

Special Issue Reprint

Mechanical Behavior and Reliability of Engineering Ceramics

Edited by
Malika Saadaoui

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Mechanical Behavior and Reliability of Engineering Ceramics

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Guest Editor

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Guest Editor

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About the Editor

Malika Saadaoui

Malika Saadaoui is a professor of Mechanical Engineering at Mohammadia Engineering School, affiliated with Mohammed V University of Rabat, Morocco. She has expertise in the thermo-mechanical behavior of engineering ceramic materials. Her main research interests include the study of the effect of the microstructure and stress-induced phase transformation in zirconia-based ceramics and composites on their mechanical properties and fracture behavior, particularly toughness and strength, crack growth resistance (R-curve effect), subcritical crack growth, fatigue behavior and impact resistance.

Mechanical Behavior and Reliability of Engineering Ceramics

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1. Introduction

Engineering ceramics are successfully used as structural or functional materials in a wide range of technical and biomedical applications [1–5] thanks to advantages such as durability, chemical stability and temperature resistance. However, they are prone to brittle fracture under mechanical or thermal stresses due to crack propagation from pre-existing flaws introduced during processing or surface machining, which serve as stress concentrators. Mechanical properties such as hardness, strength, elastic modulus and fracture toughness are incredibly important for engineering ceramics, depending on their applications. Wear and creep behavior are also key factors affecting material durability, as well as fatigue under static or cyclic stresses. Statistical analysis is necessary to estimate material reliability, often evaluated by the Weibull modulus that characterizes the flaw distribution [6,7]. Material properties depend strongly on the composition and microstructure, particularly the porosity and grain size [8,9], and this relationship must be well understood to optimize the performance of the materials.

Manufacturing processes play a key role in mechanical properties and behavior. For example, it has been shown that colloidal processing can eliminate agglomerates and organic inclusions [10], resulting in improved fracture strength. The development of new ceramic manufacturing processes, such as spark plasma sintering (SPS) [11,12], has significantly enhanced the strength of ceramic materials by increasing densification and reducing grain size. Recent advances in additive manufacturing and 3D printing processes of ceramic materials [13–15] has enabled complex shapes to be obtained that could not be produced by other technologies. Another aspect that influences the mechanical properties of engineering ceramics is surface preparation, such as surface texturing, which contributes to improving tribological performance [16,17].

Over recent decades, research has focused on material design by tailoring microstructures to obtain flaw-tolerant ceramics with enhanced fracture toughness. Different strategies have been applied based on crack shielding–toughening mechanisms such as crack bridging [18–20] and zirconia transformation toughening [21–24]. In particular, transformation toughening has been employed to increase the fracture toughness of a variety of zirconia-based ceramics and composites, including zirconia-toughened alumina (ZTA) [5] and tetragonal zirconia polycrystals (Y-TZPs), in which the metastable tetragonal phase is retained at room temperature by adding yttria (Y_2O_3), typically with a content of 3 mol% (3Y-TZPs) [25]. In these materials, stress-induced tetragonal-to-monoclinic (t-m) phase transformation, accompanied by volume expansion [26,27], may occur around a propagating crack tip. This leads to compressive stresses that prevent crack propagation and thus increase the material toughness [24,28,29]. However, the mechanical strength of zirconia ceramics is often limited by the phase transformation [30,31] and recent studies attempted to meet the challenge of obtaining zirconia ceramics that combined both high

toughness and high strength, using different strategies to optimize the rate of the t-m phase transformation [32–34].

Among the ceramic materials recently developed, high-entropy ceramics (HECs), which are potentially useful as functional materials for thermoelectric, catalytic, dielectric and magnetic applications, are rapidly growing due to their wide range of properties and behaviors [35–39]. These materials, including carbides, borides and oxides, typically contain five or more elements and form a single-phase solid-solution crystal structure. The concept of HECs was applied to ultra-high-temperature ceramics (UHTCs), known for their high melting points ($>3000\text{ }^{\circ}\text{C}$), to form multiple-component systems [40,41] with high mechanical performance, particularly in a high-temperature environment. The mechanical behavior of these materials, which has been scarcely studied, need to be understood to ensure their reliability.

Engineered cementitious composites (ECCs) are fiber-reinforced materials that can provide enhanced tensile strength, ultra-high ductility and crack resistance without steel reinforcement [42]. This is due to crack bridging by high-strength fibers which dissipate the fracture energy and prevent sudden brittle failure under tensile loads. The application of 3D printing technology to these materials has received great attention [43,44] as it reduces the construction time and cost. The challenges in the development of 3D-printed ECC materials include tailoring them to balance printability, buildability, mechanical strength, and durability.

The aim of this Special Issue is to bring together papers that advance recent understanding of the mechanical behavior and reliability of engineering ceramics, in relation to their microstructure and manufacturing processes.

2. Overview of the Contributions

This collection brings together 1 comprehensive review and 13 research papers that address different types of engineering ceramic materials, including zirconia-toughened ceramics and composites, high-entropy ceramics, and engineered cementitious composites. Their important mechanical properties or reliability are discussed in terms of composition, microstructure and manufacturing process. Here we present a brief overview of selected contributions that cover the key topics of this Special Issue. Five focused on zirconia-based ceramics and it was shown that optimizing the stress-induced t-m phase transformation rate increases their mechanical performance. In the case of Y-TZP ceramics, it is known that 3Y-TZPs may have high strength ($>1\text{ GPa}$) but only a moderate fracture toughness ($4\text{--}6\text{ MPa}^{1/2}$) [45,46]. In their contributions, Kern and Osswald [47] and Imariouane et al. [48] showed that reducing the Y_2O_3 content in new alumina-doped Y-TZPs to 2 and 1.5 mol%, respectively, increased the t-m phase transformation rate significantly, which enabled the combination of high strength and relatively high toughness, which reached $8.5\text{ MPa}^{1/2}$ for 1.5Y-TZPs. In [48], it was also reported that the t-m phase transformation is beneficial for the impact resistance of zirconia-based ceramics. By comparing the impact behavior of 3Y-TZPs, 1.5Y-TZPs and a Ce-TZP composite, the authors showed that the higher the transformability, the greater the ability to absorb energy upon impact and the higher the impact resistance. The Ce-TZP composite exhibited the highest impact resistance due to a high phase transformation rate, with ductile behavior. In [49], the relationship between the composition, microstructure and mechanical properties of zirconia–magnesia–alumina composites ($\text{ZrO}_2\text{--MgO--Al}_2\text{O}_3$) was investigated. It was shown that adjusting the material composition leads to the formation of metastable tetragonal and cubic zirconia phases and significantly improves the biaxial bending strength. In [50], the authors reported beneficial effects of the t-m phase transformation on the reliability of a zirconia–ceramic composite, stabilized with yttria and ceria and reinforced with alumina platelets ($\text{ZrO}_2\text{CeYAl}_2\text{O}_3$),

which exhibited a high Weibull modulus (16.8) and fatigue resistance. In [51], a finite element analysis was used to explore the influence of surface texturing on wear and friction in zirconia ceramic-on-ceramic hip implants, which are important for their durability. It was shown that using textured surfaces with dimples induced a significant wear reduction (17%), compared to smooth surfaces. This is particularly linked to the fact that dimples act as lubricant reservoirs and trap wear debris.

In the field of high-entropy ceramics, the creep behavior of (Co, Cu, Mg, Ni, Zn)O transition metal high-entropy oxide ceramics (TM-HEO) was reported in [52]. Samples with grain sizes ranging from coarse to nano-scale were deformed under compressive stresses (5 to 31 MPa) at temperatures between 600 and 850 °C. Shear-thickening superplastic transitions were identified and the results enabled the construction of mechanism maps that could predict the deformation behavior of TM-HEO for a wide range of deformation conditions. In [53], it was demonstrated that the combined action of adding Ni and SiC whiskers improved the fracture toughness of boride HECs, due to crack bridging. Moreover, adjusting the sintering temperature to promote densification increased their fracture strength. In [54], it was shown that the wear resistance of carbide UHTCs synthesized by SPS was improved by adding components to form a multiple-component system. The wear resistance of ternary (Ta, Nb, Hf)C and quaternary (Ta, Nb, Hf, Ti)C increased respectively by 29% and 49% compared to binary (Ta, Nb)C. This was attributed to high densification, high hardness and complete solid-solution formation in the quaternary system.

Tulliani's review paper [55] was dedicated to recent advancements in 3D-printed engineered cementitious composites (3DP-ECCs). The author analyzes, in particular, the potential of 3D printing technologies and the mechanical properties and durability of the materials. They showed that 3D printing enables the design of complex structures, like Bouligand, knitted or tilted structures, that may improve fracture performance for specific applications. 3DP-ECCs exhibit anisotropic properties due to fiber alignment in the printing direction. In particular, the compressive strength and stress–strain relationships are different in the parallel and perpendicular directions to the printing direction. Among the parameters influencing mechanical properties of 3DP-ECC, the composition, the fiber-reinforcing index and the loading direction play a crucial role. Internal curing may also improve the mechanical strength of the materials.

3. Conclusions

The contributions compiled in this Special Issue provide recent research developments on mechanical behavior and properties of a variety of engineering ceramics including zirconia-toughened ceramics and composites, high-entropy ceramics, and engineered cementitious composites. They show that tailoring the microstructures and compositions of materials or using advanced manufacturing techniques as SPS or 3D printing may enhance the mechanical performance of materials depending on their applications.

Conflicts of Interest: The author declares no conflicts of interest.

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Article

Shear-Thickening Superplastic Transitions in High-Entropy Oxides

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Abstract

Despite significant interest in their functional properties, the mechanical behavior of high-entropy oxides (HEOs) is not well studied, particularly at elevated temperatures. Bulk (Co,Cu,Mg,Ni,Zn)O (transition metal (TM)-HEO) samples were deformed under compression at applied stresses and temperatures ranging from 5 to 31 MPa and 600 to 850 °C, respectively. All of the deformation conditions result in creep stress exponents of $n < 3$, indicating that TM-HEO exhibits superplastic deformation. A transition from structural to solution-precipitation-based superplasticity is observed during deformation above 650 °C. Additionally, TM-HEO exhibits shear-thickening behavior when deformed at stresses above 9 MPa. The formation and behavior of a Cu-rich tenorite secondary phase during deformation is identified as a key factor underpinning the deformation mechanisms. The microstructure and phase state of TM-HEO before deformation also influenced the behavior, with finer grain sizes and increasing concentrations of Cu-rich tenorite, resulting in the increased prevalence of solution-precipitation deformation. While complex, the results of this study indicate that TM-HEO deforms through known superplastic deformation mechanisms. Superplasticity is a highly efficient manufacturing method and could prove to be a valuable strategy for forming HEO ceramics into complex geometries.

Keywords: high-entropy oxide (HEO); superplasticity; high temperature deformation; mechanical behavior; shear-thickening

1. Introduction

Since their discovery in 2016, high-entropy oxides (HEOs) have been intensely researched due to their wide range of properties and behaviors [1]. HEOs typically contain five or more oxide components and form a single-phase solid-solution crystal structure after processing. The large number of elements in HEOs, and their ability to form stable solid solutions, have greatly expanded the compositional design space available to material engineers. As such, HEOs are being studied for a wide range of applications. For example, HEOs have garnered particular attention in battery [2,3] and catalysis applications [4].

Some HEOs have been found to exhibit a reversible phase transformation. For example, the transition metal HEO (Cu, Co, Mg, Ni, Zn)O (referred to here as TM-HEO) segregates a Cu-rich tenorite phase and a Co-rich spinel phase during its transformation [5,6]. This transformation occurs during heat treatment within the temperature window of 650–850 °C. Above 850 °C, TM-HEO returns to its single-phase state consisting of a rocksalt crystal

structure. In our previous study, we observed that this phase transformation was sensitive to microstructure, with smaller grain sizes leading to greater amounts of secondary phase forming [6]. We also observed that the phase transformation in nanocrystalline TM-HEO (grain sizes < 100 nm) initiated at temperatures 200 °C lower than their coarse-grain counterparts. Additionally, we have found that the Cu-rich tenorite phase forms ubiquitously in the grain boundaries of TM-HEO [5].

Compared to their functional properties, the mechanical properties of HEOs are not well studied. Through simulations, Pitike et al. found that TM-HEO should exhibit greater ductility compared to other conventional ceramics [7]. Our group confirmed the existence of this ductility by experimentally demonstrating that TM-HEO exhibits significant dislocation activity during deformation at room temperature [8]. While dislocations form readily in coarse-grain TM-HEO, this is not the case in nanocrystalline TM-HEO. We observed that nanocrystalline TM-HEO forms few dislocations and fails primarily through intergranular fracture [8]. This intergranular fracture contributes to TM-HEO exhibiting inverse Hall–Petch behavior at fine grain sizes [9].

Ceramics are known to exhibit a variety of mechanical behaviors at elevated temperatures. A small subset of ceramics has the capacity for superplastic deformation, where the ceramic exhibits substantial plastic deformation without strain localization [10]. Superplasticity represents a potentially revolutionary avenue for fabricating ceramics with complex geometries. Previous studies have demonstrated that ceramics with superplastic behavior can be successfully formed into net-shaped parts. For example, Zhou et al. were able to forge sharp channels into Al₂O₃-containing carbon nanotubes [11]. Luo et al. successfully formed SiAlON into functional gears [12]. In both scenarios, the superplastically formed parts had smooth surfaces and were defect-free.

In our previous study, we demonstrated that TM-HEO could be formed into net shapes at 800 °C and pressures as low as 70 kPa [13]. Our investigation found that TM-HEO exhibited superplastic deformation facilitated through a solution-precipitation mechanism. Most interestingly, we observed that TM-HEO exhibited shear-thickening-based deformation, which is rare in inorganic solids. However, our previous study only explored a narrow set of deformation conditions, with many details underpinning the deformation behavior of TM-HEO still being unknown. In the present study, we perform compressive deformation experiments on TM-HEO under a wide range of stress and temperature values. We find that TM-HEO exhibits transitions in deformation mechanisms, which are triggered by both stress and temperature. Additionally, we find that some of these deformation mechanisms are sensitive to microstructure. Our findings provide additional insight into the underlying deformation mechanisms operative in TM-HEO, which could facilitate the efficient manufacturing of these important materials.

2. Materials and Methods

2.1. Synthesis and Processing

TM-HEO samples were prepared using solid-state synthesis followed by powder consolidation using sintering. Samples were prepared with a range of grain sizes (coarse, fine, and nanocrystalline) as well as phase states (single-phase and multi-phase). First, the five binary oxide nanopowders of CoO (50 nm, 99.7 wt% purity), CuO (25–55 nm, 99.95%), MgO (50 nm, 99.95%), NiO (18 nm, 99.98%), and ZnO (18 nm, 99.95%) (US Research Nanomaterials, Houston, TX, USA) were blended in equimolar amounts using a mortar and pestle. This blended powder was then planetary ball milled using a Pulverisette 7 planetary ball mill (Fritsch, Idar-Oberstein, Germany) for 3 h at 300 rpm. The powders were suspended in isopropanol and milled using Si₃N₄ media. The powder was then heat-treated in a furnace at 900 °C for 20 min to complete the solid-state reaction and form

TM-HEO. This TM-HEO powder was once again milled in the PBM for 12 h in order to refine the particle size. More details about our powder synthesis and processing procedures can be found in our previous work [6].

These powders were consolidated into cylindrical samples that were approximately 14 mm in diameter and 2 mm in height. Different sintering routes were used to achieve the different desired microstructures. For the coarse-grain samples (CG, target grain size of $\sim 20 \mu\text{m}$), the powder was conventionally sintered at 1100°C for 12 h. For the fine-grain samples (FG, target grain size of $\sim 1 \mu\text{m}$), the powders were consolidated using spark plasma sintering (SPS) at 900°C for 10 min with a heating rate of $200^\circ\text{C}/\text{min}$. For the nanocrystalline samples (NC, target grain size of $\sim 100 \text{ nm}$), the powder was consolidated using SPS at 700°C for 10 min with a heating rate of $200^\circ\text{C}/\text{min}$.

After consolidation, the as-sintered TM-HEO samples were polished down to $1 \mu\text{m}$ diamond suspension. Density measurements were performed on the polished samples using the Archimedes method at room temperature. Each sample was measured five times in deionized water. The measurements were performed using an AG204 balance (Mettler Toledo, Greifensee, Switzerland) with an accuracy and repeatability of 0.1 mg. All processing routes yielded samples that were fully dense ($\geq 98\% \pm 1\%$ dense according to Archimedes measurements). Guided by our previous work [6], some of the samples were heat-treated at 700°C for 12 h to form multi-phase microstructures. These multi-phase samples (-MP) were compared to the as-sintered single-phase (-SP) samples. Heat treatment of the nanocrystalline samples resulted in significant grain growth, and as such, multi-phase nanocrystalline samples were not investigated in this study. The sample labels used in this study, as well as the sample characteristics, are summarized in Table 1.

Table 1. TM-ESO samples for high-temperature compression tests.

Sample ID	Microstructure	Phase State	Grain Size	Cu-Rich Tenorite (at%)
NC-SP	Nanocrystalline	Single-phase	$90 \pm 60 \text{ nm}$	0
FG-SP	Fine-grain	Single-phase	$1.1 \pm 0.3 \mu\text{m}$	0
FG-MP	Fine-grain	Multi-phase		14 ± 1
CG-SP	Coarse-grain	Single-phase	$22 \pm 10 \mu\text{m}$	0
CG-MP	Coarse-grain	Multi-phase		14 ± 1

2.2. High-Temperature Compression Experiments

To carry out high-temperature compression experiments, a custom-built high-temperature mechanical testing system was constructed inside an Instron load frame. Custom compression rods were machined out of Inconel 718. A clamshell furnace was used to heat the samples, and the compression rods and Instron load frame were kept cool through two water-cooled adapters that attached to the compression rods. The samples were compressed between Si_3N_4 platens. These platens were coated in boron nitride lubricant spray before each experiment. The sample–platen assembly was held in place using an Inconel die. A through-hole was drilled into the Inconel die and was used to hold a thermocouple. This thermocouple was positioned to touch the bottom platen and was set $\sim 1 \text{ mm}$ away from the sample. Before deformation, the as-fabricated TM-HEO samples were polished down to $1 \mu\text{m}$ diamond suspension. The cylindrical TM-HEO samples were approximately 14 mm in diameter and 2 mm in height.

Single-phase and multi-phase samples were each compressed at stress values of 5, 9, 13, 20, and 31 MPa and at deformation temperatures ranging from 600°C to 850°C in 50°C increments (with the exception of sample NC-SP, which was deformed at temperatures up to 700°C to avoid grain growth at elevated temperatures). The samples were first heated

to the desired temperature under no load and then allowed to equilibrate at temperature for several minutes. Once the temperature stabilized, a uniaxial pressure was applied to the samples at a rate of 0.5 MPa/min. During preliminary testing, it was found that a steady-state strain rate was achieved after ~5 min at pressure. Based on this short time to achieve steady-state conditions, the samples were held at each pressure for 10 min. All data reported here are based on these 10 min holds at pressure. The samples were deformed continuously with increasing stress values to generate a strain–time curve for each compression experiment. These strain–time curves were then used to calculate the steady-state strain rate at each applied stress. The total experiment time at each temperature was ~2 h. The validity of our high-temperature compression apparatus and testing methods was verified by performing deformation experiments on N-BK7 glass (Schott, Mainz, Germany). These cylindrical glass samples were tested under the same conditions used to test our TM-HEO samples. The deformation behavior of the glass cylinders closely resembles studies presented in the literature [14,15].

2.3. Characterization

X-ray diffraction (XRD) and Rietveld refinement were used to determine if a phase transformation occurred during high-temperature deformation, and how much secondary phase formed during the high-temperature deformation experiments. XRD was performed with a SmartLab X-ray Diffractometer (Rigaku, Tokyo, Japan) with a 2θ range of 30° to 80° . Rietveld refinement was performed on the acquired XRD data using the Maud software (v2.9995) [16] to estimate the relative atomic fraction of the primary rocksalt phase and the secondary Cu-rich tenorite for each test condition.

Scanning electron microscopy (SEM) was used to observe the fracture surfaces of the samples to understand how deformation affected the grain morphology. The fracture surfaces were imaged with a Magellan 400 XHR SEM (FEI, Hillsboro, OR, USA), using an accelerating voltage of 5 kV and a current of 50 pA. The average grain size was calculated from the fracture surface micrographs by measuring the diameter of >300 grains with the FIJI/ImageJ software (v2.9.0) [17]. It is important to note that the various phases observed in TM-HEO are all multi-cation oxides [18]. Consequently, the phases have similar composite Z-numbers, making back-scatter electron microscopy unsuitable for detecting phase contrast in TM-HEO. Energy-dispersive X-ray spectroscopy (EDS) mapping was used to observe the morphology of the secondary phases in the fine-grain TM-ESO before and after high-temperature deformation. Samples were prepared for EDS analysis by polishing down to 1 μm diamond suspensions. The polished samples were mounted onto SEM stubs with colloidal silver paste (Ted Pella Inc., Redding, CA, USA) and sputter-coated with 3 nm of iridium. EDS was performed in a GAIA SEM-FIB microscope (Tescan, Brno, Czech Republic) using a silicon drift detector with an area of 150 mm^2 (Oxford Instruments, Abingdon, UK).

3. Results

3.1. Microstructure and Phase State

The microstructure and phase state of the as-sintered samples were controlled through sintering conditions. All as-sintered samples exhibit equiaxed grain structures and full density. As listed in Table 1, the as-sintered single-phase coarse-grain, fine-grain, and nanocrystalline samples (labeled as CG-SP, FG-SP, and NC-SP, respectively) exhibit average grain sizes of $22 \pm 10 \mu\text{m}$, $1.1 \pm 0.3 \mu\text{m}$, and $90 \pm 60 \text{ nm}$, respectively. Representative fracture surface micrographs are presented in Figure 1. It is important to note that voids visible in the fracture surface micrographs for sample NC-SP are not pores, but are instead caused by bulk material being dislodged during fracture surface preparation. The microstructure–processing relationship observed here is consistent with our previous study [6].

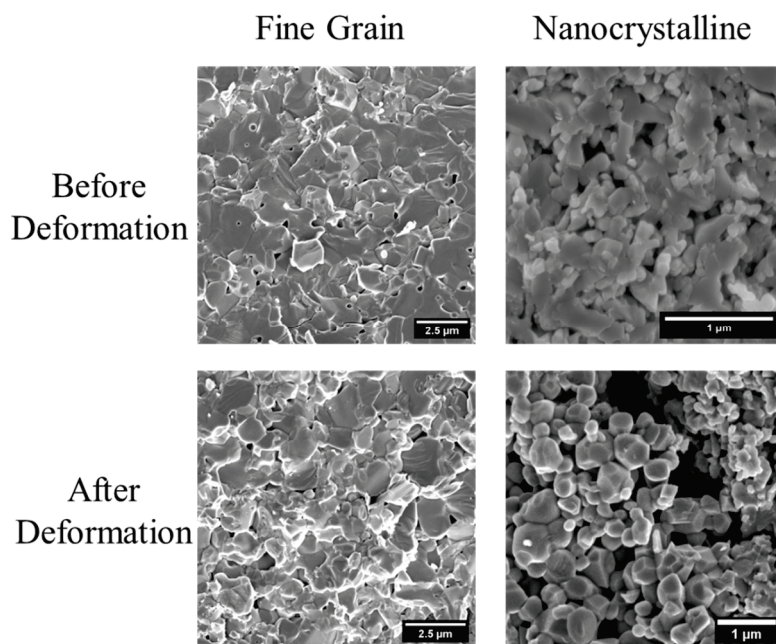


Figure 1. Fracture surface micrographs of the single-phase fine-grain (FG-SP) and nanocrystalline (NC-SP) samples, both before deformation (as-sintered) and after deformation at 700 °C.

As observed in previous studies [5,6,18], the three as-fabricated samples exhibit the expected single-phase primary rocksalt crystal structure for TM-HEO, and the heat-treated samples exhibit the primary rocksalt phase as well as the Cu-rich tenorite and Co-rich spinel secondary phases. The phase state for samples FG-SP and FG-MP before and after deformation are presented in Figures 2 and 3. We note that the concentration of the Cu-rich tenorite secondary phase is higher than that of the Co-rich spinel secondary phase. Cu-rich tenorite secondary phase is observed in the grain boundaries, whereas the Co-rich spinel secondary phase is only observed in the grain interior [5,18]. Because all of the deformation mechanisms discussed in this study involve deformation facilitated through grain boundary diffusion or related mechanisms, we focus on the Cu-rich tenorite secondary phase and neglect the Co-rich spinel secondary phase in our analysis. Future research should investigate the role of this Co-rich spinel secondary phase on high-temperature deformation by modifying the composition of the TM-HEO such that the Cu-rich tenorite secondary phase formation is suppressed [19].

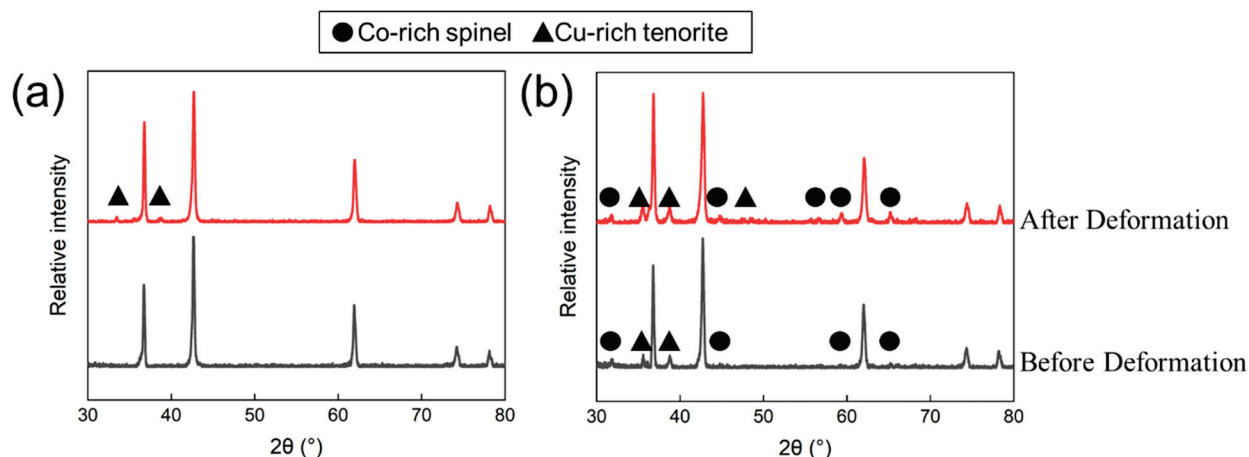


Figure 2. XRD patterns for the fine-grain (a) single-phase (FG-SP) and (b) multi-phase (FG-MP) samples before and after deformation. Secondary phase peaks are denoted with triangles (Cu-rich tenorite secondary phase) and circles (Co-rich spinel secondary phase).

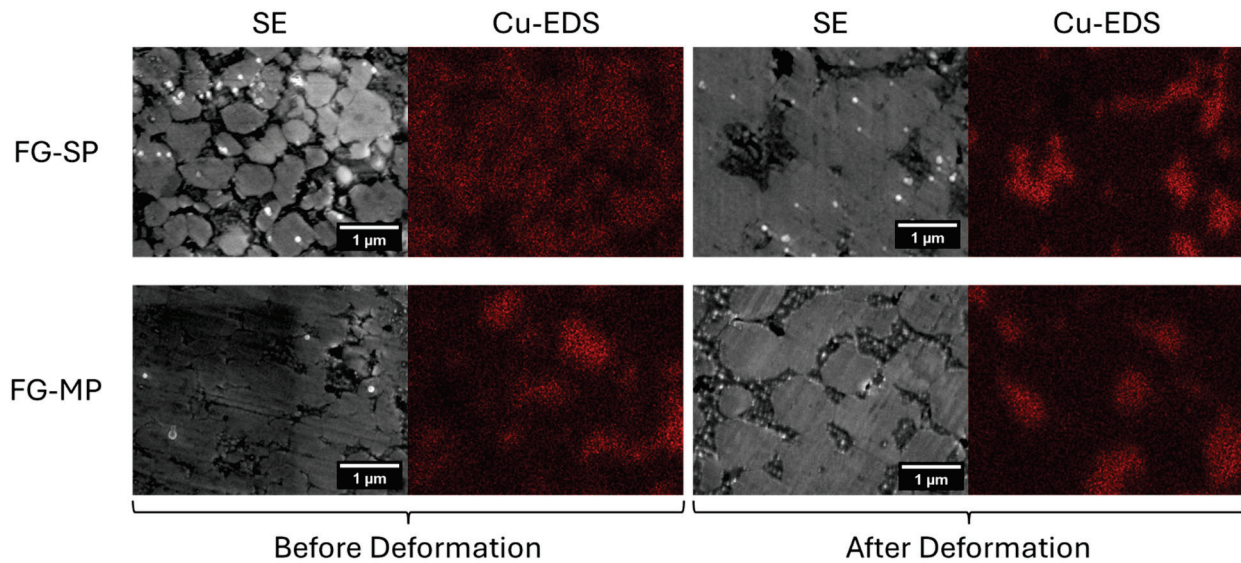


Figure 3. Secondary electron (SE) and Cu elemental maps for the fine-grain single-phase (FG-SP) and multi-phase (FG-MP) samples before and after deformation.

3.2. Deformation

Our as-fabricated samples were compressed at applied stresses in the range of 5 to 31 MPa while exposed to temperatures of 600 to 850 °C. These conditions resulted in measurable deformation, which we used to analyze the deformation behavior in TM-HEO. It is important to note that nanocrystalline TM-HEO exhibits significant grain growth when deformed at temperatures above 700 °C. Such grain growth could convolute the identification of the deformation mechanisms in nanocrystalline TM-HEO. Consequently, sample NC-SP was only deformed at 600, 650, and 700 °C. The strain rate was calculated at each applied stress and temperature condition. We observe that the role of stress on strain rate in TM-HEO is dependent on both applied pressure and temperature. For further analysis, we apply the standard Norton power-law creep model [20], which defines the strain rate due to creep as

$$\dot{\epsilon} = A\sigma^n \quad (1)$$

where A is a constant and n is the stress exponent. Qualitatively, n provides crucial insight into the mechanisms underpinning high-temperature deformation in materials by describing the role of applied stress on strain rate [20].

The role of applied stress on strain rate for samples FG-SP and FG-MP deformed at 600 °C can be seen in Figure 4a. Strain rate increases with increasing stress for both samples. When deformed at 600 °C, both samples exhibit a transition at ~9 MPa, where the role of stress on strain rate changes. This sensitivity to applied stress can be quantified using n from Equation (1). At stresses ≤ 9 MPa, the strain rate is highly sensitive to applied stress, with samples FG-SP and FG-MP having values of $n = 2.1 \pm 0.3$ and 1.4 ± 0.2 , respectively. Conversely, at stresses ≥ 13 MPa, the strain rate becomes mostly insensitive to pressure, with both samples exhibiting a stress exponent of $n = 0.6 \pm 0.1$. We note that this transition from stress-sensitive to stress-insensitive was observed in all samples deformed at 600 °C. At stresses ≤ 9 MPa, all samples had values of $n = 1$ to 2.5, while at stresses ≥ 13 MPa, all samples had values of $n = 0.5$ to 0.7.

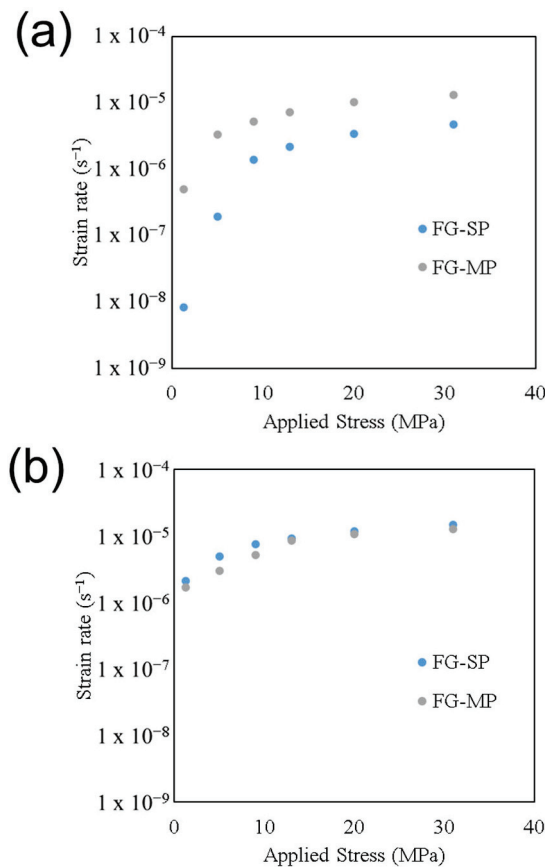


Figure 4. The role of applied stress on deformation strain rate for the fine-grain single-phase (FG-SP) and multi-phase (FG-MP) samples deformed at (a) 600 °C and (b) 850 °C.

The role of applied stress on strain rate for samples FG-SP and FG-MP deformed at 850 °C can be seen in Figure 4b. Similarly to the deformation at 600 °C, a transition in stress sensitivity is observed between 9 and 13 MPa. The samples deformed at 850 °C exhibit lower overall stress exponents compared to those deformed at 600 °C. At stresses ≤ 9 MPa, the stress exponents are $n = 0.4 \pm 0.2$ for sample FG-SP and $n = 0.3 \pm 0.1$ for sample FG-MP. At stresses ≥ 13 MPa, the stress exponents are $n = 0.3 \pm 0.1$ for sample FG-SP and $n = 0.2 \pm 0.1$ for sample FG-MP. While a decrease in n is observed at stresses ≥ 13 MPa, all of the stress exponent values observed at 850 °C are $n < 0.4$, making TM-HEO mostly insensitive to stress at this deformation temperature.

We observe that all samples in this study exhibit a transition in stress sensitivity between 5 and 13 MPa regardless of the deformation temperature. The role of temperature on n for every material deformed in this study is shown in Figure 5. For clarity, we divide our analysis into two datasets: stress exponents acquired below the transition (≤ 9 MPa, Figure 5a) and stress exponents acquired above the transition (≥ 9 MPa, Figure 5b). The value of n generally decreases with increasing temperature. Below 9 MPa, the stress exponent ranges from $n = 1.1$ to 2.5 at 600 °C and decreases with increasing temperature, ranging from $n = 0.3$ to 0.4 at 850 °C. The stress exponent values generally decrease with increasing temperature at stresses > 13 MPa, ranging from $n = 0.5$ to 0.7 at 600 °C and decreasing to $n = 0.2$ to 0.3 at 850 °C. Overall, the observed stress exponents vary from $n = 0.2$ to 2.5 depending on deformation pressure and temperature.

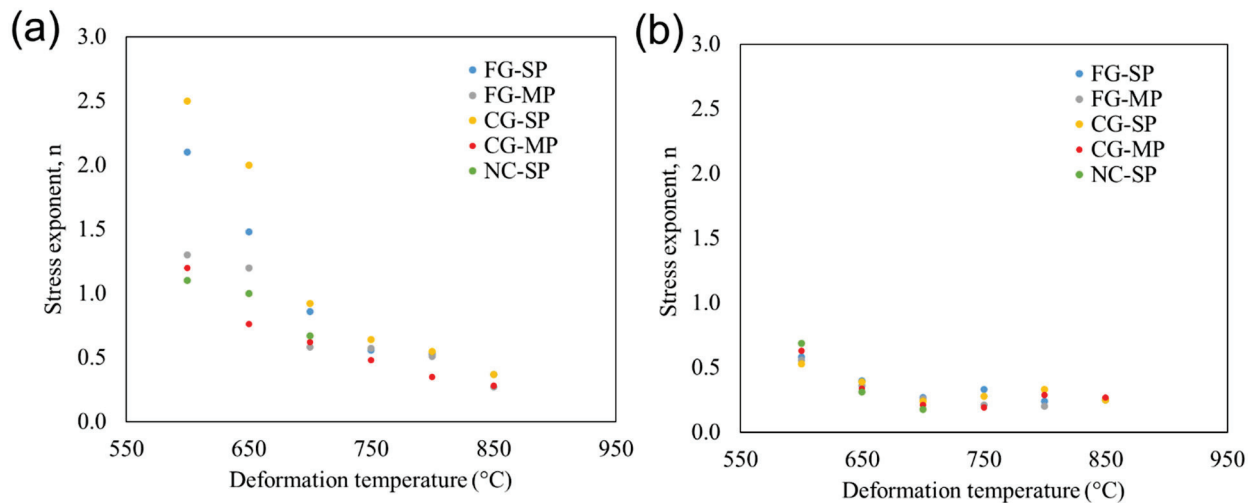


Figure 5. Role of deformation temperature on stress exponent, n , for deformation (a) below the stress transition (≤ 9 MPa) and (b) above the stress transition (≥ 9 MPa).

High-temperature deformation in ceramics is often compensated through diffusion-based mechanisms, making the strain rate highly sensitive to temperature. These diffusion-based deformation mechanisms follow an Arrhenius law, with strain rate having the form of

$$\dot{\epsilon} \propto e^{-\frac{Q}{RT}} \quad (2)$$

where T is the temperature during deformation, R is the gas constant, and Q is the activation energy for deformation. The activation energy represents the role of temperature on strain rate. Qualitatively, Q can be used to identify the mechanisms that are contributing to the high-temperature deformation.

The role of temperature on strain rate for samples FG-SP and FG-MP deformed at 9 MPa are shown in the Arrhenius plot in Figure 6a. The strain rate increases with increasing temperature for both samples. Both samples exhibit a transition in temperature dependance at distinct temperatures. This temperature dependance can be quantified using Q from Equation (2). At temperatures ≤ 650 °C, sample FG-SP has a value of $Q = 250 \pm 70$ kJ/mol. At temperatures ≥ 650 °C the activation energy decreases to $Q = 95 \pm 10$ kJ/mol, indicating that there is a significant decrease in temperature sensitivity at higher temperatures. Sample FG-MP has a value of $Q = 240 \pm 45$ kJ/mol at temperatures ≤ 700 °C and $Q = 60 \pm 5$ kJ/mol at temperatures ≥ 700 °C. The role of temperature on strain rate for samples FG-SP and FG-MP deformed at 31 MPa are shown in the Arrhenius plot in Figure 6b. The transition in temperature dependance is much more subtle compared to that observed for the deformation at 9 MPa. Additionally, both samples FG-SP and FG-MP exhibit similar temperature sensitivities under these deformation conditions. At temperatures ≤ 650 °C, both samples have activation energies of $Q = \sim 100 \pm 10$ kJ/mol. At temperatures ≥ 650 °C their activation energies decrease to $Q = \sim 40 \pm 5$ kJ/mol.

We observe that most of the samples in this study exhibit a transition in temperature sensitivity between 650 and 700 °C. The nanocrystalline samples (NC-SP) were not deformed above 700 °C, and thus their temperature transition was not explored in this study. For most samples, this transition is characterized by a higher activation energy below the transition compared to activation energy values above the transition. We observe that the activation energy associated with deformation is highly dependent on applied stress. The role of stress on activation energy can be seen in Figure 7. Deforming TM-HEO at 5 MPa and at temperatures below the temperature transition (Figure 7a) results in activation energies of $Q > 150$ kJ/mol. The activation energy decreases with increasing pressure,

reaching values as low as $Q = 50$ kJ/mol at 31 MPa. In contrast, deformations above the transition temperature (Figure 7b) are lower, having values of $Q = 80$ to 150 kJ/mol at 5 MPa and $Q = 20$ to 50 kJ/mol at 31 MPa.

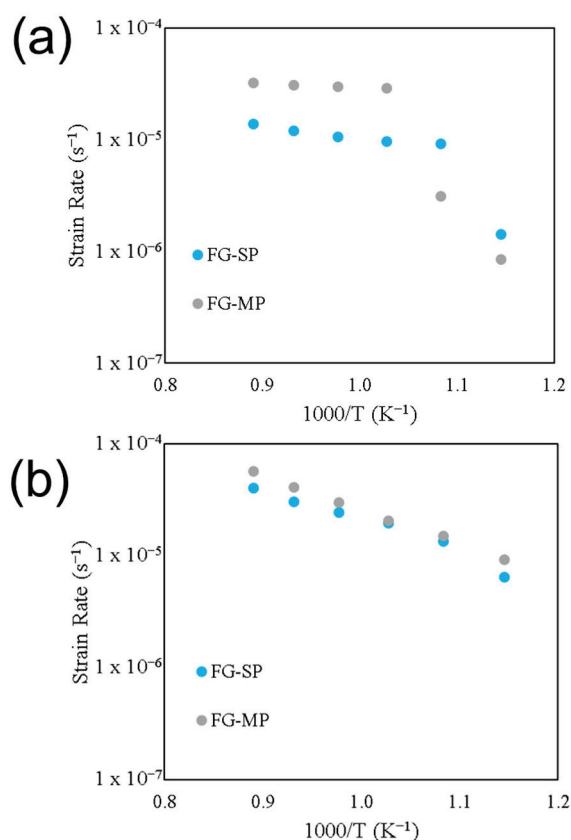


Figure 6. The role of temperature on the deformation strain rate for the fine-grain single-phase (FG-SP) and multi-phase (FG-MP) samples deformed at (a) 9 MPa and (b) 31 MPa.

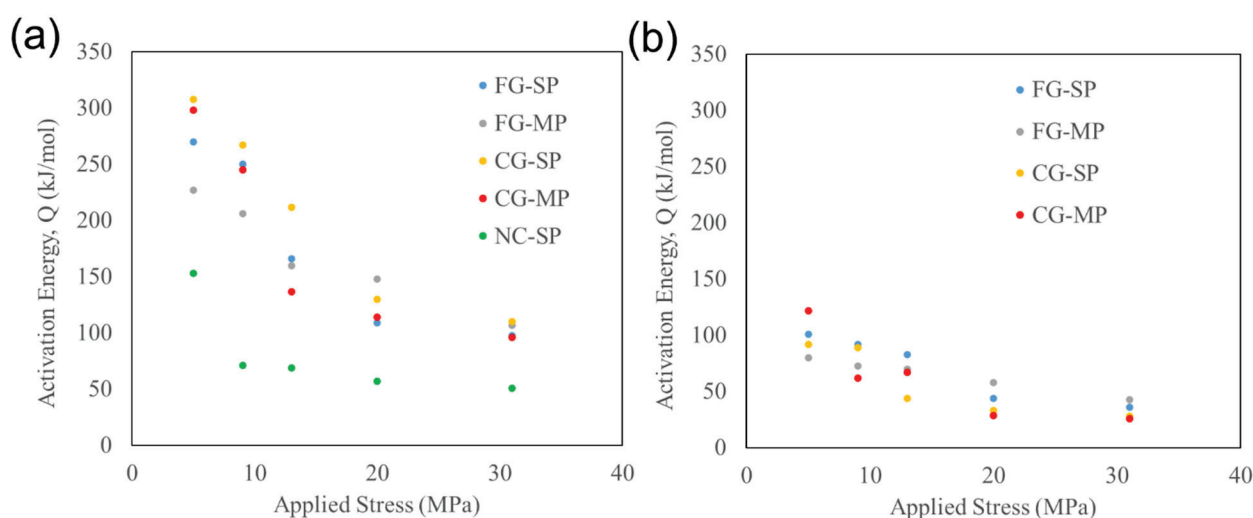


Figure 7. Role of applied stress on activation energy, Q , for deformation (a) below the transition temperature (≤ 700 °C) and (b) above the transition temperature (≥ 700 °C).

3.3. Post-Deformation Microstructure Characterization

The post-deformation microstructure for samples FG-SP and NC-SP can be seen in the fracture surface micrographs in Figure 1. The average grain size in sample FG-SP does not increase during deformation, and the grains retain their equiaxed morphology

after deformation. The microstructures of the FG and CG samples look similar before and after deformation, indicating that the deformation process does not meaningfully alter the microstructure. In contrast, the average grain size for sample NC-SP grows from 90 ± 60 nm to 260 ± 140 nm during deformation at 700 °C, as observed in Figure 1. Similarly to the fine-grain samples, the microstructure of sample NC-SP after deformation is also equiaxed. It is also important to note that there is no sign of cavitation or fracture in the microstructure after deformation.

Our previous studies have shown that TM-HEO forms a Cu-rich tenorite secondary phase when heat-treated between 650 and 850 °C [6]. Additionally, our previous study on superplastic deformation in TM-HEO demonstrated that the Cu-rich tenorite phase forms during deformation and influences its mechanical behavior [13]. In the current study, our TM-HEO samples are deformed within the temperature range for Cu-rich tenorite formation. As such, we expect the Cu-rich tenorite secondary phase to form during deformation and play a significant role in the deformation process. XRD patterns for samples FG-SP and FG-MP after deformation at 700 °C are shown in Figure 2. After deformation, sample FG-SP has peaks corresponding to the Cu-rich tenorite phase, indicating that this secondary phase formed during deformation. For sample FG-MP, the intensity of the secondary phase peaks is greater after deformation compared to before deformation, indicating the formation of additional secondary phase during high-temperature deformation. EDS elemental maps for Cu confirm the increased concentration of Cu-rich tenorite secondary phase after high-temperature deformation (Figure 3).

4. Discussion

Our compression experiments indicate that TM-HEO exhibits time-dependent deformation when deformed at elevated temperatures. Time-dependent deformation is common in inorganic solids at elevated temperatures. The two most important categories of time-dependent deformation are creep and superplasticity, both of which have a variety of potential mechanisms. The stress exponent, n (Equation (1)), is an important parameter for identifying deformation mechanisms. For example, creep mechanisms typically have values of $n > 3$, while superplasticity has values of $n < 3$. All of the stress exponents observed in this study are $n < 3$, indicating superplastic deformation. In addition to our deformation behavior, our post-deformation microstructures further support deformation through superplasticity. All of the samples in this study exhibit equiaxed microstructures with no signs of cavitation after deformation, which is a defining feature of superplasticity. We will therefore limit our discussion of deformation in TM-HEO to only superplastic deformation mechanisms.

4.1. Deformation Mechanisms

There are multiple mechanisms that can contribute to superplastic deformation. These mechanisms are defined based on how the grain boundary sliding is accommodated. Each mechanism is characterized by a stress exponent. For example, structural superplasticity, the most common form of superplasticity in ceramics, is characterized by a stress exponent of $n = \sim 2$. Structural superplasticity involves grain boundary sliding accommodated by grain boundary diffusion. The strain rate due to structural superplasticity in ionic solids can be estimated by [21]

$$\dot{\epsilon}_{st} = \left(2 \times 10^9\right) \frac{D_{eff}}{d^2} \left(\frac{\sigma}{E}\right)^2 \quad (3)$$

where D_{eff} is the relevant diffusion coefficient (often the grain boundary diffusion coefficient), d is the grain size, and E is the modulus of elasticity. While the room-temperature elastic modulus of TM-HEO is known (~ 125 GPa) [9,19], the temperature dependance

of the elastic modulus is not known. However, the elastic behavior of MgO, one of the constituents of TM-HEO, has been well studied [22,23]. The room temperature modulus of TM-HEO is known to be lower than MgO [7]. However, TM-HEO and MgO possess similar crystal structures and bonding behavior, and we propose that their mechanical properties will scale similarly with temperature. For our estimations of structural superplasticity (Equation (3)), we assume that the elastic modulus of TM-HEO exhibits the same temperature sensitivity as MgO, leading to an estimated modulus on the order of 10 GPa for TM-HEO under the deformation temperatures used in this study.

As a diffusion-driven process, proper estimation of D_{eff} is important for the accurate estimation of strain rate values due to structural superplasticity. However, the diffusion behavior in TM-HEO is not well studied. Previous work by Grzesik et al. measured the diffusion coefficient of TM-HEO during oxidation and reduction reactions [24]. However, their measured values ($8 \times 10^{-8} \text{ cm}^2/\text{s}$ at 700°C) are very high for a complex oxide, which the authors attribute to the diffusion of oxygen and oxygen defects. Using their diffusion coefficients in Equation (3) results in strain rates more than five orders of magnitude greater than our measured strain rate values. In our previous study, we calculated the diffusion coefficient for the growth of the Cu-rich tenorite secondary phase, finding that it was on the order of $D_{eff} = 1 \times 10^{-12} \text{ cm}^2/\text{s}$ at 700°C [18]. This diffusion coefficient closely resembles the cation diffusion coefficients in CoO ($10^{-11} \text{ cm}^2/\text{s}$ at 700°C) and MgO ($10^{-14} \text{ cm}^2/\text{s}$ at 700°C) rocksalt oxides [25,26], indicating that the growth of the Cu-rich tenorite secondary phase in TM-HEO is controlled by cation diffusion. We use this cation-based diffusion coefficient for D_{eff} in our calculations for the following reasons. First, structural superplasticity is rate-limited by the slow-moving element (in this case the cations) along their fastest path [20]. Second, the fastest diffusion path for structural superplasticity is along the grain boundaries, which are known to contain Cu-rich phases in TM-HEO [5].

The results of Equation (3) at 600 and 850°C , using our previously calculated diffusion coefficients, are shown in Figure 8a and Figure 8b, respectively. The experimentally measured strain rates for sample FG-SP are denoted with filled circles. Our estimated structural superplasticity strain rates closely match the experimental strain rate at 600°C , indicating that structural superplasticity is likely the dominant deformation mechanism under these conditions. Conversely, our estimated structural superplasticity strain rates overestimate the experimental strain rates at 850°C , indicating that the dominant deformation mechanism changes at elevated temperatures. As mentioned above, our estimated strain rates due to structural superplasticity use our previously calculated diffusion coefficients, as opposed to the much higher values measured by Grzesik et al. [24]. The close match to our experimentally measured strain rates indicates that structural superplasticity in TM-HEO is dominated by cation diffusion. Such an observation is consistent with observations that structural superplasticity is controlled by the diffusion of the slowest element along its fastest path [19].

While less common than structural superplasticity, ceramics with stress exponents $n \approx 1$ have also been observed. This linear dependence on stress, referred to as Newtonian flow, occurs due to grain boundary sliding accommodated by the action of a secondary phase [27]. The most well-studied Newtonian flow superplastic ceramic is Si_3N_4 , which forms an amorphous (glassy) secondary phase in the grain boundary due to the incorporation of sintering aids [28]. This amorphous phase facilitates grain boundary sliding due to a solution-precipitation mechanism. The solution-precipitation mechanism in Si_3N_4 operates as follows. Grain boundaries under compression dissolve solute from the Si_3N_4 phase into the amorphous phase. This solute diffuses through the amorphous phase along the grain

boundaries toward grain boundaries under tension. The solute then redeposits back into the Si_3N_4 phase.

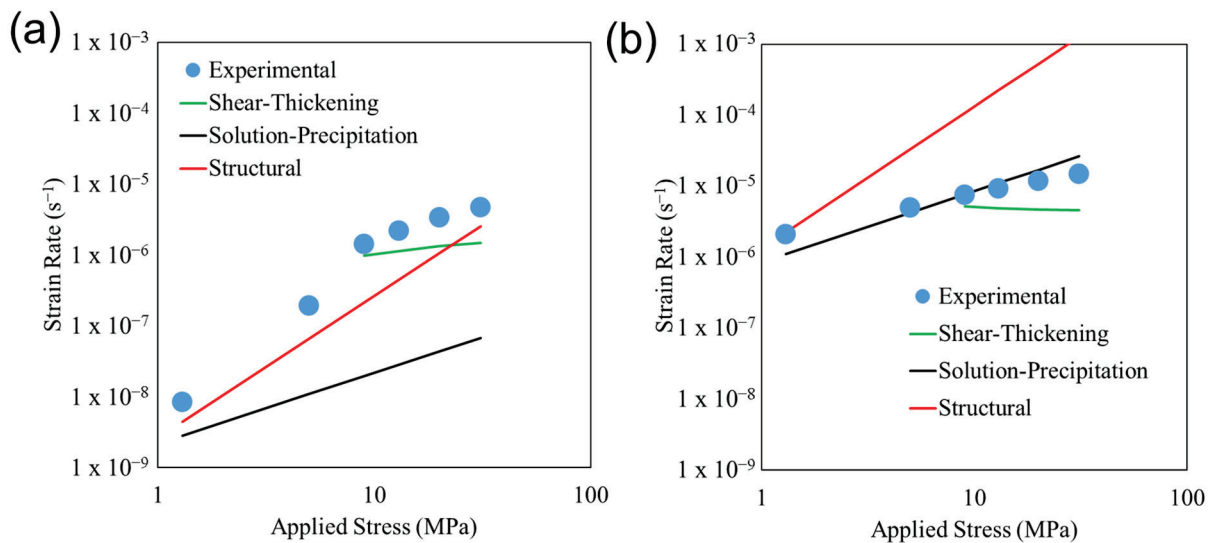


Figure 8. Role of applied stress on the deformation strain rate for the fine-grain single-phase sample (FG-SP) after deformation at (a) 600 °C and (b) 850 °C. The experimentally determined strain rates (circles) are compared to the strain rates calculated on the basis of the various proposed models (solid lines).

Our previous studies demonstrate that TM-HEO forms a Cu-rich tenorite secondary phase when heat-treated in the temperature range of 600–850 °C [5,6,18]. While the Cu-rich tenorite secondary phase forms throughout the microstructure, it forms most readily in the grain boundaries, leading to an interconnected secondary phase network. While the Cu-rich tenorite secondary phase does not form as a liquid or amorphous phase, we still hypothesize that its presence is influencing the superplastic deformation in TM-HEO. In our previous study, we identified that deformation of TM-HEO at 800 °C occurs through a solution-precipitation method facilitated by the Cu-rich tenorite secondary phase [13].

The strain rate due to the solution-precipitation mechanism can be estimated using [29]

$$\dot{\epsilon}_{SP} = \frac{\Omega}{2kT} \frac{\sigma k_t}{d} \quad (4)$$

where k is Boltzmann's constant. The term k_t is a rate constant representing the rate of exchange of atoms between the primary phase (rocksalt in TM-HEO) and the secondary phase (Cu-rich tenorite in TM-HEO). For this study, we use the kinetic constant for the coarsening of the Cu-rich tenorite secondary phase determined in our previous study [18]. These kinetic constants were calculated from experimentally measured particle-coarsening data. Our use of these kinetic constants in our calculations is justified since the coarsening of the Cu-rich tenorite phase is based on the diffusion between the Cu-rich tenorite phase and the primary rocksalt TM-HEO phase. We hypothesize that a solution-precipitation-based deformation process could be facilitated through the Cu-rich tenorite phase located in the grain boundaries of TM-HEO. The estimated strain rate derived from Equation (4) is shown in Figure 8. The solution-precipitation model underestimates our experimental strain rates during deformation at 600 °C, indicating that the deformation is not driven by a solution-precipitation mechanism under these conditions. Conversely, the solution-precipitation model closely matches our experimental strain rates during deformation at 850 °C, indicating that the deformation is dominated by the solution-precipitation mechanism at this temperature.

Stress exponent values of $n < 1$ indicate shear-thickening behavior, where deformation is inhibited by particle–particle friction. Greater applied stresses will result in greater

particle–particle friction, and thus, a resistance to deformation. While shear-thickening behavior is common in liquids and slurries, it is comparatively uncommon in bulk ceramic materials. Shear-thickening behavior with a stress exponent of $n = 0.5$ has been observed in SiAlON [30,31]. The shear-thickening effect occurs in SiAlON due to the applied stress resulting in the amorphous phase being compressed and the thickness of the phase decreasing. This reduction in the thickness of the amorphous phase increases the probability of contact between the SiAlON grains, and in turn, leading to increased friction during deformation. In our previous study, we identified that TM-HEO exhibits shear-thickening behavior during deformation at 800 °C [13].

A defining characteristic of shear-thickening behavior is the observation of a transition stress, σ_c , above which the shear-thickening behavior becomes active. Previous researchers have observed that shear-thickening behavior occurs in SiAlON at stresses > 20 MPa [30]. At stresses < 20 MPa, SiAlON exhibits Newtonian flow ($n = 1$). It is important to note that shear-thickening behavior is not an accommodation mechanism for superplastic deformation on its own. Instead, shear-thickening effects modify the stress dependence of existing deformation mechanisms. For example, SiAlON deforms through a solution-precipitation mechanism, even when the applied stress is higher than the transition stress.

The strain rate associated with shear-thickening deformation can be estimated using [28]

$$\dot{\epsilon}_{ST} = \frac{\sigma}{\eta} \left(\frac{1}{4} + \frac{\sigma_c}{2\sigma} \right)^{5/4} \quad (5)$$

where η is the apparent viscosity and σ_c is the transition stress. The apparent viscosity can be estimated using $\eta = \sigma/\dot{\epsilon}$, which results in values on the order of 1×10^{14} to 1×10^{12} Pa·s. We observe that the transition in the stress exponent (and thus deformation mechanism) occurs between 5 and 13 MPa regardless of the deformation temperature (Figure 4). While we do not know the exact value of transition stress, for our calculations, we assume a value of $\sigma_c = 9$ MPa (halfway between 5 and 13 MPa). We note that selecting a different transition stress value between 5 and 13 MPa does not meaningfully alter our results and interpretation of the data. Using Equation (5), we calculate the strain rate due to shear-thickening at deformation stresses ≥ 9 MPa (Figure 8). Our estimated strain rates closely match our measured strain rates, indicating that shear-thickening is influencing the high-temperature deformation behavior at pressures $> \sigma_c$.

While the stress exponent, n , reflects the stress dependence of the strain rate, it also provides insight into the operative deformation mechanisms. Changes in n imply that the deformation mechanism is changing. For most inorganic solids, n increases with increasing pressure and increasing temperature [20]. For example, in many superplastic alloys, n will increase with increasing temperature due to a transition from structural superplasticity to power-law creep [32]. In contrast, n values for shear-thickening in Si_3N_4 are not sensitive to temperature, indicating that the shear-thickening mechanism is stable across a range of temperatures [30]. TM-HEO exhibits the opposite behavior, with n decreasing with increasing deformation temperature (Figure 5).

We observe a change in the activation energy associated with deformation at approximately 650 to 700 °C (Figure 6). We refer to this temperature as the “transition temperature”. Based on our comparison to existing superplasticity models (Figure 8), we determine that TM-HEO deforms through structural superplasticity below the transition temperature and solution-precipitation above the transition temperature. However, the results in Figure 5 show a gradual decline in n with increasing temperature, and not a discrete transition. As temperature increases, the deformation mechanism gradually transitions from structural superplasticity deformation to solution-precipitation. Similar transition behavior with temperature has been observed in Si_3N_4 ceramics [33]. The extent of our observed

decrease in n with temperature is dependent on the applied stress. The decline in n is most pronounced when TM-HEO is deformed below the stress transition (Figure 5a). Above the stress transition, n decreases with increasing deformation temperature up to 700 °C. The values for n do not change significantly above 700 °C. This more muted decrease above the stress transition is due to the influence of the shear-thickening behavior. Above the stress transition, the high-temperature deformation behavior in TM-HEO is dictated by the shear-thickening behavior, which is mostly insensitive to temperature.

As a diffusion-driven process, superplastic deformation in ceramics is often highly sensitive to temperature, with higher temperatures leading to greater strain rates (Equation (2)). As expected, increasing deformation temperature leads to increasing strain rates during the deformation of TM-HEO (Figure 4). Unexpectedly, however, our TM-HEO samples exhibit a transition in temperature sensitivity (activation energy) above 650 to 700 °C. We observe this transition in all samples except for sample NC-SP. At temperatures below this transition, the deformation in TM-HEO is highly sensitive to temperature. Above the temperature transition, the deformation becomes comparatively insensitive to temperature.

The samples with as-fabricated grain sizes of 1.1 μm (FG-SP and FG-MP) and 22 μm (CG-SP and CG-MP) exhibit activation energy values of 230 to 310 kJ/mol when deformed below the transition temperature at 5 MPa. These activation energy values fall within the range of activation energies associated with diffusion in rocksalt-structured MgO, indicating that the high-temperature deformation is compensated by cation diffusion in the rocksalt structure. As described above, we hypothesize that TM-HEO exhibits structural superplasticity when deformed below the stress and temperature transitions. Our measured activation energies further support our conclusion that structural superplasticity is operative under these conditions.

The samples with as-fabricated grain sizes of 1.1 μm (FG-SP and FG-MP) and 22 μm (CG-SP and CG-MP) exhibit activation energy values of 80 to 120 kJ/mol when deformed above the transition temperature at 5 MPa. These activation energy values fall within the range of activation energies associated with diffusion in copper oxides [34,35]. Our TM-HEO samples form a Cu-rich tenorite secondary phase when exposed to temperatures between 650 and 850 °C [6]. Additionally, the Cu-rich tenorite secondary phase forms most readily in the grain boundaries. Our measured strain rates closely resemble those expected from a solution-precipitation mechanism (Figure 8). From our measured activation energies, we propose that above the transition temperature, TM-HEO deforms through a solution-precipitation mechanism involving the Cu-rich tenorite secondary phase at the grain boundaries. This secondary phase then acts as a solvent during high-temperature deformation, dissolving, transporting, and reprecipitating the TM-HEO phase.

Activation energy decreases with increasing pressure for all of the samples measured in this study. Below the transition temperature, the activation energy is as low as $Q = 50$ kJ/mol. Above the transition temperature the activation energy is as low as $Q = 20$ kJ/mol at 31 MPa. Such low activation energies are not commonly observed during superplastic deformation of ceramics, and do not correspond to any relevant diffusion scenario. However, low activation energies for deformation are commonly observed in shear-thickening slurries, such as melts containing slag (~40 kJ/mol) [36] and polymer slurries with high solid loading (40–70 kJ/mol) [37]. In shear-thickening slurries, these low activation energies are interpreted as the deformation being insensitive to temperature. The flow of these slurries is restricted by friction between the solid particles, which, even at elevated temperatures, dominates the rheological behavior.

We hypothesize that the deformation in TM-HEO exhibits shear-thickening behavior above the transition stress. Our observation of low activation energies above the transition stress further supports this argument. The transition to shear-thickening behavior would

be expected to be discrete in materials with uniform grain size and morphology, occurring at a specific value of stress where particle–particle friction initiates. However, real materials will have a distribution of grain sizes and morphologies and, therefore, the influence of shear-thickening will occur gradually as stress increases. We propose that the decrease in activation energy with increasing pressure occurs due to the shear-thickening behavior becoming more important as the pressure increases.

4.2. Role of Microstructure on Deformation

Structural superplastic deformation is known to be highly dependent on microstructure. The role of grain size on superplastic deformation has been well studied, with smaller grain sizes leading to increased strain rates. For example, Wakai found that decreasing the grain size of yttria stabilized zirconia from 2.6 μm to 0.5 μm and increased the strain rate by one order of magnitude during deformation at 10 MPa [38]. Various researchers demonstrated strain rates on the order of 10^{-2} s^{-1} in fine-grain ceramics [39]. For example, Kim et al. achieved strain rates on the order of 10^{-1} s^{-1} in a ceramic composite consisting of tetragonal zirconium oxide, magnesium aluminate spinel, and alumina, all with grain sizes < 300 nm [40]. Additionally, reducing the grain size can reduce the temperature required for superplastic formation. For example, CaF_2 and TiO_2 with grain sizes on the order of <10 nm were found to deform at temperatures as low as 80 $^\circ\text{C}$ and 180 $^\circ\text{C}$, respectively [41].

In contrast to structural superplasticity, solution-precipitation deformation is less sensitive to grain size. For example, Xu et al. performed superplastic deformation experiments on Si_3N_4 with grain sizes as small as 70 nm [42]. They observed strain rates on the order of 10^{-4} s^{-1} , compared to 10^{-6} s^{-1} observed in Si_3N_4 having grain sizes of 1 μm [28]. While not intensely studied, grain size is thought to have little-to-no influence on shear-thickening behavior [30]. It is important to note that shear-thickening does not directly accommodate superplastic deformation on its own. Shear-thickening only modulates the stress dependence of the operative deformation mechanism, usually solution-precipitation-based deformation. Thus, any observed influence of grain size on deformation in shear-thickening materials is the result of the underlying accommodation mechanism, and not the role of shear-thickening directly. For example, Wananurksawong et al. found that finer grain sizes increased the observed strain rates in SiAlON due to solution-precipitation deformation but did not directly modify the shear-thickening behavior [43].

However, changes in grain size can also lead to changes in the deformation mechanisms, such as the transition from creep to superplastic deformation mechanisms with decreasing grain size in many metals [19]. Such changes in the mechanism with changes in grain size occur in both engineering materials as well as geological materials [44]. We observe a decrease in n value with decreasing grain size during high-temperature deformation of TM-HEO below the transition stress and transition temperature (Figure 5). While the change in n between sample CG-SP ($22 \pm 10 \mu\text{m}$ grain size) and sample FG-SP ($1.1 \pm 0.3 \mu\text{m}$ grain size) is relatively small ($n = 2.5$ to 2.1), there is a substantial decrease in n for sample NC-SP ($n = 1.1$), implying a change in the high-temperature deformation mechanism.

While superplastic deformation is highly sensitive to grain size, the activation energies for deformation are often not strongly influenced by grain size. Superplasticity in ceramics is facilitated through one or more diffusion mechanisms, making the activation energy a reflection of the rate-limiting diffusion mechanism. As such, changes in grain size would not be expected to influence activation energy unless there was a change in the mechanism. While there is little difference in activation energies between sample FG-SP ($Q = 240$ to 270 kJ/mol) and sample CG-SP ($Q = 270$ to 310 kJ/mol), the activation energy for deformation in sample NC-SP (70 – 150 kJ/mol) is significantly lower at all applied stresses. The observed decrease in activation energy in sample NC-SP indicates the

emerging influence of another deformation mechanism. We do not observe a grain size dependence in activation energy during deformation above the transition temperature.

The presence of secondary phases is known to influence superplastic behavior. The most common example of this is the use of Zener-pinning particles, which limit grain growth and extend the duration of superplastic formation [20]. In ceramics such as ZrO_2 and Si_3N_4 , the presence of an amorphous phase in the grain boundary is known to enhance superplastic deformation [28,45]. In TM-HEO, we attribute the solution-precipitation and shear-thickening-based superplastic behavior to the presence of the Cu-rich tenorite secondary phase, which forms during heating. As a result, it would be expected that the amount of Cu-rich tenorite secondary phase in TM-HEO would directly influence the high-temperature deformation mechanisms. During deformation at 600 to 650 °C (below the stress transition), samples FG-SP and CG-SP exhibit higher stress exponents of $n \geq 1.5$ compared to their multi-phase counterparts, which exhibit stress exponents of $n = 0.7$ to 1.2 (Figure 5). From this comparison, it might be expected that the single-phase samples deform through a structural superplasticity mechanism below the stress and temperature transition, while the multi-phase samples deform through a solution-precipitation mechanism. However, under these conditions, there is little difference between the activation energies of the four samples (Figure 7), indicating that the phase state is not changing the dominant deformation mechanism. We hypothesize that both structural and solution-precipitation superplastic deformation mechanisms are operative in the multi-phase samples under these conditions.

In our previous study, we observed that smaller grain sizes lead to increased secondary phase formation and enhanced transformation kinetics in TM-HEO, with nanocrystalline samples exhibiting transformation temperatures 200 °C lower compared to their coarse-grain counterparts [6,18]. We attributed this increase in transformation kinetics to the higher concentration of grain boundaries in the nanocrystalline samples, with the Cu-rich tenorite secondary phase forming most readily on the grain boundaries. We would, therefore, expect significantly more Cu-rich tenorite secondary phase to form during deformation in sample NC-SP compared to in the samples with larger grain sizes. For samples FG-SP and CG-SP, the observed deformation behavior fits well with a structural superplasticity model. However, the significantly lower activation energy and stress exponent (Figures 5 and 7) in sample NC-SP indicates the emerging influence of another deformation mechanism with a lower activation energy. We propose that nanocrystalline TM-HEO deforms through the solution-precipitation mechanism instead of through a structural superplasticity mechanism.

The solution-precipitation mechanism requires a secondary phase in the grain boundaries. The high grain boundary concentration, and thus high Cu-rich tenorite concentration, will result in the deformation in nanocrystalline TM-HEO being predominantly facilitated by solution-precipitation through the Cu-rich tenorite grain boundary secondary phase. While the nanocrystalline grain size results in a transition to a new deformation mechanism, it does not alter the shear-thickening transition also observed in the samples with larger grain sizes. The deformation behavior of the nanocrystalline sample is significant in that it demonstrates that the role of as-fabricated grain size on deformation mechanisms in TM-HEO is not straightforward. Instead, there is an interplay between grain size, phase transformation, and deformation behavior that needs to be further investigated.

4.3. Deformation Mechanism Map

In our previous study, we demonstrated that superplastic deformation was a viable method of forming TM-HEO into net-shaped parts [13]. The present study provides insight into the mechanisms underpinning that superplastic deformation. While com-

plex, TM-HEO deforms through known superplasticity mechanisms. As a result, the high-temperature deformation of TM-HEO can be modeled and predicted using existing equations. Combining Equations (1) and (2) results in the full temperature-dependent Norton model:

$$\dot{\epsilon} = B\sigma^n e^{-\frac{Q}{RT}} \quad (6)$$

where B is a constant and $A \neq B$. Our experimental high-temperature deformation results show that both n and Q are stress- and temperature-dependent. Additionally, the dependence of these values changes depending on the stress and temperature regime used during deformation, and the resulting operative deformation mechanisms.

Using Equation (6), we calculate the expected strain rates during the deformation of TM-HEO. Lines of constant strain rate (strain rate contours) are presented in the form of an experimentally derived Ashby deformation mechanism map, as seen in Figure 9 [32]. It is important to note that Ashby deformation mechanism maps are commonly prepared using the equations associated with the deformation model (such as Equations (3)–(5) in this study). However, TM-HEO exhibits superplastic deformation modified by shear-thickening behavior. It is currently unknown how to calculate the combined effects of superplastic deformation and shear-thickening. As a result, our deformation mechanism map is prepared by applying regression analysis to the experimental data. The solid red lines in Figure 9 denote the estimated transition stress and transition temperature values used in this study. We note that the transition stress and transition temperature values are not calculated but are instead estimated based on experimental observations. The gray box in Figure 9 denotes the stress and temperature values investigated experimentally in this study. All data outside the gray box are extrapolated based on the experimental data. To our knowledge, this is the first report of such a deformation mechanism map for a high-entropy ceramic.

Our experimentally derived Ashby deformation mechanism map can be used to estimate the deformation conditions required to form TM-HEO at specific strain rates. Additionally, a qualitative examination of the map can provide some insight on how the high-temperature deformation in TM-HEO differs from other materials. In particular, the relative positioning of the strain rate contours differs compared to other materials. The strain rate contours in TM-HEO become further spread apart from one another as the temperature and pressure increase (the upper-right quadrant of the map), indicating that higher stress and temperature are required to increase strain rate. Most metals exhibit the opposite behavior. The strain rate contours in metals group closer together as temperature and stress increase due to the transition to power-law creep and the activation of dynamic recrystallization [32].

In contrast to metals, ceramics often have highly complex deformation mechanism maps due to their limited dislocation plasticity and more complex diffusion. However, similar to TM-HEO, many ceramics exhibit strain rate contours that spread apart as stress and temperature increase [46]. This increasing spread in strain rate contours in ceramics is often attributed to changes in defect chemistry with temperature. In MgO, for example, increasing temperature leads to a transition in the dominant defects [47]. As a result, the diffusion of oxygen becomes rate-limiting at high temperatures, decreasing the temperature sensitivity of creep in MgO. We can rule out a similar defect-induced transition in TM-HEO for two reasons. First, in contrast to MgO, TM-HEO has been shown to predominantly form oxygen vacancies as its primary defect throughout the temperature range used in this study [24]. Second, the activation energies we observe above the transition temperature are much lower than the activation energy for any known diffusion mechanism in a rocksalt oxide [25,26].

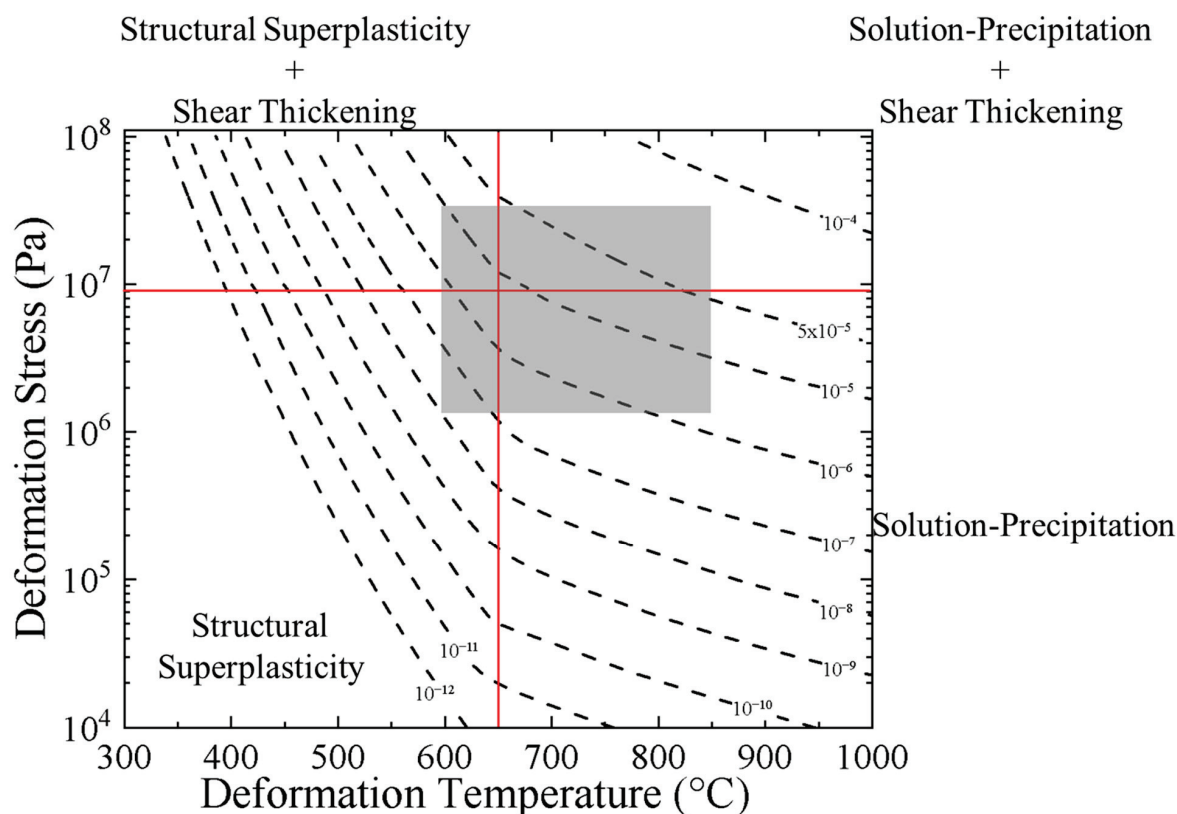


Figure 9. Experimentally derived Ashby deformation mechanism map for the fine-grain single-phase sample (FG-SP). Dashed lines correspond to lines of constant strain rate (strain rate contours). Solid red lines denote the estimated transition stress and transition temperature used in this study, which are used to divide the deformation diagrams into quadrants based on the predominant deformation mechanisms. The gray box denotes the stress and temperature values investigated in this study. All data outside the gray box are extrapolated based on the experimental data.

5. Conclusions

Bulk TM-HEO samples were prepared with variable grain sizes and as-fabricated phase states. These TM-HEO samples were deformed in compression under an applied stress of 5 to 31 MPa and temperatures ranging from 600 to 850 °C. Under all deformation conditions, these TM-HEO samples exhibited stress exponents of $n < 3$, indicating that the deformation occurred through superplasticity. Notably, the mechanism facilitating the superplastic deformation varied based on the temperature and stress. At stresses ≤ 9 MPa and temperatures ≤ 650 °C, the values of the stress exponent ($n = 1$ to 2.5) and activation energy (230 to 310 kJ/mol) indicate that the deformation proceeds through a structural superplastic deformation mechanism. A transition to a solution-precipitation mechanism is observed for deformation at temperatures > 650 °C. We attribute this transition to the observed formation of the Cu-rich tenorite secondary phase during deformation. The deformation in TM-HEO exhibits shear-thickening behavior at applied stress values > 9 MPa. The as-fabricated microstructure influences the deformation behavior, with smaller grain sizes and greater quantities of secondary phase leading to an increased prevalence of solution-precipitation deformation. From our current understanding of the deformation mechanisms, we are able to construct a deformation mechanism map for TM-HEO, the first of its kind for a high-entropy ceramic. Our mechanism map allows for the deformation behavior of TM-HEO to be predicted across a wide range of deformation conditions. Additional variables should be investigated in future research, including chemical compositions beyond the equimolar composition, a wider range of grain sizes, pressures, and

temperatures, and alternative sample geometries, to further elucidate and confirm these deformation mechanisms.

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Article

Compositional Effects on Mechanical Performance of Zirconia–Magnesia–Alumina Ceramics

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Abstract

The study of the relationship between the composition and mechanical properties of structural ceramics based on zirconium, magnesium and aluminum oxides is an important scientific and technological task. In this study, ceramics of the composition $x\cdot\text{ZrO}_2\text{--}(90\text{--}x)\cdot\text{MgO}\text{--}10\cdot\text{Al}_2\text{O}_3$ ($x = 10\text{--}80$ wt.%) were obtained using standard ceramic technology. XRD, SEM, Vickers hardness and biaxial flexural strength measurements were performed to determine the effect of concentration x on the phase composition, microstructure and mechanical characteristics of the sintered samples. The results show that with an increase in the starting concentration x in experimental samples, the fraction of the stabilized ZrO_2 phase grows, and the grain size decreases. These two factors determine the values of microhardness and biaxial bending strength. Experimental investigation on the ternary oxide ceramics shows that for ceramics sintered at 1500°C , the microhardness values varied within the range of 815–1300 HV1 and the biaxial bending strength of 110–250 MPa.

Keywords: alumina; zirconia; composite ceramics; microhardness; flexural strength

1. Introduction

In modern industry, technology, and medicine, engineering structural ceramics occupy an important place, and their advantages are their high thermal resistance, mechanical strength, and chemical inertness [1–3]. Among others, ceramics based on Al_2O_3 , ZrO_2 , and their composites stand out [4,5]. Due to their unique mechanical, thermal, optical and electrical properties, these types of ceramics are used as refractory materials [6], structural materials for work in aggressive environments [7], and have uses in the energy sector and as biomedical materials [8].

Alumina-based ceramics have been among the most readily available and widely used ceramic materials for many years due to their high hardness, high modulus of elasticity, chemical resistance and abrasion resistance [9]. The weak points of Al_2O_3 ceramics include low bending strength and resistance to cracking, which limits their use under conditions of higher mechanical loads [10,11]. Zirconium ceramics, in turn, are known for their unique mechanical properties, such as high hardness, heat resistance, and resistance to cracking due to the mechanism of transformation hardening caused by the phase transition from the tetragonal to the monoclinic phase ($t \rightarrow m$ transition) [12–14]. However, pure ZrO_2 is subject to phase transformations with volumetric change, which can cause microcracks and destruction of the material upon cooling [15].

To stabilize high-temperature phases at room temperature, additives of Y_2O_3 [16], CaO [17], and MgO [18] oxides and rare earth elements [19,20] are used. Yttrium-stabilized zirconium (YSZ), the most studied material of this class, has high mechanical strength, but its application is limited by its high cost [21]. Magnesium oxide stands out as an economical and technologically convenient option, providing an extension of the stability range of t-ZrO_2 and a reduction in the effects of hydrothermal aging characteristic of Y-TZP [22].

Composites based on the $\text{ZrO}_2\text{--MgO--Al}_2\text{O}_3$ system are of wide interest due to the fact that the magnesium oxide in it simultaneously promotes the stabilization of t-ZrO_2 at room temperature and improves the sinterability of Al_2O_3 , and also reacts with Al_2O_3 to form a MgAl_2O_4 spinel, which ensures the formation of a microstructure with a controlled grain size, which further improves crack resistance [23,24]. It is noted that magnesium oxide can stabilize t-ZrO_2 not only directly through the introduction of Mg^{2+} ions into the crystal lattice, but also due to the formation of an amorphous $\text{MgO--Al}_2\text{O}_3$ matrix, which limits the growth of ZrO_2 grains and ensures stability up to 1200°C [25].

An additional factor that has a significant impact on the properties of ceramics is the particle size of the magnesium oxide used as a dopant [26]. In [27], it was shown that the use of MgO nanoparticles (about 80 nm in size) promotes the accelerated sintering of ceramics and the formation of a denser and more uniform microstructure, which has a positive effect on the maximum microhardness of the samples. At the same time, excessive particle size reduction is accompanied by a decrease in crack resistance associated with the agglomeration of nanoparticles and their uneven distribution in the volume of the material. It is noted that the optimal particle size of the MgO dopant is critical to achieve balanced mechanical properties of the composite.

Despite significant progress in the study of $\text{ZrO}_2\text{--MgO--Al}_2\text{O}_3$ ceramics, some aspects remain insufficiently studied. In particular, optimization of the component ratio and temperature treatment conditions are important to achieve a balance between the mechanical characteristics of the obtained composite ceramics. For example, researchers K.L. Meena et al. [28] note that sintering temperatures above 1300°C can lead to a decrease in the strength of $\text{ZrO}_2\text{--MgO--Al}_2\text{O}_3$ ceramics as a result of overheating and grain growth, which also emphasizes the importance of temperature control during annealing. In addition, the study of possible phase transformations, spinel formation and degradation of t-ZrO_2 at high temperatures is a promising direction for further research to develop a material with improved characteristics [29].

This work is devoted to the synthesis of composite ceramics $x\cdot\text{ZrO}_2\text{--}(90-x)\cdot\text{MgO--}10\cdot\text{Al}_2\text{O}_3$ in order to study their microstructure, phase composition and mechanical properties. Despite the wide application of $\text{ZrO}_2\text{--MgO--Al}_2\text{O}_3$ ternary oxide ceramics, there is a lack of comprehensive property–composition–structure studies in the scientific literature for this system. It is known that the ternary system $\text{ZrO}_2\text{--MgO--Al}_2\text{O}_3$ has metastable phases that can significantly change properties such as hardness and strength. As mentioned above, the formation of the MgAl_2O_4 spinel can positively influence the formation of the microstructure of ZrO_2 ceramics. By introducing a fixed concentration of Al_2O_3 , this work investigates the effect of corundum additive on the known binary system $\text{ZrO}_2\text{--MgO}$. The main focus of the research is on the study of the formation of metastable phases, such as c-ZrO_2 and t-ZrO_2 , and their influence on the mechanical characteristics of $x\cdot\text{ZrO}_2\text{--}(90-x)\cdot\text{MgO--}10\cdot\text{Al}_2\text{O}_3$ ceramics. Also, zirconium oxide and magnesium oxide are more refractory materials than corundum. For this reason, the work examines the variation in concentrations between ZrO_2 and MgO with a low content of aluminum oxide. The results of this study are extremely important for the creation of new types of refractories with variable thermodynamic and mechanical characteristics.

2. Materials and Methods

For the synthesis of ceramics from a mixture of oxides $x \cdot \text{ZrO}_2 - (90 - x) \cdot \text{MgO} - 10 \cdot \text{Al}_2\text{O}_3$, where $x = 10, 20, 30, 40, 50, 60, 70, 80\%$ (mass concentration of initial component ZrO_2), a standard ceramic technology was chosen. ZrO_2 , MgO , and Al_2O_3 (Sigma Aldrich, 99.99% purity) were mixed in a Pulverisette 6 planetary mill (Fritsch, Idar-Oberstein, Germany) with tungsten carbide (WC) grinding sets for 30 min at a speed of 250 rpm. To obtain homogeneous compositions, ethanol was added to the mass of dry powders before milling. After mixing, the mixture was dried in a drying cabinet at a temperature of 45 °C for several hours to remove all ethyl alcohol from the composition after milling. To initiate the formation of new phases, the resulting dried powders were pre-annealed at a temperature of 1300 °C for 5 h in a Nabertherm LHT 08/18 muffle furnace (Nabertherm, Lilienthal, Germany) in an air atmosphere in corundum crucibles (“Alita” LLP, Ust-Kamenogorsk, Kazakhstan). After the first annealing, powder X-ray diffractometry (XRD) was performed on a Rigaku SmartLab diffractometer (Rigaku, Tokyo, Japan) to determine the phase compositions using the PDF-2 2024 database. The sintered powders were ground in an ethyl alcohol medium in a Pulverisette 7 premium line planetary micromill (Fritsch, Idar-Oberstein, Germany) at 400 rpm for 30 min using a tungsten carbide grinding jar and grinding balls (Fritsch, Idar-Oberstein, Germany) (grinding ball diameter Ø 1.6 mm). At the outlet, the obtained suspension was analyzed for particle size distribution using a laser particle meter Analysette 22 MicroTec (Fritsch, Idar-Oberstein, Germany) plus with a liquid dispersion unit. Polyvinyl alcohol (PVA) (Sigma Aldrich, 95%, Darmstadt, Germany) was chosen as a plasticizer for the production of green powders. The powders were poured into a hot aqueous solution of PVA at ~90 °C and stirred using a magnetic anchor IKA C-MAG HS7 (IKA-Werke GmbH & Co. KG, Staufen, Germany). Then the pre-dried pressed powders were ground in an agate mortar until a homogeneous powder without obvious large agglomerates was obtained. The collected green powders were completely dried in a drying cabinet at a temperature of 90 °C for 10 h. The concentration of PVA in the finished green powder was 2% of the mass of the synthesized powders. To obtain experimental green tablets, the required amount of powder was poured into a hardened stainless steel mold, previously lubricated with oil. The mold for pressing was placed in an automatic hydraulic press (Paratus, Yekaterinburg, Russia) and a pressure of 5 tons was applied from above to the punch for 5 s, and the same time for 10 tons. Tablets with a diameter of Ø 20 mm and a thickness of 1.5 mm were obtained after pressing. The geometrical parameters of disks after sintering are listed in Supplementary Table S1. Geometrical density was calculated by using measured geometrical parameters of disks and measured mass of the ceramic disks. Archimedes density was calculated after crushing a ceramic disk into pieces with a length of 2–3 mm by using a picnometer and deionized water.

The PVA binder was removed from the ceramic composition by preliminary annealing in a muffle furnace with heating at a rate of 1.6 °C/min and holding at 500 °C for 2 h. The final annealing of the tablets was performed in a Nabertherm LHT 08/18 resistance furnace (Nabertherm, Lilienthal, Germany) in an air atmosphere in corundum crucibles at a temperature of 1500 °C for 5 h. A repeated X-ray phase analysis of the samples after sintering was carried out on the sintered final tablets, which was necessary to determine the formed phases. The microstructure of the sample surface and the elemental composition were studied using a Thermo Fisher Phenom X electron microscope (Thermo Fisher Scientific, Eindhoven, The Netherlands) by acquiring backscattered electron images (accelerating voltage 10 and 15 kV, working distance 8.720 mm). The Vickers method was used to determine the microhardness using a Dupoline-M1 microhardness tester (Duroline-M METKON instruments, Bursa, Turkey) with a load of 1000 gf and dwell time of 10 s in 5 random areas. During the measurements, it was observed that the diamond pyramidal

indenter created indentations covering different grains, so the values of microhardness can be considered as effective values of the composite (see illustrations in Supplementary Figure S19). Prior to microhardness tests, the surfaces of the samples underwent a grinding process on a Tegramin (Struers, Ballerup, Denmark) unit with diamond disks of different roughness and diamond paste. The mechanical strength of the tablets was determined by calculating the biaxial flexural strength [30] (ISO 6872, piston-on-three-ball), which was determined by the formula

$$\sigma_{flex} = \frac{3(1+\nu)P}{4\pi t^2} \left[1 + 2\ln \frac{a}{b} + \frac{(1-\nu)}{(2+\nu)} \left(1 - \frac{b^2}{2a^2} \right) \frac{a^2}{R^2} \right] \quad (1)$$

where σ_{flex} is the biaxial bending strength,

P—the load in N;

ν —Poisson's ratio (0.305);

t—the tablet thickness;

a—the radius of the circle on which the spherical supports are located;

b—the radius of the pin pressing on the tablet;

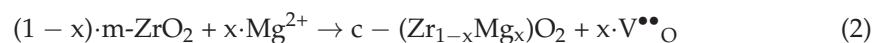
R—the radius of the ceramic tablet.

The test fixture for flexural strength used in the study had the following values of geometrical parameters: $a = 6.5$ mm, $b = 1.13$ mm. The disk compression tests were carried out on a universal electromechanical single-column WalterBai LFM-L 10 kN machine (WalterBai, Lohningen, Switzerland) with a crosshead speed of 0.05 mm/s by compression of 3 disks of the same composition. The sample was mounted on spherical supports, and a movable metal pin was moved from above until the tablet was destroyed.

3. Results and Discussion

Figure 1a shows the particle size distributions after pre-annealing and milling. The distribution histograms are asymmetrical, and the particle sizes range from 0.1 to 5 μm . The wider distribution for samples with a concentration of $x = 10, 20$ wt.% is explained by the large size of agglomerates for the MgO particles, which were used as the starting material (Figures S1c,d and S2b). This may also be due to the solid state reaction occurring with particle coarsening. In addition, at low zirconium oxide concentrations, there is good contact between MgO particles, which apparently leads to better sinterability. With an increase in the ZrO_2 concentration, the sinterability of MgO and Al_2O_3 particles deteriorates, since neither MgO nor Al_2O_3 form new compounds with ZrO_2 under pre-annealing conditions [31]. Also, the size of the initial ZrO_2 powder was less than 1 μm , which determined the small size and narrow distribution of the pre-annealed particles. The dependence of the average particle size on the starting concentration x is shown in Figure 1b. The increase in the average particle size at the last concentration $x = 80$ wt.% can also be associated with better sinterability of the zirconium dioxide particles, which constitute the basis of the mixture.

Figure 2 reveals the XRD patterns for all pre-annealed powders. The main phases on the figure are depicted by special symbols, and dotted drop lines were added to indicate the peaks of each phase. The XRD patterns show the presence of peaks of four main phases: monoclinic zirconia m- ZrO_2 , periclase (magnesium oxide), spinel MgAl_2O_4 and stabilized cubic zirconia c- $(\text{Zr}_{1-x}\text{Mg}_x)\text{O}_2$. It can be stated that during pre-annealing in the $x\cdot\text{ZrO}_2$ -(90- x)-MgO-10- Al_2O_3 mixture, the following solid-state chemical reactions occur [32]:



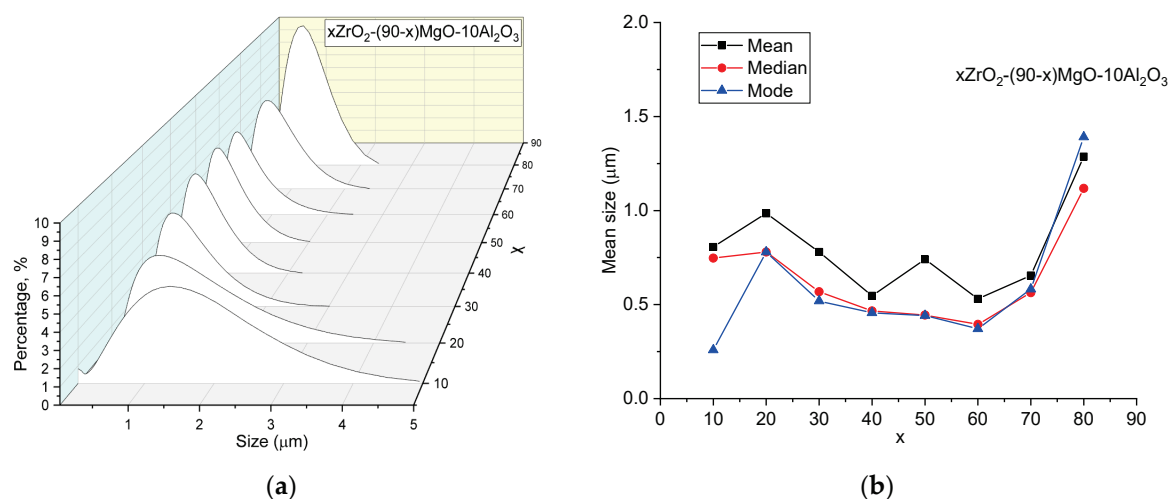


Figure 1. Size distribution of milled powders after pre-annealing at 1300 °C (a) and the dependence of mean and median sizes and modes of distributions from starting concentration x (b).

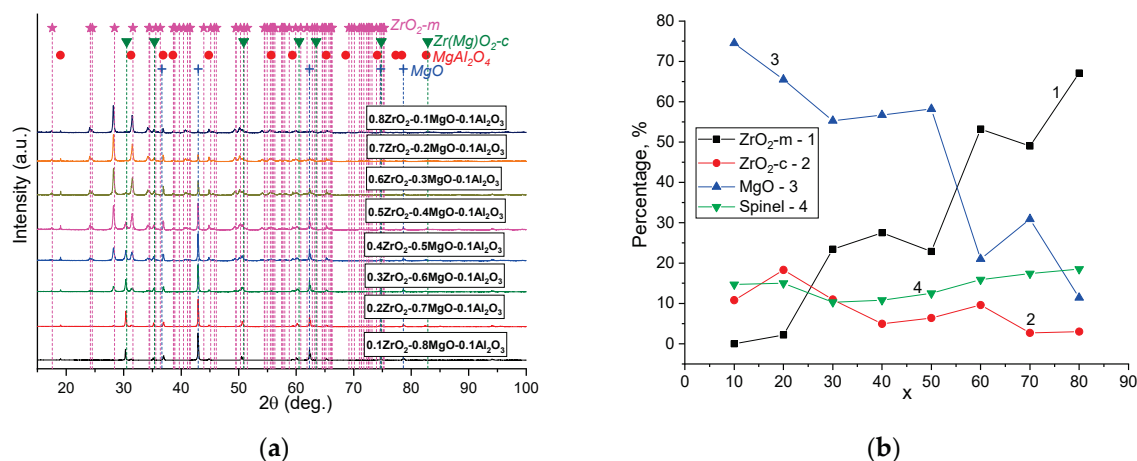


Figure 2. XRD patterns (a) and phase composition of powders after preliminary annealing (b).

A full-profile analysis was performed on the experimental diffraction patterns using the Rietveld method [33]. Statistical parameters of fitting, such as R_{wp} and R_p , were in the range of 6.88–8.61 and 5.19–6.71, respectively. The results of the analysis are presented as dependences of the concentration of each of the above-mentioned phases on the concentration x (Figure 2b). Some discrepancies in the phase composition according to the diffraction pattern analysis from the nominal composition of the batch are explained by the high adsorption coefficient of X-rays of magnesium oxide. From the obtained dependencies it is important to highlight that the proportion of stabilized zirconium dioxide is within 5–18 wt.%. This indicates an insufficient temperature for the formation of substituted stabilized zirconium dioxide.

The density and volume shrinkage of the tablets sintered at 1500 °C were estimated by measuring the thickness, diameter, and weight before and after sintering. The results of the density and shrinkage calculations are shown in Figure 3a,b. As is evident from Figure 3a, the density of the sintered ceramic tablets increases as the concentration x grows according to a linear relationship. This tendency of the curve can be explained by the fact that the composition of the ceramics changes in such a way that the component with a lower physical density (periclase, MgO) is substituted by a component with a high density (ZrO_2). Volume shrinkage, on the other hand, decreases with increasing concentration x , and on the curve one can distinguish two slopes, which can correspond to different sintering mechanisms. Explanations for this will be given below.

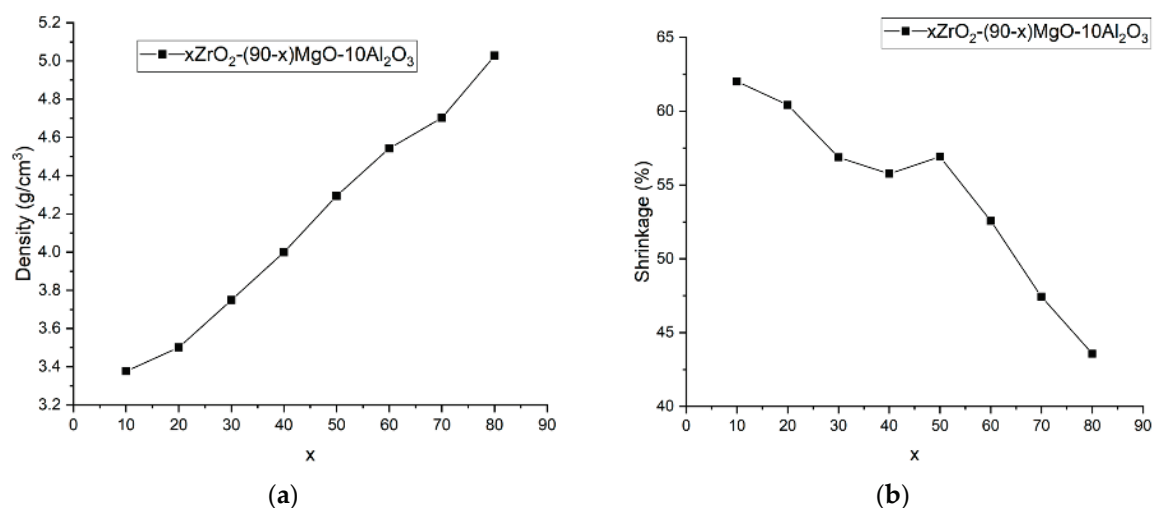


Figure 3. Dependence of apparent density (a) and volume shrinkage (b) on x.

The XRD patterns in the $2\theta = 15\text{--}100^\circ$ range of the sintered tablets are shown in Figure 4a. To clarify the main features, XRD patterns were also plotted in the $2\theta = 20\text{--}50^\circ$ range in Figure 4b and separately in the Supplementary Files (Figures S3–S10). As can be seen from Figure 4a,b, the XRD patterns show reflections from the periclase phases, magnesium–aluminum spinel, and monoclinic zirconium, as well as cubic and tetragonal zirconium dioxide. Small peaks of the secondary phases of silica, CaWO_4 and Mg_2SiO_4 also are presented in the XRD pattern due to possible contamination from the corundum crucible or muffle lining. The intensities of the reflections corresponding to the c- ZrO_2 phases are significantly higher compared to the diffraction patterns recorded on pre-annealed powders, indicating an intense reaction (2) at 1500°C . An unexpected result is that for the sample with a concentration of $x = 60$ wt.%, a significant increase in the intensities of the reflections of the monoclinic phase of ZrO_2 is observed. Some XRD patterns show the presence of a CaWO_4 phase, which occurred after the decomposition of tungsten carbide. The tungsten carbide particles contaminated pre-annealed powders during grinding and oxidized with the formation of CaWO_4 .

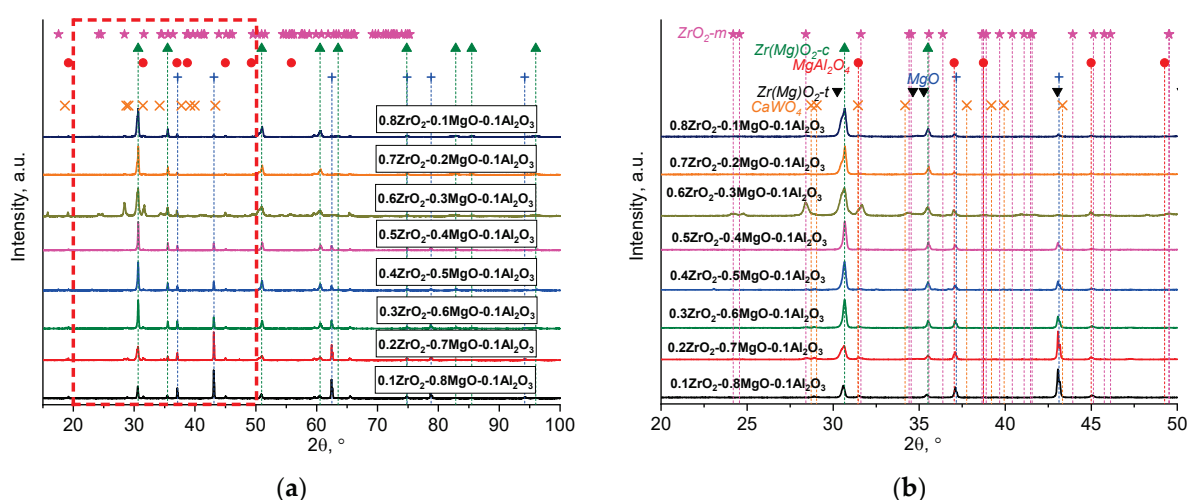


Figure 4. XRD patterns of tablets sintered at 1500°C in the range of angles $15\text{--}100^\circ$ (a) and $20\text{--}50^\circ$ (b).

The microstructure of the sintered tablet's unpolished surface is shown in the SEM images in Figure 5. As can be seen from the images, two contrasting areas can be distinguished—light grains and dark grains. The dark areas correspond to MgO and

Mg-Al spinel grains, while the light ones correspond to the c-ZrO₂ phase. For better illustration, EDX elemental maps are also shown in Supplementary Figures S11–S18. MgO grains are rounded and larger in size, reaching 10 µm at low concentrations, while spinel grains are polygonal. Some micrographs show grains of tungsten oxide or wolframite. The surface of the zirconium dioxide grains, starting with a concentration of $x = 20$ wt.%, has a developed morphology with extended pores, grooves and convolutions. Based on the results of ZrO₂-MgO ceramics, where high-resolution electron microscopy images are available, this type of zirconium dioxide grain is acquired due to the eutectoid decomposition $c\text{-(Zr}_{1-x}\text{Mg}_x\text{)O}_2 \rightarrow m\text{-(1-x)ZrO}_2 + x\text{MgO}$ [34,35]. In addition, high-temperature annealing can cause the volatilization of Mg atoms from the ceramic surface [36]. During the volatilization process, defective regions with a high concentration of vacancies are created, which migrate along the grain surface and form extended voids.

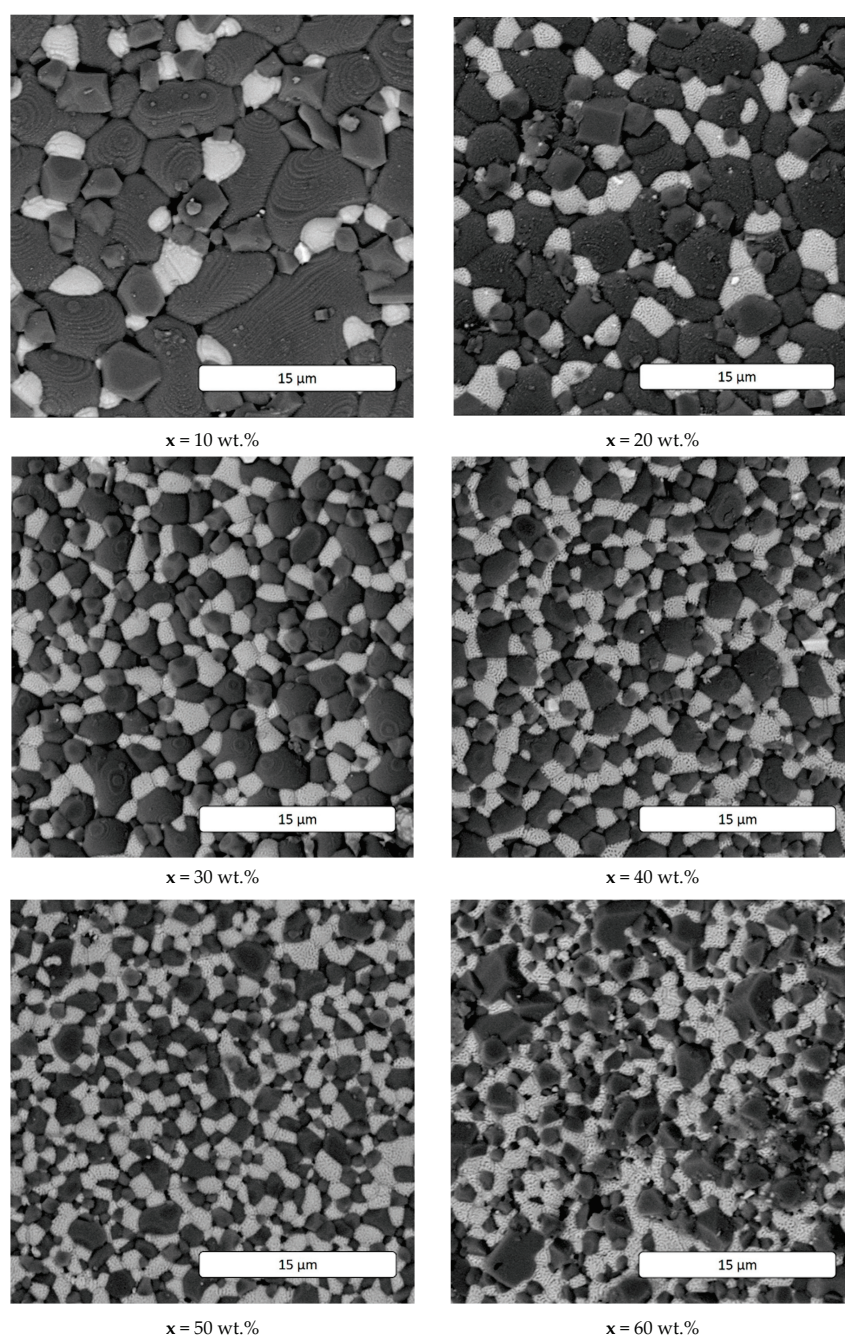


Figure 5. Cont.

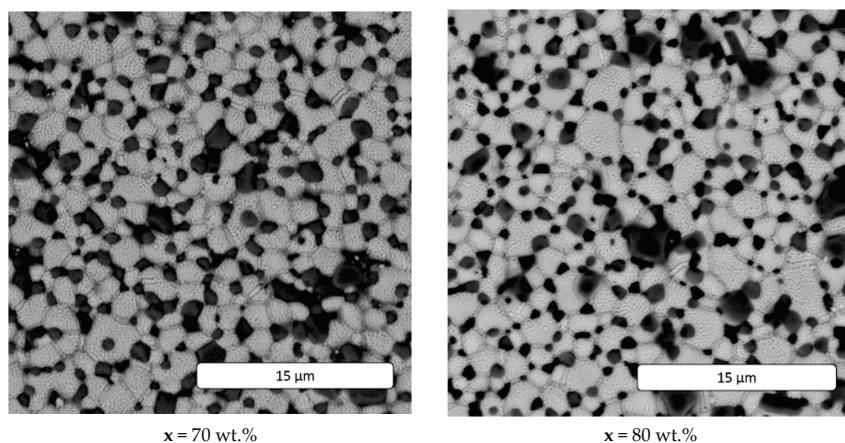


Figure 5. SEM images of the surface of sintered tablets.

As the concentration x increases, the grain size of the zirconia (inclusion phase) grows and the matrix phase $\text{MgO}/\text{MgAl}_2\text{O}_4$ changes places with ZrO_2 and becomes the inclusion phase. The change in grain size distribution with elevation of concentration x can also be traced in the grain size distribution histograms in Figure 6. Samples with a large amount of periclase have wide distributions and high shrinkage values (Figure 3b). As concentration x increases, MgO particles present in the powders can act as inhibitors of zirconium dioxide grain growth [25]. In this case, the shrinkage of the samples will decrease, and the grain size will be smaller than in ceramics with excess MgO .

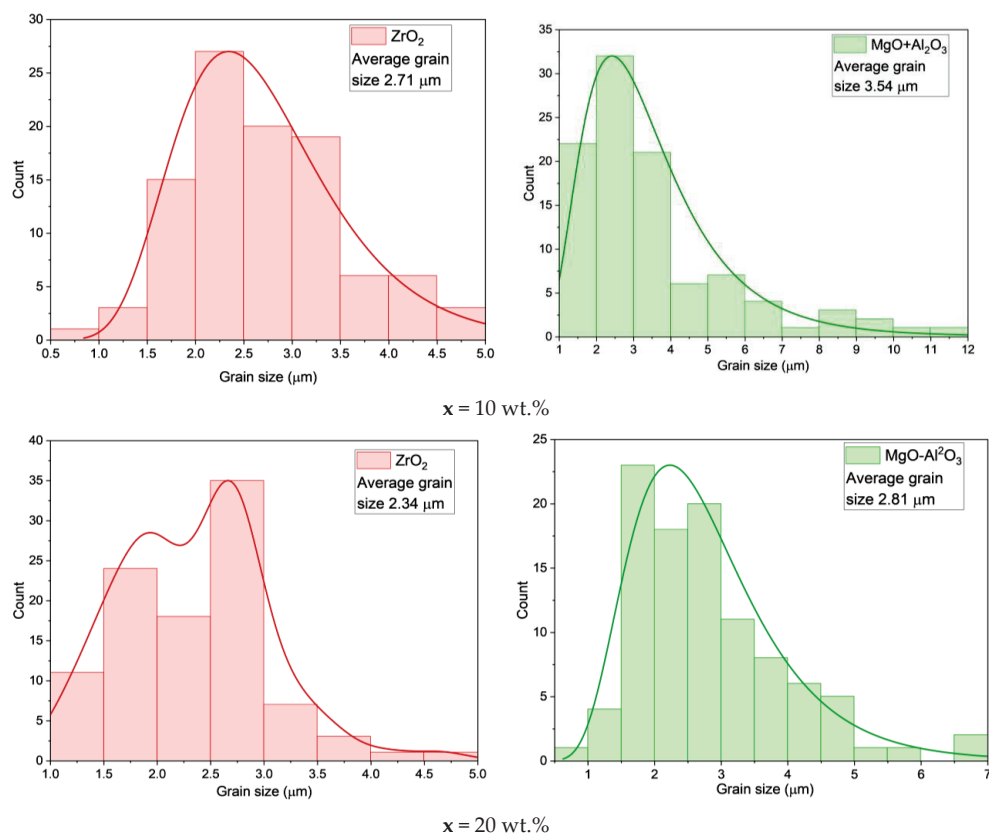


Figure 6. *Cont.*

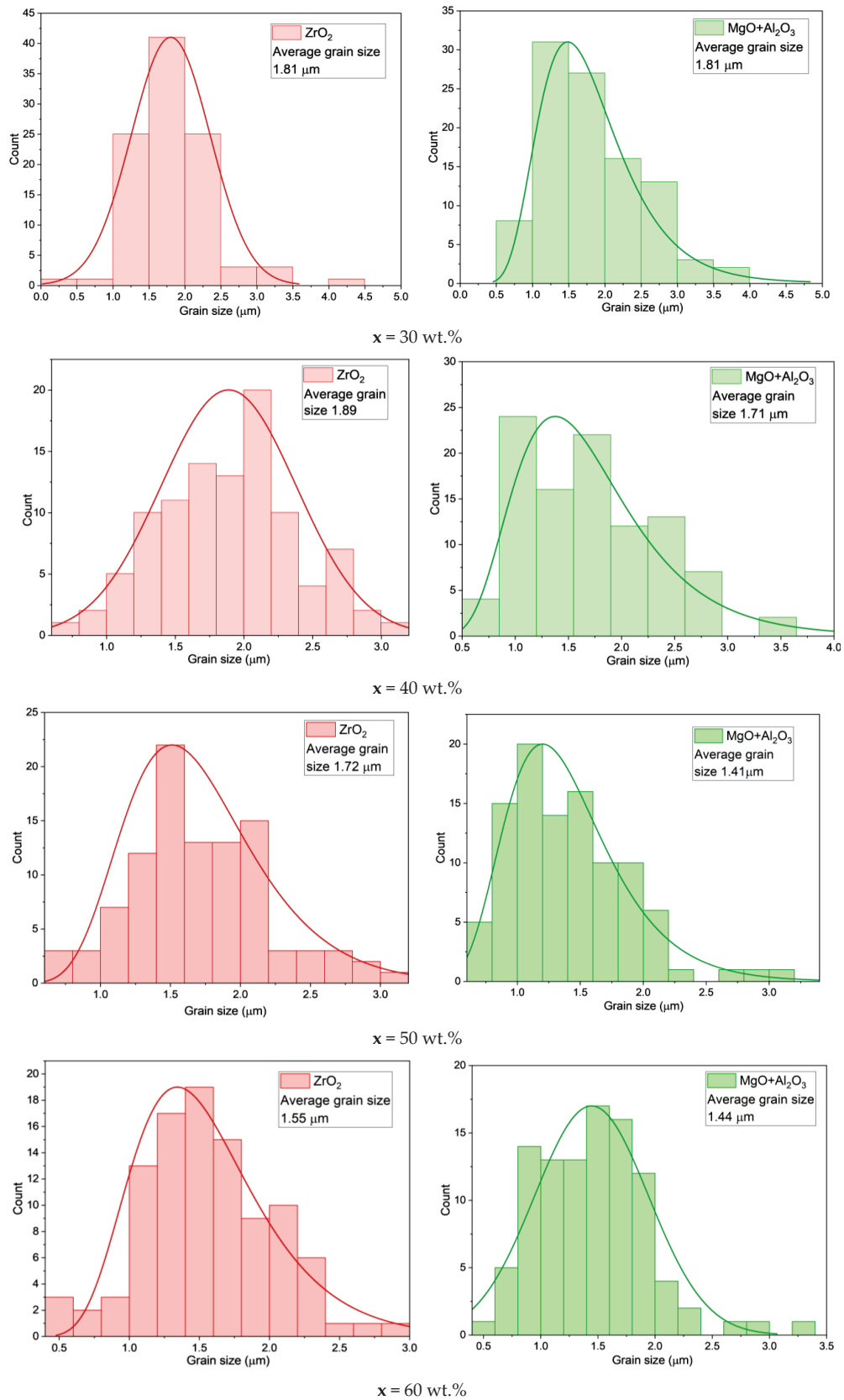


Figure 6. Cont.

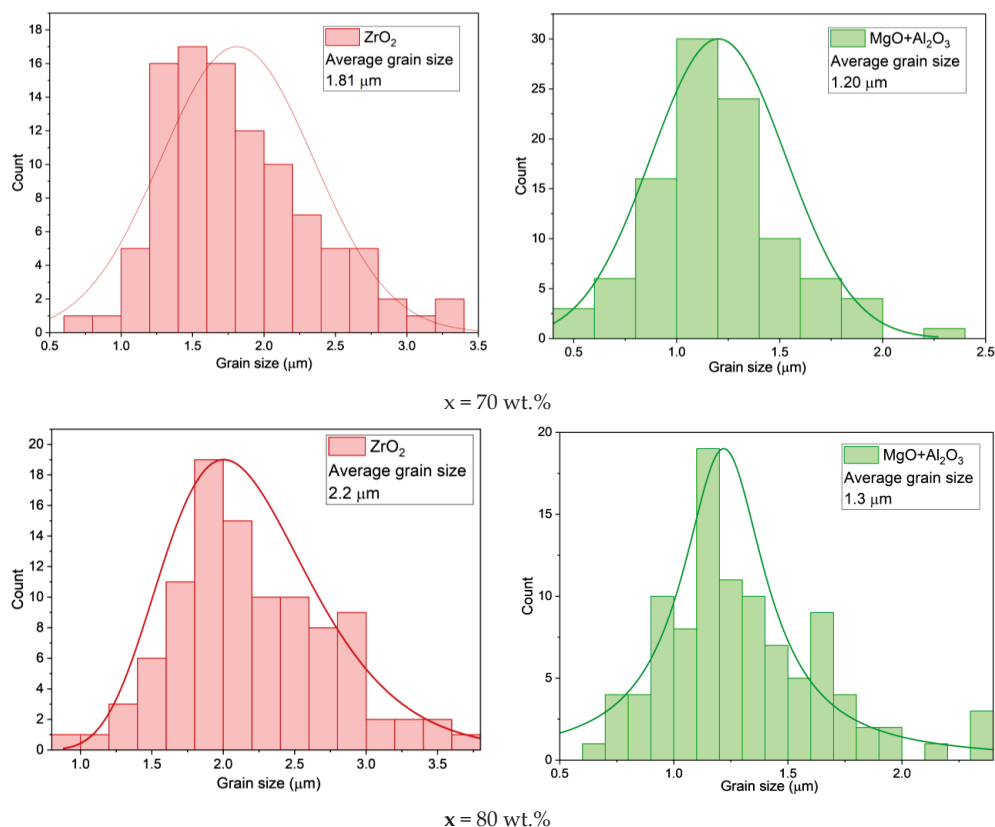


Figure 6. Distribution of grain sizes of zirconium dioxide and MgO, Al₂O₃.

The mechanical characteristics of the sintered ceramics were assessed by measurement of the Vickers microhardness and the biaxial flexural strength. Table 1 illustrates the obtained values of the above characteristics for all concentrations of x . A comparison of these dependences shows that the changes in HV and σ_{flex} have sections with the same characteristic bends. At initial concentrations ($x = 10$ wt.%), a slight increase with a plateau was observed for the HV dependence. For $\sigma_{flex}(x)$, a continuous growth up to the point $x = 50$ wt.% was observed. Such behavior is associated with a change in the phase composition and microstructure.

Table 1. The comparison of phase composition, phase content, statistical parameters of Rietveld refinement, HV microhardness, and σ_{flex} among obtained ceramics.

x , wt. %	Phase Name	Phase Content, %	Statistical Parameters				ρ_{exp} , g/cm ³	Open Porosity, %	HV1	σ_{flex} , MPa
		R_{wp} , %	R_p , %	R_e , %	χ^2					
10	c-ZrMgO ₂	11.53 ± 0.09	8.04	6.02	7.3	1.2106	3.3368	6.86	830 ± 38	122 ± 4.76
	MgO	74.05 ± 0.02								
	MgAl ₂ O ₄	13.09 ± 0.17								
	CaWO ₄	1.33 ± 0.09								
20	c-ZrMgO ₂	12.2 ± 0.03	8.05	6.03	7.3	1.2123	3.5012	5.59	832 ± 51	146 ± 11.41
	MgO	56.7 ± 0.05								
	MgAl ₂ O ₄	18.5 ± 0.02								
	m-ZrO ₂	5.2 ± 0.02								
	t-ZrO ₂	6.21 ± 0.03								
30	CaWO ₄	1.19 ± 0.07	10.49	7.54	6.82	2.3663	3.7488	5.39	898 ± 70	150 ± 6.57
	c-ZrMgO ₂	40.1 ± 0.03								
	MgO	32.2 ± 0.03								
	MgAl ₂ O ₄	26.4 ± 0.04								
	m-ZrO ₂	0.0								
	CaWO ₄	1.30 ± 0.16								

Table 1. Cont.

x, wt. %	Phase Name	Phase Content, %	R _{wp} , %	Statistical Parameters R _p , %	R _e , %	χ ²	ρ _{exp} , g/cm ³	Open Porosity, %	HV1	σ _{flex} , MPa
40	c-ZrMgO ₂	46.3 ± (5)	11.15	7.68	6.69	2.7734	3.9999	5.91	1037 ± 12	208 ± 11.07
	MgO	28.2 ± (4)								
	MgAl ₂ O ₄	13.2 ± (3)								
	CaWO ₄	7.2 ± (6)								
	Mg ₂ SiO ₄	5.1 ± (6)								
50	c-ZrMgO ₂	47.2 ± 0.04	7.62	5.78	6.64	1.3124	4.2942	2.78	1037 ± 12	250 ± 15.16
	MgO	25.6 ± 0.05								
	MgAl ₂ O ₄	26.8 ± 0.03								
	CaWO ₄	0.4 ± 0.03								
60	c-ZrMgO ₂	38.5 ± 0.03	10.38	7.74	6.57	2.4932	4.5432	0.34	736 ± 19	113 ± 3.73
	MgO	10.1 ± 0.02								
	MgAl ₂ O ₄	18.3 ± 0.03								
	m-ZrO ₂	26.5 ± 0.02								
	Si ₁₉₂ O ₃₈₄	6.6 ± 0.03								
70	c-ZrMgO ₂	42.9 ± 0.03	8.78	6.94	6.54	1.7977	4.7018	11.93	777 ± 7	151 ± 6.47
	MgO	0.46 ± 0.07								
	MgAl ₂ O ₄	5.34 ± 0.04								
	m-ZrO ₂	4.3 ± 0.03								
	t-ZrO ₂	47 ± 0.02								
80	c-ZrMgO ₂	44.6 ± 0.02	8.05	6.07	6.34	1.6058	5.0280	1.61	1312 ± 14	211 ± 10.24
	MgO	6.7 ± 0.04								
	MgAl ₂ O ₄	11.9 ± 0.07								
	m-ZrO ₂	7.4 ± 0.05								
	t-ZrO ₂	29.4 ± 0.10								

The increase in the values of mechanical properties may be associated with an elevation in the proportion of the stabilized zirconium dioxide phase c-ZrO₂ and a decrease in the average grain size. As can be seen from Figure 7a the average grain size for the ZrO₂ phase and the MgO, Al₂O₃ phases decreases, and the proportion of the stabilized phase c-ZrO₂ grows in the concentration range of x = 10–40 wt.%. It is important to highlight that despite the increase in porosity from ~10 to 13.5% (see Supplementary Table S4), the values of microhardness and flexural strength grow, indicating that it is the phase composition that determines the strength characteristics of sintered ceramics. It is known from the literature that the microhardness of magnesium oxide and spinel is lower than that of stabilized zirconium dioxide [37,38]. Since the object of study is composite ceramics, then according to the effective medium theory, the properties of the composite will be determined by the concentration of the components of the composite [39]. As the proportion of periclase decreases, the proportion of stabilized zirconium dioxide increases, enhancing the strength of the sintered ceramic. The contribution to the effective values of HV1 and σ_{flex} from the MgAl₂O₄ phase is not decisive due to the fact that its concentration is in the range of 5–25%. Also, in zirconium dioxide, there is a known transformation strengthening mechanism in which there is a phase transition to a monoclinic phase, in which the crack loses its energy and has no ability to propagate further [15,40]. For this reason, the content of stabilized zirconium dioxide can determine the final properties of composite ceramics. An additional mechanism leading to strengthening can be attributed to the following. As the average grain size shrinks, the area of intergranular boundaries, which have a higher concentration of dislocations, grows. High concentrations of dislocations can also stop cracks and increase the values of microhardness and bending strength [41,42].

Since pores are dislocation concentrators, the propagation of cracks will inevitably occur through their accumulations in the volume [43]. This is what causes the low values of mechanical properties of ceramics with concentrations of x = 10–30 wt.% (see Figure 7b and Table 1). The porosity of the above samples is in the range of 10–14%, while HV has a value of less than 1000, and σ_{flex} < 200 MPa. The porosity values above are due

to the asymmetrical wide distribution of particles after annealing and milling (Figure 1). The maximum value of $\sigma_{flex} = 250$ MPa in Table 1 is directly related to the decrease in porosity in the ceramic disks. For the sample with a concentration of $x = 50$ wt.%, the minimum porosity was found with a value of 3% (Figure 7b). The porosity was calculated using the formula $(1 - \rho_{exp} / \rho_{theo}) \cdot 100\%$, where the geometrical density from Figure 3a was used as the experimental density. More information about porosity calculation can be found in Supplementary Tables S2–S4. In addition to low porosity, sintered ceramics with a concentration of $x = 50$ wt.% have a high stabilized zirconium dioxide content, which also determines the highest biaxial flexural strength value. Overall, it can be seen that mechanical characteristics mainly depend on open porosity in sintered ceramics (see Supplementary Table S4). This is due to the connectivity of pores which results in creating a path for crack propagation [43,44].

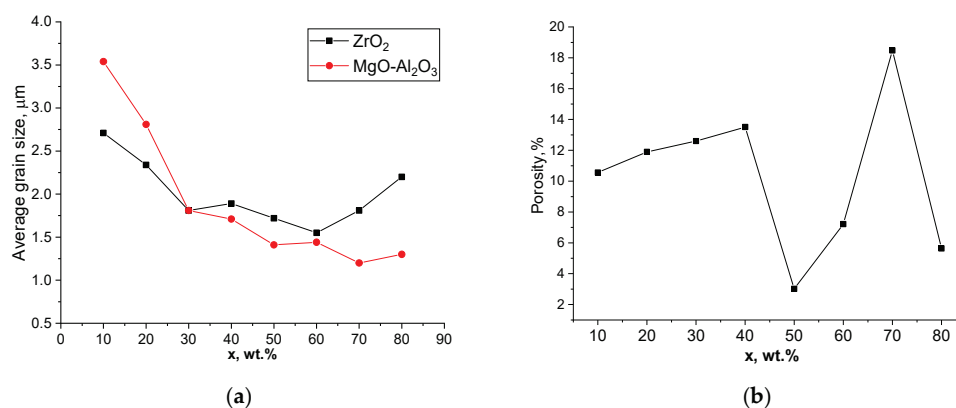


Figure 7. Dependence of the average grain size (a) and total porosity (b) on the starting concentration x .

As the concentration x grows to 60 wt.%, a dramatic decrease in the HV and σ_{flex} values is observed. This change correlates with a sharp increase in the proportion of the monoclinic phase of ZrO_2 , which was found by analyzing the experimental XRD patterns using the Rietveld method (see Table 1). A possible explanation for this effect can be found by analysis of the SEM images (Figure 5). As the study of the microstructure showed for the sample with $x = 60$ wt.%, there is an uneven distribution of the components of the composite ceramics compared to the other samples. Apparently, the clusters of MgO and MgAl_2O_4 grains are the main reason for the transition of the stabilized $c\text{-ZrO}_2$ phase to the monoclinic ZrO_2 . This may occur by the following mechanism. During annealing, Mg atoms possibly volatilize on the grain surface. If there are no MgO periclase grains near the $c\text{-ZrO}_2$ grain, then the diffusion of Mg ions from the grains in the ceramic volume into the ZrO_2 crystal lattice does not occur. This subsequently leads to an increase in the proportion of the monoclinic phase and a decrease in the HV and σ_{flex} values, because of the absence of the stabilizing dopant. Regarding the reasons for the uneven distribution of grains in the microstructure, it can be noted that for the sample $x = 60$ wt.%, a fairly high concentration of MgAl_2O_4 was found in the pre-annealed powders. Since MgAl_2O_4 is a highly stable oxide, then at a sintering temperature of 1500°C , stabilization of zirconium dioxide according to Equation (2) is unlikely, since Mg ions will not leave the MgAl_2O_4 grains [45]. A surprising fact is that for the sample with the highest porosity of 18% ($x = 70$ wt.%), the mechanical property values are comparable with less porous samples. This observation can be explained by the increased content of the tetragonal phase $t\text{-ZrO}_2$, which is characterized by the highest crack resistance among oxide technical ceramics. This surprising fact also points to the decisive contribution of the phase composition to the final properties of $x\text{-ZrO}_2\text{-(}90-x\text{)-MgO-}10\text{-Al}_2\text{O}_3$ ceramics.

A comparison of the measured values of mechanical properties with the results from recent studies is given in Table 2. As can be seen from the table, the values of biaxial flexural strength of some ceramics based on aluminum oxides and zirconium oxide exceed the values obtained in this work by 2–6 times. However, to obtain these ceramics, sintering regimes with much lower heating rates and controlled cooling were used. In addition, most studies used commercial nanoscale or submicron powders as starting materials. The use of micron pre-annealed powders in this work results in high porosity, which reduces the σ_{flex} values. However, conducting experiments with micron powders brings the laboratory experiment closer to production conditions. We believe that by selecting the sintering mode, it is possible to achieve comparable results in such indicators as flexural strength and compressive strength. This assumption is also supported by the fact that the ceramics obtained in this work achieve microhardness values comparable to those obtained by other researchers. The sintering regimes used in this work are suitable for producing porous ceramics, for example for thermal insulation applications.

Table 2. Comparison between composition of ceramics, synthesis method, starting powder size, σ_{flex} , microhardness, and porosity in recent publications and this work.

Composition of Ceramics	Synthesis Method	Starting Powder Size, μm	σ_{flex} , MPa	Microhardness	Porosity, %	Reference
$\text{Al}_2\text{O}_3\text{:ZrO}_2 = 3:1$ with SrO , Cr_2O_3 doping	Conventional processes with pressing and sintering, 1600 °C	0.15–0.20	501 ± 21	$\text{HV}1658 \pm 28$	Low, fully dense	[46]
ZTA- Cr_2O_3	Conventional processes with pressing and sintering, 1450 °C, 2 °C/min heating rate, 3 h hold, 10 °C/min cooling rate	-	546 ± 59	-	4.09	[47]
ZTA-MgO	Conventional processes with pressing and sintering, 1450 °C, 2 °C/min heating rate, 3 h hold, 10 °C/min cooling rate	-	915 ± 41	-	6.17	[47]
ZrO_2 92.5; Al_2O_3 0.07; SiO_2 0.58; MgO 0.14; Na_2O 0.14; K_2O 0.07; SnO_2 0.15; Y_2O_3 4.67; HfO_2 1.64.	Printed via digital light processing, Ramp-up rate 0.2–0.5 °C/min, 1500 °C, 2 h sintering	-	650 ± 76	$\text{HV}1359 \pm 35$	-	[48]
1 mol% Y_2O_3 ; 12 mol% Al_2O_3 ; 1 mol% CoO ; 7 mol% CeO_2 ; 1 mol% Fe_2O_3	Conventional processes with pressing and sintering 1550–1620 °C	0.01–0.04	606 ± 148	-	-	[49]
Zirconia	DLP printed, 30 h of debinding 1100 °C, 1500 °C with dwell time 5 h of sintering	-	1238 ± 327	-	Fully dense	[50]
5Y-PSZ	DLP printed, 30 h of debinding 1100 °C, 1500 °C with dwell time 5 h of sintering	-	1059 ± 178	$\text{HV}1590 \pm 24$	Fully dense	[51]

Table 2. Cont.

Composition of Ceramics	Synthesis Method	Starting Powder Size, μm	σ_{flex} , MPa	Microhardness	Porosity, %	Reference
Zirconia	FDM printed and milled, conventional sintering at 1500 °C with dwell time 2 h	0.4–0.6	1241 ± 200	$\text{HV}1622 \pm 216$	-	[52]
$x\text{-ZrO}_2\text{-(90-x)-MgO-10-Al}_2\text{O}_3$	Conventional processes with pressing and sintering, 10 °C/min, 1500 °C, 5 h	0.8–1.25	250 ± 15.16	$\text{HV}1312 \pm 14$	3–18.5	This Work

The main novelty of this work is the study of the property–composition–structure interactions in multicomponent ceramics $\text{ZrO}_2\text{-MgO-Al}_2\text{O}_3$. In particular, it was found that the formation of the metastable phase $t\text{-ZrO}_2$ and $c\text{-ZrO}_2$ significantly improves the mechanical characteristics and helps to reduce porosity. It was found that despite the high porosity in ceramics with $t\text{-ZrO}_2$ and $c\text{-ZrO}_2$ phases, higher values of bending strength and microhardness are observed compared to dense samples with a high content of the $m\text{-ZrO}_2$ phase.

4. Conclusions

In this work, ternary oxide ceramics with the composition of $x\text{-ZrO}_2\text{-(90-x)-MgO-10-Al}_2\text{O}_3$ ($x = 10\text{--}80$ wt.%) were obtained using the standard ceramic technology with preliminary annealing of powders. A comprehensive study using XRD, SEM and mechanical tests showed that with a change in the concentration of x , the microstructure, microhardness and flexural strength varied significantly. Preliminary annealing at 1300 °C initiates the formation of MgAl_2O_4 and $c\text{-ZrO}_2$ phases, but the concentration of the latter does not exceed 20 wt.% according to the results of Rietveld analysis. After sintering the tablets at 1500 °C, the phase composition changes and the content of the stabilized zirconium dioxide phase can reach 90 wt.%. At low x concentrations in the range of 10–40 wt.%, the high porosity of the ceramics is due to the large initial size of the MgO particles. Despite the relatively high porosity, the high HV and σ_{flex} values are mainly due to the change in phase composition. With a decrease in the proportion of periclase MgO and an increase in the proportion of $c\text{-ZrO}_2$ at a concentration of $x = 50$ wt.%, high values of microhardness of 1000 HV and biaxial bending strength of 250 MPa were found. In the microstructure of sintered ceramic disks above the concentration of $x = 10$ wt.%, ZrO_2 grains with a developed morphology, which arises due to the volatilization of Mg atoms and eutectoid decomposition, were found. The uneven distribution of grains of different phases in the volume leads to a significant deterioration in mechanical properties. This is due to the formation of an unstabilized $m\text{-ZrO}_2$ phase in the composition of the final ceramics.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/ceramics8030114/s1>, Figure S1: Size distribution of initial powders obtained by SEM (a), (c), (e) and by laser analyzer (b), (d), (f) for ZrO_2 , MgO and Al_2O_3 , respectively; Figure S2: SEM images of starting powders ZrO_2 (a), MgO (b) and Al_2O_3 (c); Figures S3–S10: XRD patterns with corresponding phases from PDF database (a) and results of Rietveld fitting (b) for the samples with concentration $x = 10\text{--}80$; Figures S11–S18: Surface EDX maps for $x = 10\text{--}80$ wt.%. (a) SEM; (b) Zr; (c) Al; (d) Mg; Figure S19: Representation view of the indents; Table S1: Values of geometrical parameters of sintered tablets (R —radius of tablet, t —thickness of tablet); Table S2: Values of theoretical density used for effective theoretical density calculations; Table S3: Comparison between geometrical density (ρ_{exp}), Archimedes density (ρ_A) and effective theoretical density (ρ_{theo}) of sintered disks; Table S4: Comparison between total porosity, closed porosity and open porosity of sintered disks.

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Article

Synergistic Effects of SiC_w and Ni Addition on the Densification and Mechanical Properties of (M_{0.2}Ti_{0.2}Ta_{0.2}V_{0.2}Nb_{0.2})B₂ (M=Hf, Zr, or Cr) High-Entropy Ceramics

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Abstract

The improvement of densification and fracture toughness in high-entropy ceramics is important to realizing their practical applications. In this study, SiC whiskers and metal Ni additions were incorporated to solve these problems of high-entropy boride ceramics. The influence of sintering temperatures (1450–1650 °C) on the densification, microstructure, hardness, fracture toughness, and bending strength of (M_{0.2}Ti_{0.2}Ta_{0.2}V_{0.2}Nb_{0.2})B₂-SiC_w-Ni (M = Hf, Zr, or Cr) composites prepared by hot-pressing technology were studied. Results showed that when SiC whiskers and metal Ni additions were used as additives, increasing sintering temperatures from 1450 to 1600 °C promoted the densification of high-entropy boride ceramics. This was mainly attributed to the high sintering driving force. However, when the temperature further increased to 1650 °C, their densification behavior decreased. At a sintering temperature of 1600 °C, these high-entropy borides ceramics all had the highest densification behavior, leading to their high hardness and fracture toughness. The highest relative density was 96.3%, the highest hardness was 22.02 GPa, and the highest fracture toughness was 13.25 MPa·m^{1/2}, which was improved by the co-function of SiC whiskers and plastic metal Ni. Meanwhile, in the adopted sintering temperature range of 1450 to 1650 °C, the highest bending strength at room temperature of these high-entropy boride ceramics could reach 320.8 MPa. Therefore, this research offers an effective densification, strengthening, and toughening method for high-entropy boride composites at a low sintering temperature.

Keywords: high-entropy boride ceramic; SiC whiskers; metal Ni; densification; hardness; fracture toughness; bending strength

1. Introduction

High-entropy boride (HEB) ceramics, as a new category of ceramics, have received significant research attention owing to their outstanding characteristics of a high melting temperature, enhanced corrosion resistance, high hardness, good oxidation resistance properties, and so on [1–5]. Meanwhile, they exhibit potential applications in the fields of cutting tools, thermal protective materials, wear-resistant materials, microwave materials, and ultra-high-temperature materials [6–8]. In 2016, high-entropy boride ceramics

were synthesized for the first time by Gild et al. [2], and their relative density could reach about 92% using spark plasma sintering (SPS) technology. Since then, the preparation (various synthesizing methods of high-entropy powders and sintering technologies of bulk materials) and properties (hardness, fracture toughness, bending strength, oxidation resistance, and so on) of high-entropy boride ceramics or composites has been a research hotspot. For high-entropy boride ceramics or composites, many studies have realized improved densification behavior and increased properties. However, high temperature ($>1800\text{ }^{\circ}\text{C}$) is still required for sintering densification owing to a high covalent bonding strength and a low interdiffusion coefficient [9–11]. Therefore, low-temperature densification is necessary to obtain high-entropy boride ceramics or composites with high densification and excellent properties.

Liquid phase sintering can realize the low-temperature densification of high-entropy boride ceramics or composites by promoting mass transfer in the formed liquid phase. In recent years, most research has also focused on the development of high-entropy ceramics using the metallic phase as a sintering aid, which can effectively improve low-temperature densification and further result in excellent properties [5,12–14]. Xu et al. [5] prepared $(\text{Hf,Zr,Ta,Nb,Ti})\text{B}_2$ composites by introducing 5 vol% cobalt as a sintering aid via spark plasma sintering (SPS) at $1500\text{ }^{\circ}\text{C}$; the relative density was 99.5% and the hardness reached $24.90 \pm 1.39\text{ GPa}$. Luo et al. [13] also fabricated $(\text{Ti,Zr,Nb,Ta,Mo})\text{C-Co}$ materials via the liquid phase sintering of SPS using Co as a sintering aid at $1350\text{ }^{\circ}\text{C}$; the hardness was $24.11 \pm 0.75\text{ GPa}$ and fracture toughness reached $4.07 \pm 0.13\text{ MPa}\cdot\text{m}^{1/2}$. Additionally, Anwer et al. [15] successfully prepared $(\text{Ti,V,Nb,Ta,W})\text{C}$ cermets with full densification using 12 vol% Ni as a binder by pressureless sintering at a temperature $> 1360\text{ }^{\circ}\text{C}$. Meanwhile, high-entropy boride composites, using Ni as a sintering aid by pressureless sintering at $1450\text{--}1650\text{ }^{\circ}\text{C}$, were successfully fabricated, and the highest relative density could reach 99.8% [16]. Therefore, it was concluded that the introduction of a metal phase could effectively realize the low-temperature densification of high-entropy diboride and improve its fracture toughness, which is beneficial for broadening its applications.

Now, fracture toughness in high-entropy ceramics or composites has been improved by introducing a metal phase as a secondary phase. For example, in high-entropy carbide composites, a $(\text{Ti,V,Nb,Ta,W})\text{C}$ composite with 12 vol% Ni had a fracture toughness of $9.2\text{ MPa}\cdot\text{m}^{1/2}$ [15] and a $(\text{Zr}_{0.25}\text{Hf}_{0.25}\text{Ta}_{0.25}\text{Ti}_{0.25})\text{C}$ composite with Ni-Co metal had a fracture toughness of $14.2\text{ MPa}\cdot\text{m}^{1/2}$ [17]. In high-entropy diboride composites, a $(\text{Hf}_{0.2}\text{V}_{0.2}\text{Ta}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2})\text{B}_2$ composite with 15 wt% Ni metal also had a fracture toughness of $9.2\text{ MPa}\cdot\text{m}^{1/2}$ [16]. Although fracture toughness has been evidently improved, some new toughening strategies need to be further developed. For example, fiber or whisker toughening is an effective method for improving the fracture toughness of composites. Using $\beta\text{-SiC}$ whiskers or nanowires as a toughening agent has realized the toughening of high-entropy ceramics [18]. Luo et al. [19] successfully prepared dense, textured, and toughened $(\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})\text{C-SiC}_w$ ceramics, and the introduction of 15 wt% SiC_w led to a fracture toughness of $4.3 \pm 0.3\text{ MPa}\cdot\text{m}^{1/2}$. Sun et al. [20] fabricated $(\text{HfZrTaTiW})\text{C-SiC}_{nw}$ (SiC nanowire) composites with a fracture toughness of $6.2\text{ MPa}\cdot\text{m}^{1/2}$ by two-step spark plasma sintering. However, there is presently no available literature on the investigation of high-entropy boride composites by incorporating SiC whiskers.

Therefore, in this study, low sintering densification and improved mechanical properties of high-entropy boride composites using metallic Ni and SiC whiskers as additives were realized by hot-pressing technology. The influence of different sintering temperatures on densification, microstructure evolution, hardness, fracture toughness, and bending strength at room temperature of three high-entropy boride composites $(\text{M}_{0.2}\text{Ti}_{0.2}\text{Ta}_{0.2}\text{V}_{0.2}\text{Nb}_{0.2})\text{B}_2\text{-SiC}_w\text{-Ni}$ ($\text{M}=\text{Hf, Zr, or Cr}$) were investigated.

2. Experimental

Three high-entropy boride powders ($(\text{M}_{0.2}\text{Ti}_{0.2}\text{Ta}_{0.2}\text{V}_{0.2}\text{Nb}_{0.2})\text{B}_2$, $\text{M}=\text{Hf}$, Zr , or Cr) were synthesized using a boro/carbothermic reduction process, and the synthetic process was based on previous research [16]. Ni metal powders (A.R., purity: 99 wt%, with a particle size range of 1~3 μm) and β -SiC whiskers (purity: 99 wt%, Shandong Hengshi New Material Technology Co. Ltd., Shandong, China, particle length: 50~100 μm) were chosen as additives. In this study, three high-entropy boride composites ($(\text{M}_{0.2}\text{Ti}_{0.2}\text{Ta}_{0.2}\text{V}_{0.2}\text{Nb}_{0.2})\text{B}_2$, $\text{M}=\text{Hf}$, Zr , or Cr) with 12 vol.% Ni and 23 vol.% SiC whiskers were prepared by hot-pressing sintering technology, and were named $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$, respectively. The 12 vol.% Ni metal additive was a reasonable amount obtained from our published literature [16] and 23 vol.% SiC whiskers were added after being supported by previous experiments. The detailed preparation process was as follows. Firstly, to realize the high dispersion of SiC whiskers in the composites, they were ultrasonically dispersed for 30 min in ethyl alcohol solution. Secondly, weighted high-entropy diboride powders, Ni metal powders, and dispersed SiC whiskers were ball-milled for 3 h. Next, the powders were mixed, dried for 24 h at 60 $^{\circ}\text{C}$, and further sieved. Finally, after as-prepared powders were pre-compacted in the graphite mold under a pressure of 3 MPa by a hydraulic machine, they were densified by hot-pressing sintering technology. The final sintering temperatures were 1450 $^{\circ}\text{C}$, 1500 $^{\circ}\text{C}$, 1550 $^{\circ}\text{C}$, 1600 $^{\circ}\text{C}$, and 1650 $^{\circ}\text{C}$. The heating rate was 5 $^{\circ}\text{C}/\text{min}$ and the holding temperature time was 1 h. The applied loading force was 30 MPa, and Ar gas was used as the protective atmosphere. After sintering, three $\text{HEB-SiC}_w\text{-Ni}$ composites with a size dimension of 40 $\times$ 40 $\times$ 40 mm were successfully prepared.

The phase compositions of as-prepared $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites were measured by X-ray diffraction (XRD, D/MAX) technology. The microstructures of the fractural surfaces of as-prepared $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites were analyzed by scanning electron microscopy (SEM, SU-4700, Hitachi, Tokyo, Japan). The corresponding elemental composition was analyzed by energy dispersive spectrometry (EDS). The densification behavior (apparent porosity and bulk density) was analyzed by the Archimedes method using the following Equation (1).

$$B = \frac{G_2 - G_1}{G_2 - G_3} \quad (1)$$

where G_1 was the mass of high-entropy samples in the dry state (g); G_2 was the mass of high-entropy samples after water absorption in air (g); and G_3 was the buoyant weight of the high-entropy samples after water absorption in water (g).

The relative density of as-prepared $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites was calculated by dividing measured bulk densities by theoretical densities estimated according to the rule of mixtures. Vickers hardness was measured and analyzed by a hardness tester (MHVD-30IS, Bony Precision Measuring Instruments Co., Ltd., Shanghai, China) for which the loading force was 30 kg and the time was set to 10 s. In addition, the fracture toughness $K_{\text{I.C.}}$ was calculated according to the following Equation (2) [16].

$$K_{\text{I.C.}} = 0.15 \sqrt[2]{\frac{H.V_{.30}}{\sum_{i=1}^4 l_i}} \quad (2)$$

The room bending strength was analyzed by a three-point bending tester, and the size of HEB composites was 4 $\times$ 3 $\times$ 35 mm. The span distance was 30 mm and the loading rate was 0.5 mm/min. The average value of five measured composites was used as the data.

3. Results and Discussion

Commercially available β -SiC whiskers showed severe agglomeration and they formed the large elliptic shape in Figure 1a. The local enlarged SEM image in Figure 1b exhibits that the SiC whiskers had a rod-like shape with a smooth surface. However, these raw agglomerated SiC whiskers were not suitable for direct application in composites, as their inclusion would work against the improvement of composites. Therefore, ultrasonic treatment was used to realize the high dispersion of SiC whiskers, and the results are shown in Figure 1c,d. The SiC whiskers had good monodispersity, showing that the ultrasonic treatment effectively opened the agglomeration of SiC whiskers. Therefore, these prepared SiC whiskers were suitable as the toughening agent in HEB composites. The average diameter of these prepared β -SiC whiskers was about $0.39\ \mu\text{m}$.

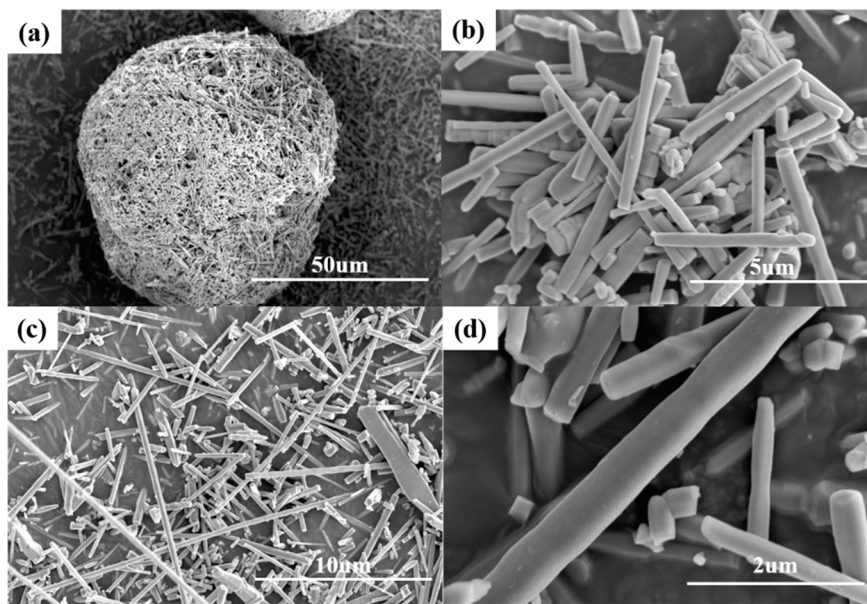


Figure 1. Morphology of raw β -SiC whiskers (a,b) before ultrasonic dispersion and (c,d) after ultrasonic dispersion.

In order not to damage the morphology of SiC whiskers, ball milling at a low rotating speed was adopted to realize the uniform mixing of HEB powders and ultrasonically dispersed SiC whiskers. The morphologies of mixed HEB_{Hf} , HEB_{Zr} , or HEB_{Cr} powders and SiC whiskers are shown in Figure 2a–c, respectively. It is seen that SiC whiskers were uniformly dispersed in HEB_{Hf} , HEB_{Zr} , and HEB_{Cr} powders, and that their rod-like morphology had no evident change. These results illustrate that ultrasonic treatment and ball milling remarkably improved the dispersion of whiskers in mixed powders, and that as-obtained mixed powders are beneficial for preparing HEB_{Hf} , HEB_{Zr} , and HEB_{Cr} composites with high properties.

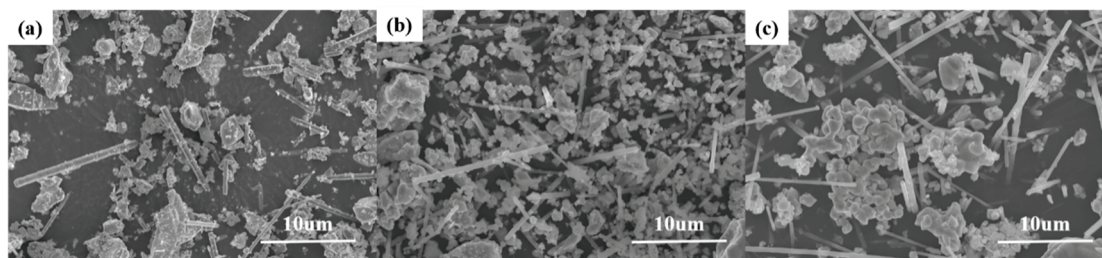


Figure 2. SEM images of mixed high-entropy diboride powders and SiC whiskers after ultrasonic treatment and ball milling: (a) $\text{HEB}_{\text{Hf}}\text{-SiC}_w$, (b) $\text{HEB}_{\text{Zr}}\text{-SiC}_w$, and (c) $\text{HEB}_{\text{Cr}}\text{-SiC}_w$.

XRD patterns of sintered $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites with SiC whiskers are shown in Figure 3a–c, respectively. For sintered $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$ composites in Figure 3a, the analysis of diffraction peaks confirmed that the $(\text{Hf}_{0.2}\text{V}_{0.2}\text{Ta}_{0.2}\text{Ti}_{0.2}\text{Nb}_{0.2})\text{B}_2$ phase, Ni phase, and SiC phase co-existed regardless of the sintering temperature, which is consistent with the phase composition of raw mixed powders. During the sintering process, the formation of no new phase illustrated that high-entropy boride (HEB_{Hf}) could not react with Ni or SiC whiskers, further confirming the stability of high-entropy borides (HEB_{Hf}). Meanwhile, when the sintering temperature was above 1550°C , it was found that the peak of the Ni phase gradually decreased, which is attributed to the outflow of molten Ni metal at high temperature during the hot-pressing process. This phenomenon has been confirmed in other high-entropy composites [13,16,21]. Similarly, in the $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$ and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites in Figure 3b,c, the HEB_{Zr} and HEB_{Cr} phases remained stable at high temperatures, and the SiC and Ni phases still existed. Comparative XRD patterns of $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites sintered at 1600°C are shown in Figure 4. Owing to the replacement of Hf (1.59), Zr (1.6), and Cr (1.27) elements with different atomic radii, the main peak positions corresponding to the high-entropy diboride were different. The peak positions of HEB_{Hf} and HEB_{Zr} had no change owing to their near atomic radii, but the peak position of HEB_{Cr} had a shift toward a big angle (right) relative to HEB_{Hf} and HEB_{Zr} , owing to the smaller atomic radii of Cr; this phenomenon has been confirmed in previous research [16].

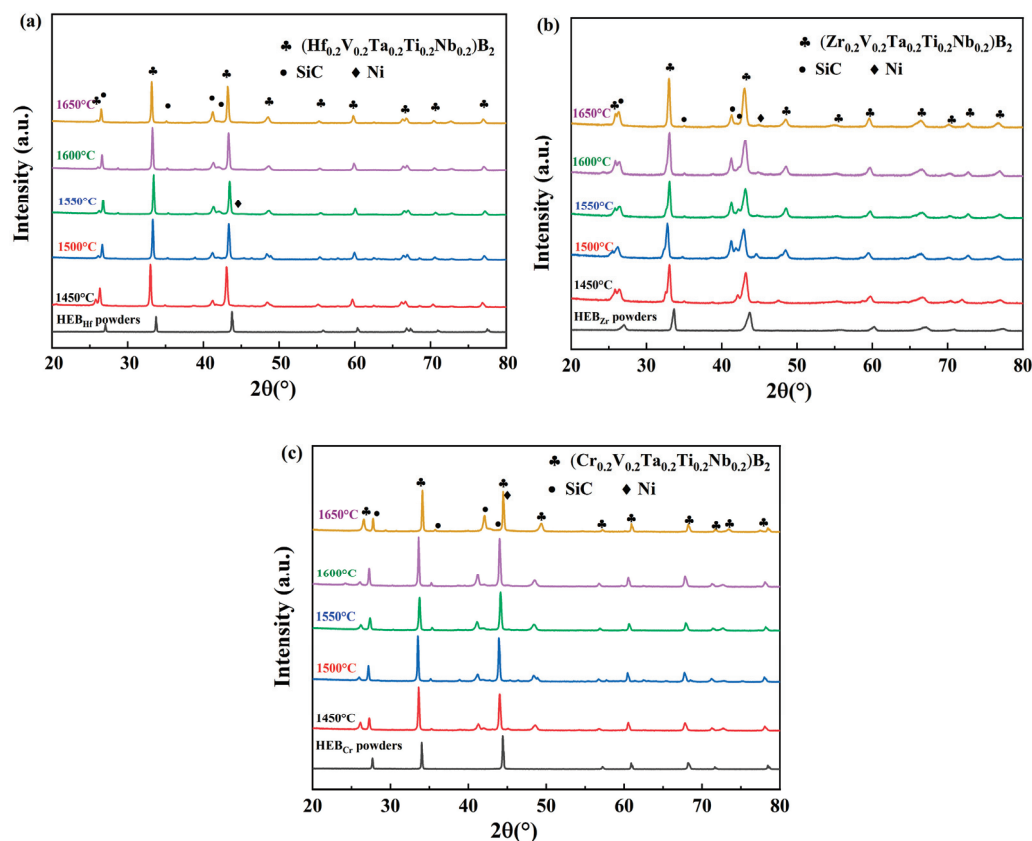


Figure 3. XRD patterns of as-sintered high-entropy composites with SiC whiskers hot pressed at different sintering temperatures: (a) $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, (b) $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and (c) $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$.

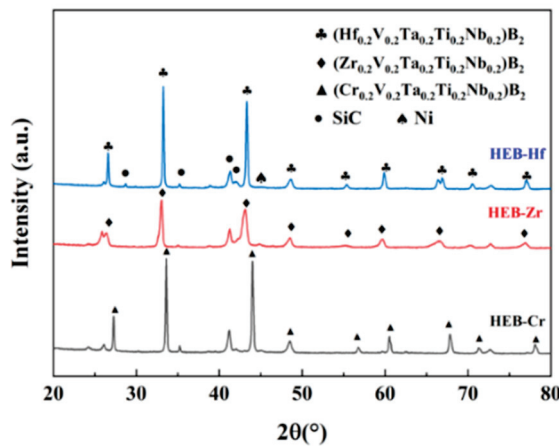


Figure 4. Comparative XRD patterns of as-sintered high-entropy boride composites with SiC whiskers hot pressed at 1600 °C.

The densification behaviors of sintered $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites were analyzed. The apparent porosities in Figure 5a illustrate that with an increase in sintering temperature the apparent porosities of sintered $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites all showed a decreasing and increasing change trend. When the sintering temperature was 1450 °C, the $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites had the highest apparent porosities, and these were 4.82%, 13.93%, and 6.37%, respectively. The reason for this is that at 1450 °C the densification process caused by the liquid phase sintering mechanism was slow because less molten Ni existed in the HEB composites and the pores could not be effectively eliminated, leading to their high porosity. When the temperature reached 1500 °C and 1550 °C, the apparent porosities of the $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites gradually decreased. Increasing the temperature facilitated the formation of more molten Ni metal, promoting the densification process of HEB composites by filling in the pores among HEB grains. The as-formed Ni liquid phase offered a pathway to mass transfer, leading to a decrease in pores accompanied by the growth of HEB grains. When the sintering temperature was 1600 °C, their apparent porosity reached the lowest values, which were 3.74%, 3.58%, and 4.76%, respectively. Oppositely, at the sintering temperature of 1650 °C, the apparent porosities increased. Although increasing temperature led to the low viscosity of molten Ni metal, the applied pressure at high temperature caused the outflow of the Ni phase, which was responsible for the appearance of low density. Similarly, in Figure 5b,c, it is seen that bulk density and relative density both increased first and then decreased as temperatures increased from 1450 °C to 1650 °C. When the sintering temperature was 1600 °C, bulk density and relative density reached their highest values. The bulk densities of $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites were 7.32, 6.42, and 6.54 g/cm³, respectively. And their relative densities were 96.3%, 96.1%, and 95.6%, respectively.

The fracture surfaces of as-sintered high-entropy $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$ composites at different sintering temperatures from 1450 °C to 1650 °C are shown in Figure 6. It was concluded that the fracture mode of $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$ composites is mainly transgranular fracture. At a temperature of 1450 °C, as shown in Figure 6a, some pores existed in the fracture surfaces of $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$ composites owing to the inadequate liquid phase sintering caused by molten Ni metal. With increases in the sintering temperature, it was found that the number of pores among high-entropy grains gradually decreased, and these pores even disappeared. An adequate Ni liquid phase at high temperature promoted the densification of high-entropy $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$ composites. The increasing temperature decreased the viscos-

ity of liquid Ni metal, which was more beneficial for the densification of composites shown in Figure 6b–d. However, when the temperature was further increased to 1650 °C, some pores appeared among the grains; this was caused by the outflow of the liquid Ni metal with lower viscosity under the hot-pressing process. Additionally, it was found that when the temperature was higher than 1550 °C, SiC whiskers could not be evidently observed. Comparing Figure 6d,e, no SiC whiskers existed in the sample sintered at 1600 °C. The reason for this may be attributed to the degradation of whiskers under high temperatures.

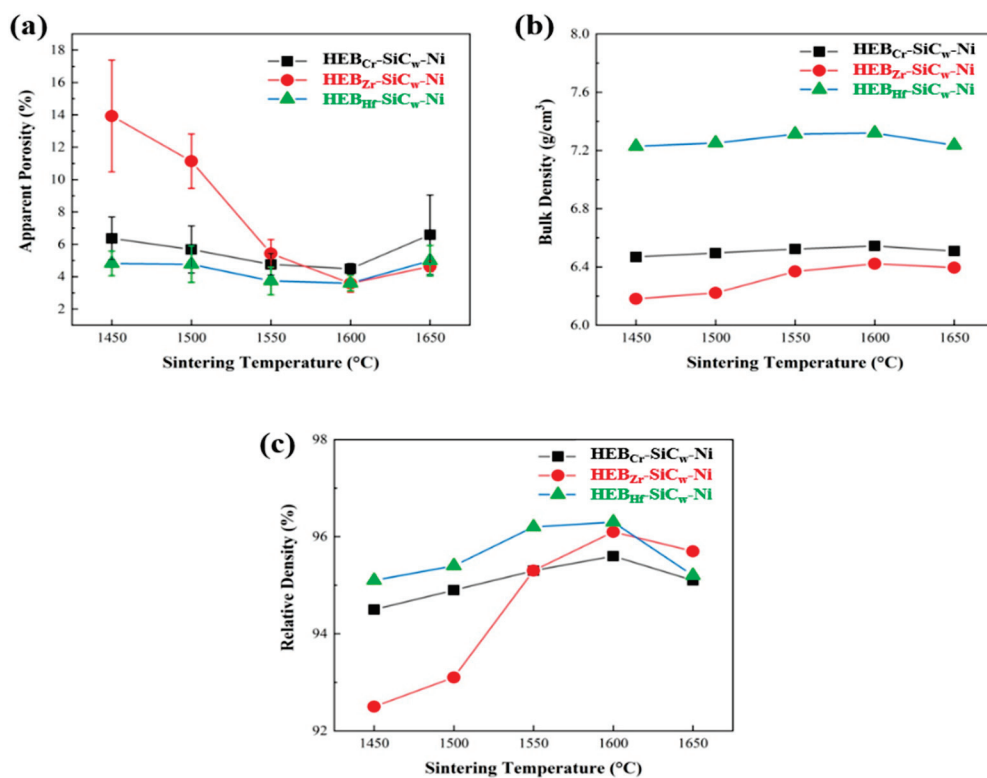


Figure 5. (a) Apparent porosity, (b) bulk-density, and (c) relative density of as-sintered high-entropy composites with SiC whiskers processed by hot pressing.

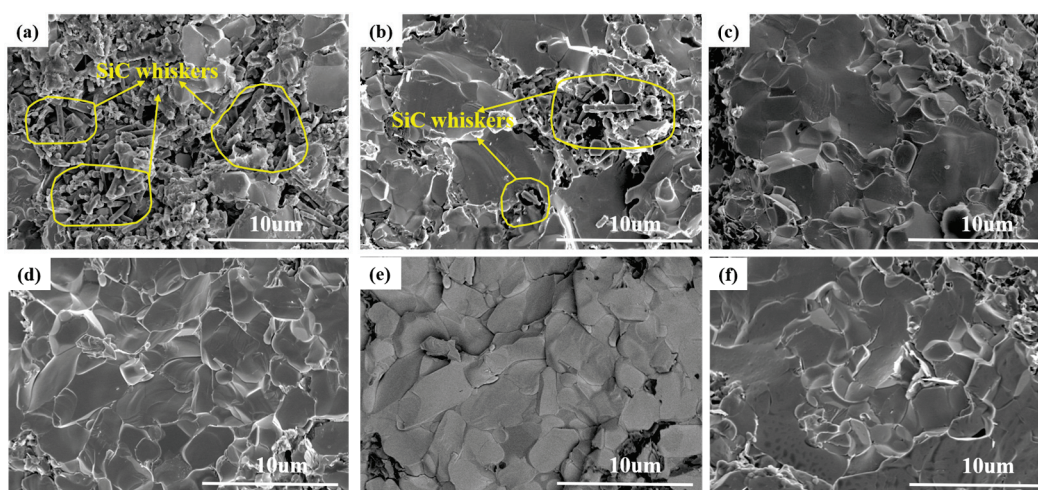


Figure 6. SEM images of fracture surfaces of as-sintered high-entropy HEB_{Hf}-SiC_w-Ni composites hot pressed at different temperatures: (a) 1450 °C, (b) 1500 °C, (c) 1550 °C, (d,e) 1600 °C, and (f) 1650 °C.

Comparative SEM images of the fracture surfaces of $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites sintered at 1600 °C are shown in Figure 7. According to the densification behavior (porosity and density) of high-entropy boride composites, high densification behavior can be obtained at 1600 °C. In Figure 7a, the grains connect tightly and only a few pores exist in the $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$ composites, corresponding to a porosity of 3.74%. In Figure 7b, a few pores still exist in the $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$ composites, corresponding to a porosity of 3.58%. By comparison, in Figure 7c, more pores appear in the $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites, which have a relative high porosity of 4.76%. Meanwhile, the grain size in the $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$ composite was far larger than those in the $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$ and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites.

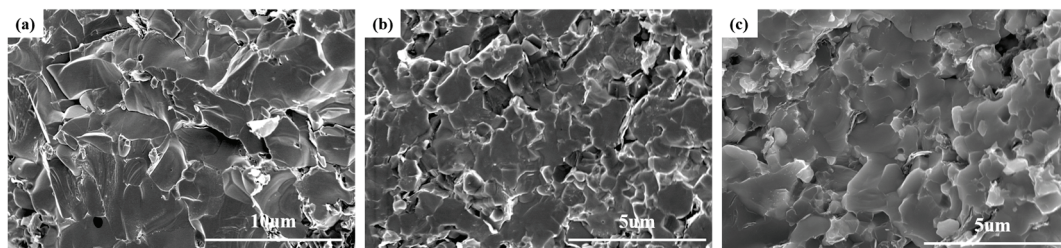


Figure 7. Comparative SEM images of fracture surfaces of as-sintered high-entropy boride composites with SiC whiskers hot pressed at 1600 °C: (a) $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, (b) $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and (c) $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$.

To further characterize the composition distribution in the microstructure of high-entropy boride composites, EDS-mapping images of the polished surfaces of $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites are shown in Figure 8. The Hf, V, Ta, Ti, and Nb elements were uniformly distributed, and Ni elements were distributed in the gaps between HEB grains on the polished surface of the $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$ composite. The same element distribution phenomenon appeared in the $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$ and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites.

Figure 9a–c show the hardness and fracture toughness of as-sintered $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites at different sintering temperatures, respectively. It can be seen that the hardness of these three HEB-SiC_w-Ni composites first showed an increasing trend, and then a decreasing trend when the sintering temperature increased from 1450 °C to 1650 °C. At a sintering temperature of 1450 °C, $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites had the lowest hardness values of 13.5, 11.8, and 13.7 GPa, respectively, which is mainly attributed to the low densification caused by the inadequate molten Ni phase. At a sintering temperature of 1600 °C, owing to high densification, their hardnesses reached the highest values, and these were 22.02, 20.98, and 21.88 GPa, respectively. Oppositely, further increasing the sintering temperature led to a decrease in hardness, which originated from the decreased density. The hardness variation law is consistent with that of density variation in these three HEB-SiC_w-Ni composites. Additionally, as the temperature increased, the fracture toughness of $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites basically increased and then decreased. At a sintering temperature of 1600 °C, their highest fracture toughnesses were 12.64, 13.25, and 11.05 $\text{MPa}\cdot\text{m}^{1/2}$, respectively.

Additionally, the bending strength of $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites at room temperature was analyzed, and results are shown in Figure 10. Figure 10a shows that for the $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$ composites, when the temperature was increased from 1450 °C to 1600 °C, the bending strength basically showed an increasing trend. At 1450 °C, the bending strength was 261.1 MPa, and when the sintering temperature was 1600 °C, the value reached 309.5 MPa. Oppositely, the bending strength slightly de-

creased to 301 MPa. Figure 10b shows that for the $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$ composites, the bending strength increased first and then decreased, and at 1600 °C the highest bending strength of 290.3 MPa was obtained. Figure 10c shows that for the $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites, the highest bending strength of 320.8 MPa was obtained at 1600 °C. It was determined that the variation trend of bending strength at room temperature vs. sintering temperature was consistent with densification behavior.

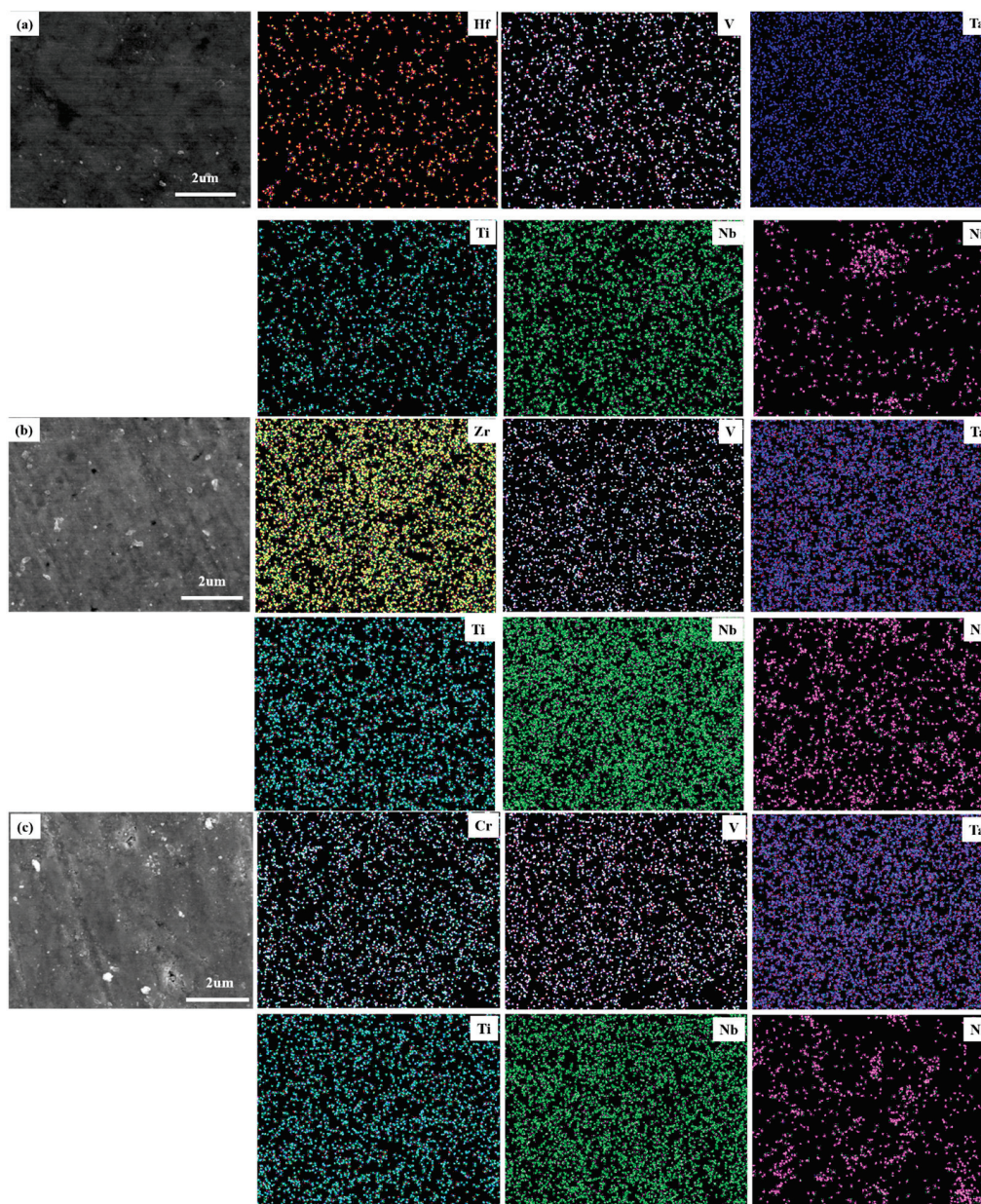


Figure 8. EDS mapping images of as-sintered high-entropy diboride composites with SiC whiskers hot pressed at 1600 °C: (a) $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, (b) $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and (c) $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$.

To further analyze the toughening mechanism in $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$ composites, crack propagation paths on the polished surfaces of $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$ composites prepared by hot pressing at 1600 °C were observed, as shown in Figure 11. In Figure 11a,b, it is seen that the crack on the polished surface shows a wriggling curve, which is beneficial for improving fracture toughness by consuming fracture energy during crack propagation. Based on the above results from Figure 6d, it was observed that for the sample at 1600 °C, SiC whiskers basically disappeared. Therefore, the high fracture toughness of the sample at 1600 °C

is believed to be mainly attributed to improved densification, the existence of a metal Ni phase, and small particles formed by the degradation of SiC whiskers in the microstructure.

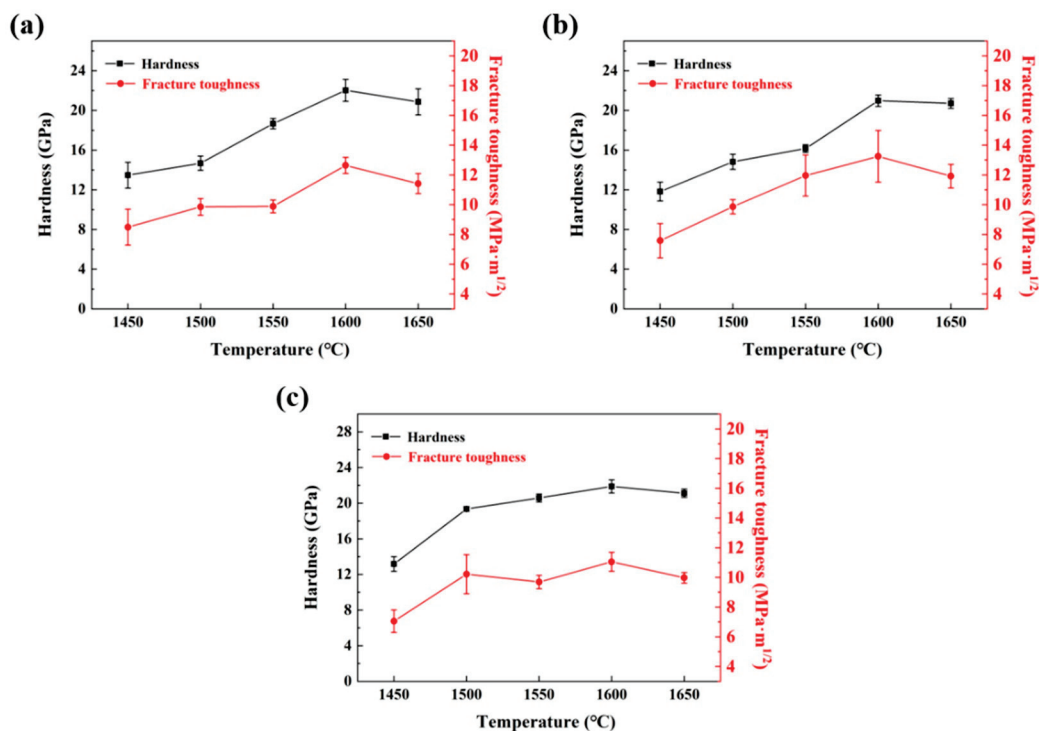


Figure 9. Hardness and fracture toughness of as-sintered high-entropy composites with SiC whiskers processed by hot-pressing: (a) HEB_{Hf}-SiC_w-Ni, (b) HEB_{Zr}-SiC_w-Ni, and (c) HEB_{Cr}-SiC_w-Ni.

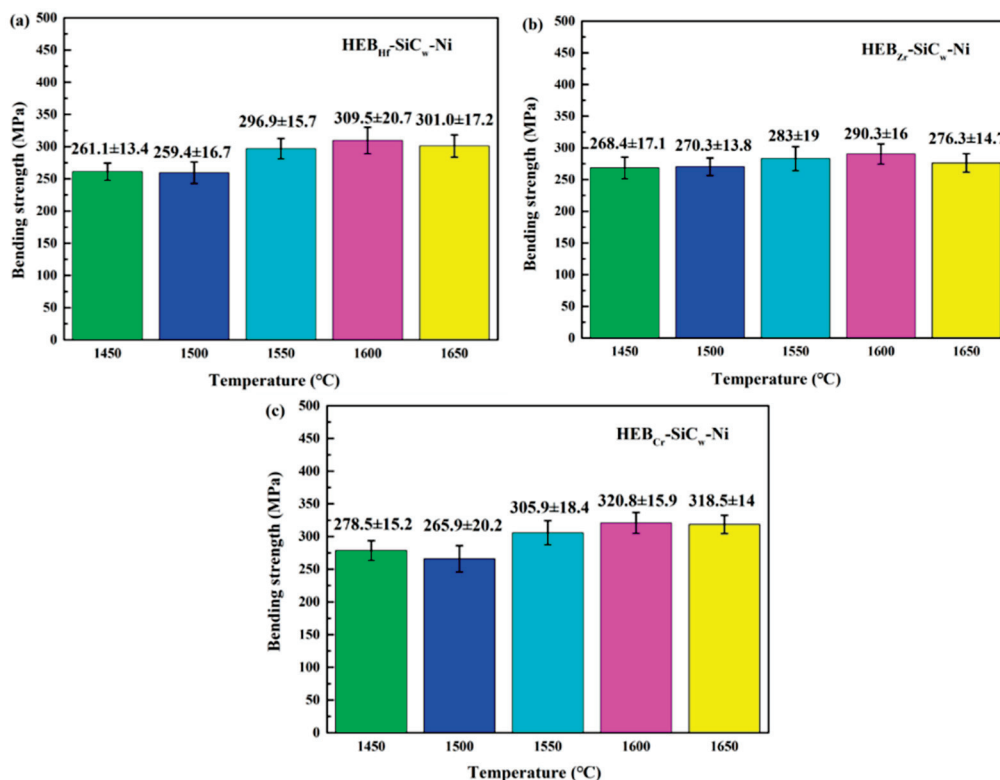


Figure 10. Bending strength of as-sintered high-entropy composites with SiC whiskers processed by hot pressing: (a) HEB_{Hf}-SiC_w-Ni, (b) HEB_{Zr}-SiC_w-Ni, and (c) HEB_{Cr}-SiC_w-Ni.

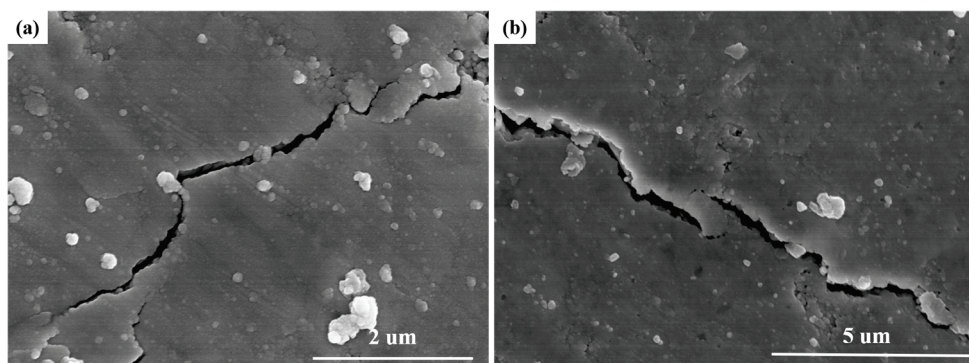


Figure 11. (a,b) Crack growth images of as-sintered high-entropy $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$ composites hot pressed at 1600 °C.

4. Conclusions

In this study, three high-entropy $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites with good hardness, fracture toughness, and bending strength were successfully prepared by hot-pressing sintering technology, in which SiC whiskers were used as the toughening agent and metal Ni was the additive. The metal Ni realized the densification of $\text{HEB-SiC}_w\text{-Ni}$ composites at low temperature; meanwhile, the combined action of metal Ni and SiC whiskers promoted the improvement of the fracture toughness of the $\text{HEB-SiC}_w\text{-Ni}$ composites. Increasing sintering temperatures from 1450 to 1600 °C improved the densification of $\text{HEB-SiC}_w\text{-Ni}$ composites. At a sintering temperature of 1600 °C, $\text{HEB}_{\text{Hf}}\text{-SiC}_w\text{-Ni}$, $\text{HEB}_{\text{Zr}}\text{-SiC}_w\text{-Ni}$, and $\text{HEB}_{\text{Cr}}\text{-SiC}_w\text{-Ni}$ composites had the highest densification, leading to high hardness and fracture toughness. It was determined that their relative densities were 96.3%, 96.1%, and 95.6%, respectively. The highest hardnesses were 22.02, 20.98, and 21.88 GPa, respectively. And the fracture toughnesses were 12.64, 13.25, and 11.05 $\text{MPa}\cdot\text{m}^{1/2}$, respectively. In the sintering temperature range of 1450 to 1650 °C, their bending strengths at room temperature were 259.4~309.5 MPa, 268.4~290.3 MPa, and 265.9~320.8 MPa, respectively. This work will provide new guidance for the development of high-entropy composites.

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Conflicts of Interest: Author Yubo Gong was employed by the company CARS Engineering Consulting Corporation Limited. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Article

Binder Jetting for Functional Testing of Ceramic Sanitaryware

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Abstract: Additive manufacturing (AM) of ceramics presents a promising approach for the production of complex sanitaryware prototypes, offering advantages in terms of cost and time to market. This study explores binder jetting (BJ) as an optimal AM technique due to its ability to process ceramic materials without thermal stress, accommodate various compositions, and produce large components without support structures. A combination of refractory cement, feldspathic sands, quartz, and calcined alumina was used to formulate 19 different compositions, ensuring adequate green strength and minimizing shrinkage during sintering. A hydration-activated binding method with a water-based binder was employed to enhance part formation and mechanical properties. The results indicate that compositions containing calcined alumina exhibited lower pyroplastic deformation, while optimized gelling agent concentrations improved green strength and dimensional accuracy. The final selected material (SA18) demonstrated high compressive strength, low shrinkage, and a surface roughness comparable to traditional sanitaryware. The application of an engobe layer improved glaze adherence, ensuring a homogeneous surface. This study highlights binder jetting as a viable alternative to traditional ceramic processing, paving the way for its adoption in industrial sanitaryware manufacturing.

Keywords: sanitaryware; additive manufacturing; binder jetting; design; ceramics

1. Introduction

Ceramic materials are broadly used in industrial applications, ranging from the production of sanitaryware to advanced mechanics. Despite their widespread use, their production process still involves inefficient product development procedures, often based on a trial-and-error approach [1].

The product development process of ceramic sanitaryware encompasses a specific sequence of steps that a company follows to bring new offerings to the market to meet a particular demand. For many years, traditional prototyping has been utilized to develop, design, and create accurate models of diverse products. This prototyping method often requires extensive training and substantial time investment. Skilled craftsmen are essential to construct temporary prototypes of complex components based on blueprints. This

approach enables the craftsmen to fabricate either a complete or partial model. Nevertheless, the prototype may not always work, leading to the creation of additional prototypes using different materials and crafting techniques. Typically, a near-final product must be produced to test its ultimate properties. This iterative cycle, spanning from conceptualization to production, entails considerable investments of time, materials, energy, and financial resources. This is precisely the stage where additive manufacturing (AM) can provide value.

AM allows for the fabrication of prototypes with greater ease and flexibility, eliminating the need for highly skilled workers. By directly translating intricate digital 3D models into tangible products, AM minimizes the time, labor, and materials traditionally expended in manual construction processes [2]. In addition to the time and cost savings of introducing AM at the pre-production stage, AM, and in particular binder jetting (BJ), have proven to be more sustainable processes than traditional manufacturing methods like casting or injection molding [3,4].

While AM processes can produce larger build parts, in the current framework, limitation on the availability of initial raw materials for obtaining feedstock is still a challenge in the AM of ceramics [5]. A significant constraint is related to the availability of printable materials suitable for glazing and that can be processed within an industrial cycle. The fabrication of large ceramic components with no cracks or deformation is still challenging [6]. In addition, during binder removal and sintering, large ceramic parts show problems that can be attributed to significant variations in sectional thickness and differences in thermal features and shrinkage.

The integration of ceramic AM continues to grow, driven by improvements in processing techniques and material properties, making it a viable solution for complex and high-performance applications [7]. Traditional ceramics have been largely overlooked in AM material development, as research and industrial applications have predominantly focused on advanced ceramics such as zirconia (ZrO_2), alumina (Al_2O_3), silicon carbide (SiC), and hydroxyapatite (HA) for their application in biomedical, aerospace, and energy applications [8]. As a result, the evolution of ceramic AM has been driven by materials that offer enhanced processability, structural integrity, and application-specific performance, resulting in the limited integration of conventional ceramics within this technological paradigm.

This study aims to develop prototypes using traditional ceramics, evaluating their feasibility in meeting the technical requirements and certification standards of conventional sanitaryware. The objective is to assess the suitability and reproducibility of the fabricated components, ensuring that additive manufacturing can effectively integrate traditional ceramic materials while maintaining industry-specific performance criteria.

In order to achieve the main objective of this project, some of the most influential factors in the development of the materials were identified as follows:

- The material must be able to be processed by BJ (more on technology selection later).
- Sufficient green strength. Printed parts do not need to have high mechanical strength at this stage, but they must be able to withstand further processing.
- Adequate pyroplastic deformation after sintering. The material must guarantee a dimensional stability after firing.
- The material must be able to withstand glazing to achieve the characteristics of the real end product.
- Adequate final roughness (after glazing). To be able to test some of the properties of the sanitaryware, the roughness of the final pieces must be equal to that obtained with pieces manufactured by the usual industrial process.
- To ensure that the glaze has the correct properties for further testing, the material needs to be fired using an industrial cycle.

In short, the required green strength was set at 2 MPa, as this was considered sufficient for the part to be handled and post-processed safely. The final mechanical strength was established at 4 MPa, as no mechanical strength tests were to be carried out. The main tests for the design would be related to fluid mechanics, and this would require the highest precision in the prototype and achieving the same surface roughness after glazing. As the part would be fired with an industrial cycle, the prototypes must withstand firing temperatures up to 1230 °C with a pyroplastic deformation lower than $15 \cdot 10^5 \text{ cm}^{-1}$.

2. Materials and Methods

2.1. Additive Manufacturing Technology

As illustrated in Table 1, a comparison is provided of the current AM technologies that are capable of processing ceramic materials. Of all the additive manufacturing technologies currently available, binder jetting was selected because it has certain advantages over other AM processes:

- It does not use heat during the build process. Other technologies use a heat source that can create residual stress that must be removed in secondary post-processing.
- It has a high compatibility with materials such as ceramics and refractory metals and a large group of material types that are difficult to process.
- There is no need for support structures, as the loose powder supports protrusions and stacked or suspended objects.
- It allows for the printing of large components and is often more cost-effective than other additive processes.

Table 1. Comparison of various 3D printing technologies for manufacturing ceramics [9].

Process	Layer Formation Technique	Accuracy/Resolution (μm)	Temperature Process/Speed	Support Structure	Build Size	Feedstock Cost/Process Cost
SLA	Photopolymerization	High/10	Very low	Required	XS/S/M	Low/Medium
FDM	Extrusion	Good/50–200	Low/Low	Required	M/L/XL	Low/Low
SLS	Powder fusion	Low/80–250	High/Low	Not required	M/L	Low/High
SLM	Sheet lamination	High/80–250	High/High	Required	M	Low/Low
BJ	Binder bonding	High/<50	Low/High	Not required	M/L/XL	Low/Medium
DED	Material deposition	Very low/-	High/	-	Versatile	Low/High

Binder jetting is an additive manufacturing process in which a liquid bonding agent is selectively deposited to join powder materials [10]. The machine comprises two platforms: the feed platform, where the raw material is placed, and the build platform, where the part is built up layer by layer.

First, a blade spreads a layer of the powder from the feed platform onto the build platform. Next, the print head, which consists of one or more inkjet nozzles, injects the binder liquid into the powder following a pattern defined by the CAD model. The binder helps to join the powder particles in the chosen areas. Once the layer is complete, the build platform lowers to a set height, the feed platform raises, and the blade spreads a new layer of fresh powder onto the build platform. The process is repeated until the part is completely built.

Once the printing process is complete, the parts are left in the machine for 60 min to facilitate drying and ensure proper binding. Subsequently, excess powder is gently brushed away, leaving a bed of powder surrounding the parts.

Figure 1 shows all the steps involved in binder jetting technology.

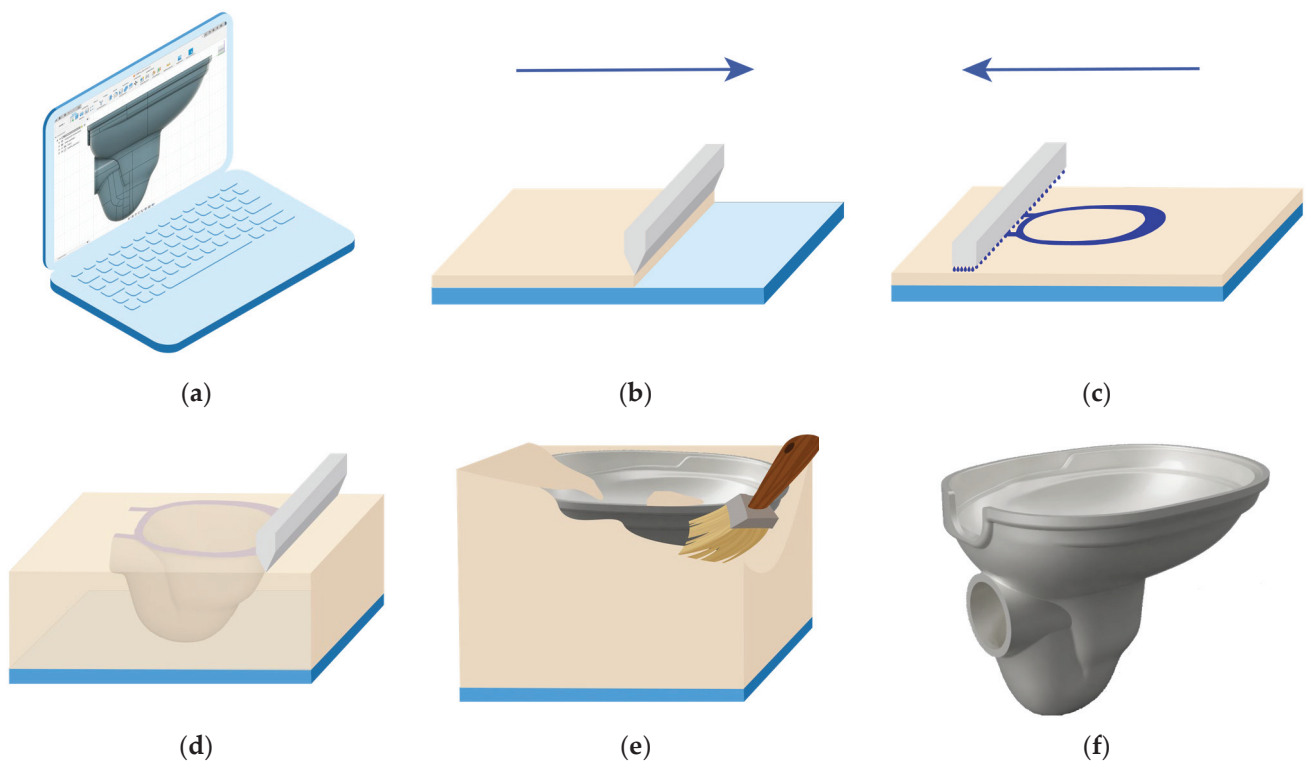


Figure 1. BJ process: (a) CAD data transfer; (b) powder application; (c) selective binder deposition; (d) steps b-c repeated until completion of part; (e) unbound powder removal; (f) finished part. The arrows on the figures represent the direction of the movement.

2.2. Specimen Preparation

2.2.1. Base Material

In order to improve the material's compatibility with the printing process, ceramic atomized materials were mixed with additives. The primary function of these additives is to maintain the structural integrity of the green body, given that compaction by pressure is not performed during the printing process. The additives provide the necessary binding power to shape the ceramic material. After removing the excess support powder, the green piece remains fragile, making the role of additives crucial at this stage.

The raw base material used was a refractory cement ($d_{50} = 15.6 \mu\text{m}$). To improve strength and hardness, a mixture of feldspathic sands and ceramic frit with two different mean particle sizes was used: FS&CF1 ($d_{50} = 184.8 \mu\text{m}$) and FS&CF2 ($d_{50} = 232.6 \mu\text{m}$). To reduce shrinkage during the drying and firing processes and to impart rigidity to the body, quartz sand ($d_{50} = 264.4 \mu\text{m}$) and micronized quartz ($d_{50} = 17.0 \mu\text{m}$) were incorporated. To provide strength against warping during firing and to add fired strength, calcinated alumina ($d_{50} = 3.0 \mu\text{m}$) was selected. The calcinated alumina was obtained from Alteo (Gardanne, France), while all other materials were supplied by ROCA Sanitario S.A. (Gavà, Spain).

Variations in the percentage of the cement and the different additives were used to create nineteen different compositions to test the printability and the properties of the printed parts (Figure 2).

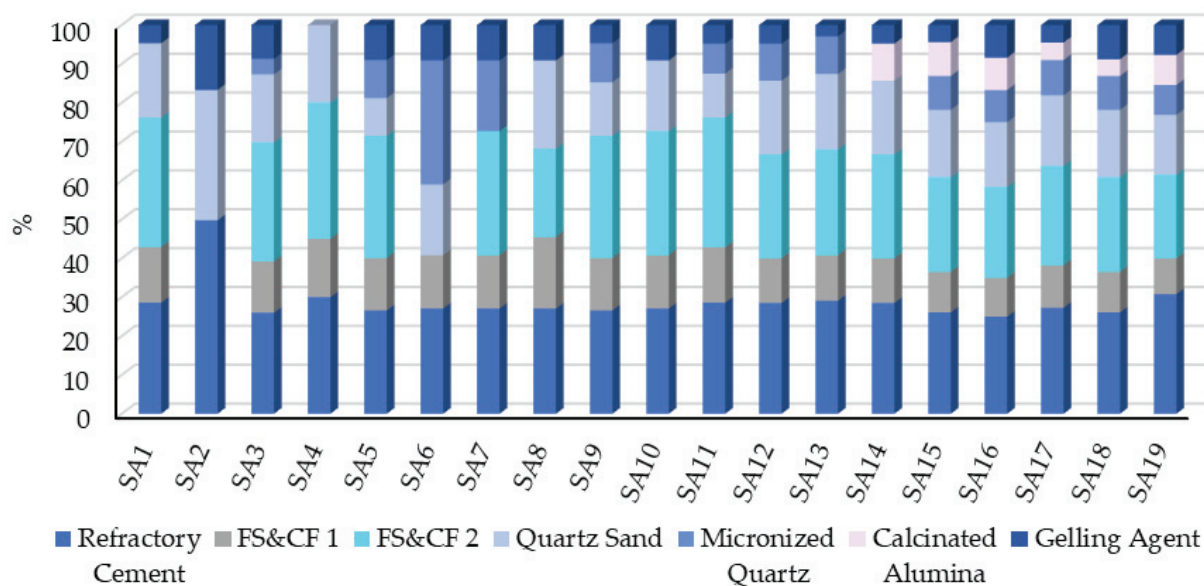


Figure 2. Various component ratios used to formulate different compositions.

2.2.2. Binder

In the present project, the hydration-activated binding method was employed. This method involves the utilization of a simple liquid (e.g., water) to selectively bind the self-binding powder bed. The absence of an adhesive is a consequence of the sufficiency of hydration for activating the setting.

A water-based liquid binder (85–95% water) was selected. As part of the liquid binder formulation, glycerol (Merck KGaA, Darmstadt, Germany, $\geq 99.5\%$) was dissolved in deionized water. Glycerol was utilized to increase the viscosity and surface tension of the liquid binder, with the objective of improving droplet definition and infiltration kinetics. The aqueous solution was magnetically stirred for 10–15 min to obtain a clear solution, a viscosity within the range of 1.1 and 1.3 Pa·s, and a surface tension of 72 ± 0.3 mN/m.

An organic gelling agent was utilized as a solid binder, exhibiting a solubility rate greater than 99.9% and a viscosity of 0.075 Pa·s (after 24 h in 25% of H_2O).

2.2.3. Preparation of Powders

In order to achieve a homogeneous mixture, the ceramic material, the additives, and the solid binder were dry-mixed with an Eirich planetary mixer for 10 min at 150 rpm.

To reduce porosity and improve printing resolution, small particle size distributions are favorable, as they allow for smaller layer thicknesses [11]. However, that same packing property, which is desirable for sintering, becomes a problem for the flowability of the material [12].

The flowability of solids is complex and linked to many parameters. It is an important property for dried particles, which is measured using the Carr Index (CI) and the Hausner Ratio (HR). The powder flowability (%), as determined by the CI value, is classified as follows: <15 very good, 15–20 good, 20–35 fair, 35–45 bad, and >45 very bad. The powder cohesiveness, as determined by the HR value is classified follows: <1.2 low, 1.2–1.4 intermediate, >1.4 high [13].

To ensure the printability, all the compositions made had a similar flowability to that shown in Table 2. In accordance with the findings of previous studies [14], a HR of 1.35 (intermediate) was considered to be correct. The Carr Index value obtained was deemed to be satisfactory according to the available bibliography. All the tested powders demonstrated comparable spreadability.

Table 2. Powder characteristics.

Humidity H (%)	Aerated Bulk Density ρ_0 (kg/m ³)	Packed Bed Density ρ_f (kg/m ³)	Carr Index CI (%)	Hausner Ratio HR (ρ_f/ρ_0)
0.92	1287 ± 28	1730 ± 21	25.61	1.35 ± 0.04

2.2.4. Printing Parameters

In addition to the powder-based parameters, there are other factors involved in BJ that impact the mechanical properties of sintered parts, such as the printing parameters [15]. In this study, the printer parameters were kept constant at the following values (Table 3).

Table 3. M10 printing parameters.

Parameter	Value
Layer height	0.16 mm
Feed box ratio	1.3
Printing	2
Nozzle	2
Slow axis	12,000 pps

The layer height was established based on the mean particle size of the compositions.

The feed box ratio parameter allows for the provision of a greater quantity of powder. The value of 1.3 means that the build platform is lowered by 1 mm, and then the feed platform is raised by 1.3 mm, creating a greater compaction of the material.

The printing parameter refers to the number of printing repetitions in the same position, which is to be adjusted according to the amount of binder used.

The nozzle parameter sets the number of nozzle slots to be used (1 to 4, with the understanding that an increase in the number of nozzle slots results in higher binder saturation).

The slow axis parameter establishes the speed of the axis where the nozzle is mounted, and this can range from 16,000 pps (3840 mm/s) to 4000 pps (960 mm/s).

2.3. Drying and Sintering

After printing, the green body and construction bed containing the remaining powder were dried in an oven at 80 °C for four hours.

The parts were then removed from the oven, and any remaining unbound powder was carefully removed with a metal bristle brush.

Finally, the parts were sintered in an electric furnace according to an industrial firing cycle (Figure 3) in a laboratory electric furnace (Carbolite RHF, Carbolite Gero Ltd., Derbyshire, UK).

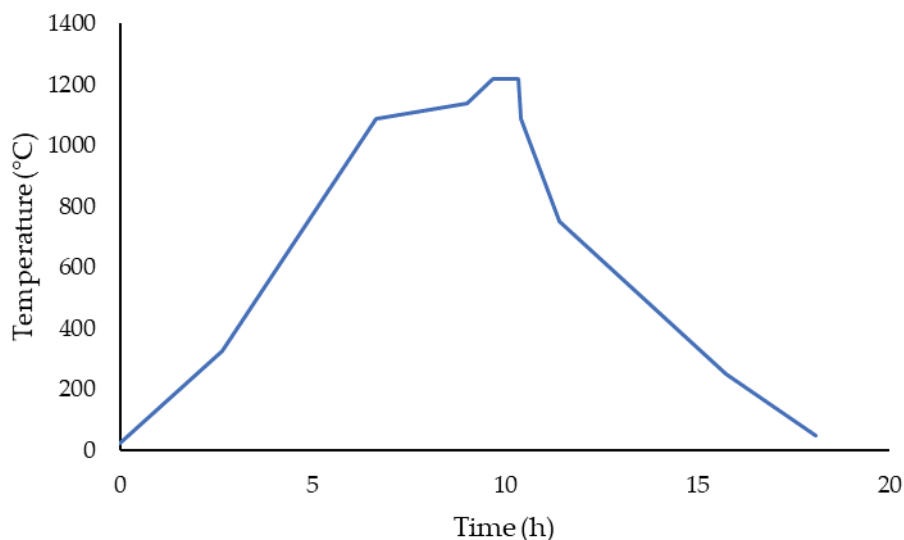


Figure 3. Sintering cycle.

2.4. Glazing

A standard sanitary glaze was used for the glazing. The glaze was sprayed onto the green parts using different grammages. After firing, it was observed that the glaze had been partially absorbed, resulting in slight deformation of the shape and an irregular surface (Figure 4).



Figure 4. Glazed parts: (a) 1230 g/m², (b) 1420 g/m².

It was therefore decided to use a highly refractory engobe that would allow the glaze to be applied and stretched correctly. The engobe was applied to the green part with a grammage of ~908 g/m² and, after drying, the glaze was applied with a grammage of ~1024 g/m². The parts were then fired according to the above firing cycle. The fired parts showed a well stretched and homogeneous glaze with no signs of distortion on the piece (Figure 5).



Figure 5. Engobed and glazed part.

2.5. Characterization of the Printed Parts

2.5.1. Pyroplastic Deformation

The magnitude of pyroplastic deformation is defined by the pyroplastic index (PI), which indicates the tendency of a specimen of given dimensions to be deformed by gravity during firing under specified conditions. The procedure used to determine the pyroplas-

ticity index consists of measuring the curvature of a specimen resting on two refractory supports during firing using the following expression (1):

$$PI = \frac{4 \cdot e^2 \cdot s}{3 \cdot L^4} \quad (1)$$

where e is the thickness of the part (cm), s is the maximum deformation (cm), and L is the distance between the supports (cm). The support spacing used in this case was 5.25 cm.

The specimens were fired at the maximum temperature of 1230 °C in an electric laboratory oven. The time spent at maximum temperature was 60 min.

2.5.2. Bulk Density

The density of the parts was measured using the Archimedes principle by submerging the specimens in a mercury bath and observing the increase in the weight of the bath following the method described by Amorós [16]. Mercury was used because it has a high degree of non-wetting properties and the parts do not need to be sealed for the measurement. The parts were measured before sintering. The bulk density is given by the following expression (2):

$$\rho = \frac{m \cdot \rho_{Hg}}{m_{fl}} \quad (2)$$

where ρ is the density measured in g/cm³, m is the weight of the part measured in g, ρ_{Hg} is the density of mercury (13.53 g/cm³), and m_{fl} is the weight of the fluid displaced by the specimen (g).

2.5.3. Dimensional Accuracy

The dimensional accuracy obtained by printing each material was analyzed by determining the linear shrinkage. The length of each part was measured, before and after sintering, using a digital caliper with an accuracy of 0.01 mm (Mitutoyo Europe GmbH, Neuss, Germany).

For the final selected material, the accuracy of the printing was also studied by scanning the green parts with a white-light-emitting hand scanner with a resolution of 50 µm (Academia 50, Creaform Inc., Quebec, Canada) and comparing them with the original digital files.

2.5.4. Compressive Strength

The compressive strength test was carried out on 8 cubic specimens measuring approximately 20 × 20 × 20 mm. The test consisted of applying a progressive compressive force perpendicular to the base of the specimens at a rate of 0.5 mm/min until the specimens broke.

The compressive strength was calculated using the following expression (3):

$$\sigma = \frac{F_{max}}{A} \quad (3)$$

where F_{max} is the maximum strength before the breaking point (N), and A is the compression area (mm²).

2.5.5. Surface Roughness

The surface roughness of the final (sintered) parts was established using a roughness meter (Hommelwerke TM 8000, Microtécnic Ibérica, Barcelona, Spain). Surface roughness measurements were performed in accordance with international standards DIN 4768 [17], BS 1134 [18], and ISO 4287 [19] to ensure consistency and comparability.

There are numerous parameters used to define roughness [20], and for this research, the roughness parameters studied were the roughness average (R_a) and the ten-point height (Rz_{ISO}). R_a is the most commonly used roughness parameter for general quality control. Rz is more sensitive to occasional high peaks or deep valleys than R_a [20]. Since using R_a alone may cause some points, such as single protrusions, to be overlooked, it is important to use both R_a and Rz together.

R_a is the arithmetic mean of the absolute values of the distance of the points that make up the profile to a mean line (4):

$$R_a = \frac{1}{l_m} \int_0^{l_m} |y(x)| dx \quad (4)$$

where l_m is the evaluated length (5/6 of the total length, eliminating the first and last points).

Rz_{ISO} is the arithmetic mean of the vertical distance between the highest peak and the deepest valley of each of the five fractions into which the evaluated profile has been divided, without the profile having been divided into equal sections (5).

$$Rz_{ISO} = \frac{1}{5} \left(\sum_{i=1}^5 |Y_{pi}| + \sum_{i=1}^5 |Y_{vi}| \right) \quad (5)$$

3. Results and Discussion

In the raw state, the primary factor influencing densification is the compaction of the powders, which is contingent, in part, on the pressure applied by the machine; in this study, the pressure applied remained constant for all compositions. The other main factor in the compaction of the compositions is the particle size distribution, which exhibited a direct correlation between the width of the particle size distribution and the bulk density obtained on the parts, as shown in Figure 6. The correlation between the width of the particle size distribution and the resulting density was therefore direct. This can be explained by a rearrangement of the particles between large and small populations.

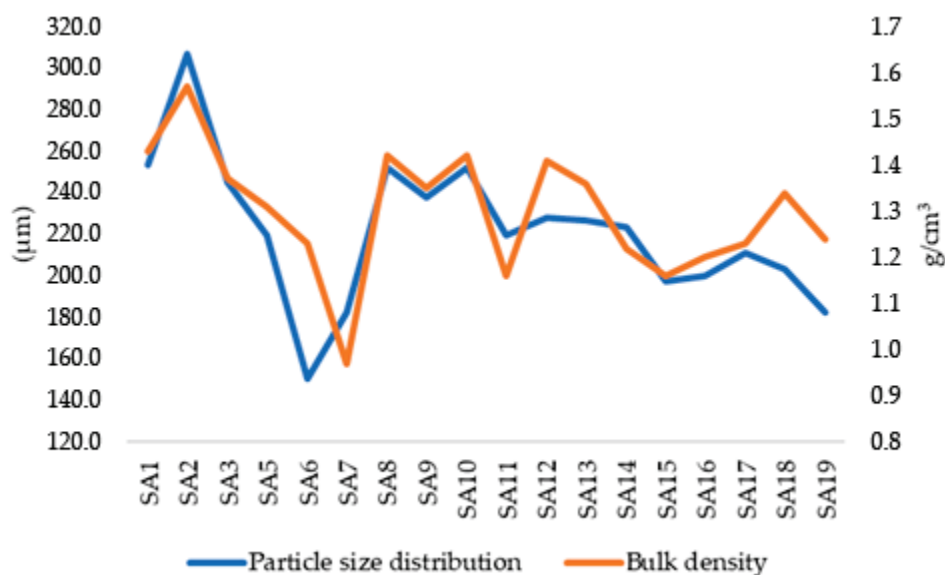


Figure 6. Particle size distribution vs. bulk density.

3.1. Pyroplastic Deformation

As the parts are required to withstand 1230 °C, materials exhibiting high pyroplastic deformation were excluded from further evaluation. It is important to note that for deformations greater than 12 mm, the pyroplastic index was deemed excessive and, consequently, was not quantified. The results are presented in Table 4.

Table 4. Pyroplastic deformation of the parts at 1230 °C.

Specimen	Pyroplastic Deformation Index
SA1	>12 mm
SA2	>12 mm (disintegrated)
SA3	>12 mm
SA4	Did not withstand handling
SA5	>12 mm
SA6	>12 mm (melted)
SA7	>12 mm (melted)
SA8	>12 mm
SA9	>12 mm
SA10	>12 mm
SA11	>12 mm
SA12	$40.9 \cdot 10^5 \text{ cm}^{-1}$
SA13	>12 mm
SA14	$11 \cdot 10^5 \text{ cm}^{-1}$
SA15	$8.9 \cdot 10^5 \text{ cm}^{-1}$
SA16	$9.3 \cdot 10^5 \text{ cm}^{-1}$
SA17	$13.2 \cdot 10^5 \text{ cm}^{-1}$
SA18	$12.2 \cdot 10^5 \text{ cm}^{-1}$
SA19	$7.1 \cdot 10^5 \text{ cm}^{-1}$

As shown in the table above, compositions SA1 to SA13 exhibited very high pyroplastic deformation. Consequently, only compositions SA14 and onwards were further analyzed in this study.

These results indicate that calcined alumina is crucial for adequate performance during the firing phase, as only the compositions containing alumina had a pyroplastic deformation index lower than $14 \cdot 10^5 \text{ cm}^{-1}$.

3.2. Compressive Strength

A critical additive in the green state is the gelling agent, which acts as a binder for the composition. However, due to its organic nature, an increased amount of gelling agent will result in higher shrinkage and/or deformation during sintering. Compositions SA1, SA4, and SA10 were identical except for the amount of gelling agent (Figure 2). As expected, the composition without the gelling agent (SA4) crumbled on contact. From the gathered data, it was determined that the optimum range for the organic gelling agent was between 5–10% to achieve adequate green strength.

Figure 7 illustrates the compressive strength of the studied compositions.

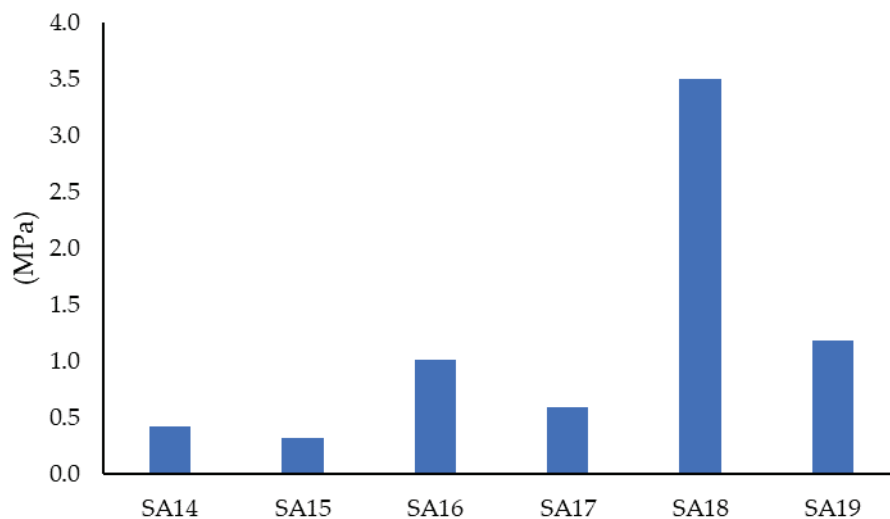


Figure 7. Compressive strength of the green parts.

3.3. Dimensional Accuracy

In addition to the need to manipulate the parts, the green strength is also needed to maintain the shape of the parts. As the prototypes must be true to scale, the amount of powder that the printed part must support during the printing process results in a significant weight that can distort the shape of the printed part (Figure 8a).



Figure 8. Comparison of the scanned printed part (yellow) vs. the original model (transparent): (a) first try-outs, (b) SA18 printed part. The red circle highlights the shape differences.

The higher compressive strength exhibited by SA18 (Figure 7) resulted in printed parts that could withstand the weight of the powder, thereby maintaining dimensional accuracy, as shown in Figure 8b.

Another critical parameter in achieving precise dimensional accuracy is contraction. Greater contraction in a printed part makes it more challenging to achieve high dimensional accuracy.

Figure 9 shows the linear shrinkage of the parts after sintering. All compositions exhibited a low shrinkage.

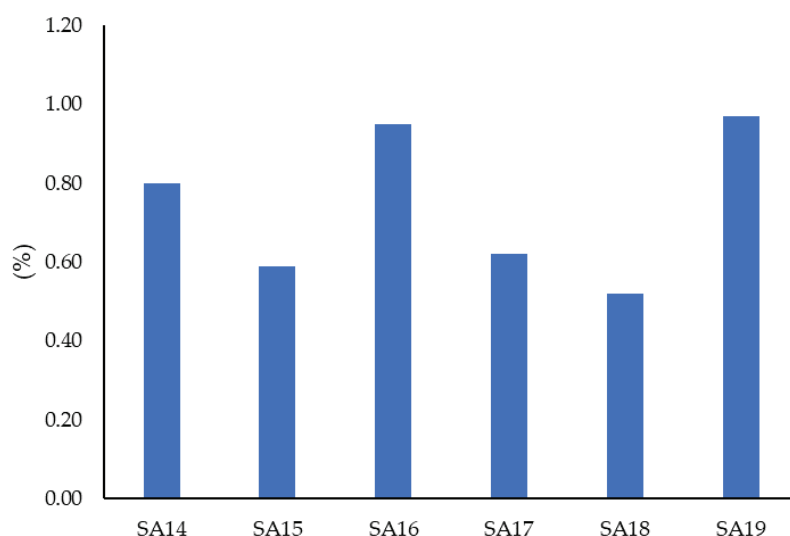


Figure 9. Linear shrinkage of the sintered parts.

3.4. Surface Roughness

The engobed and glazed parts produced with the SA18 composition were subjected to a surface roughness analysis. A sanitaryware sample was used as the reference standard for the desired roughness. Figure 10 shows the topographic maps of each part.

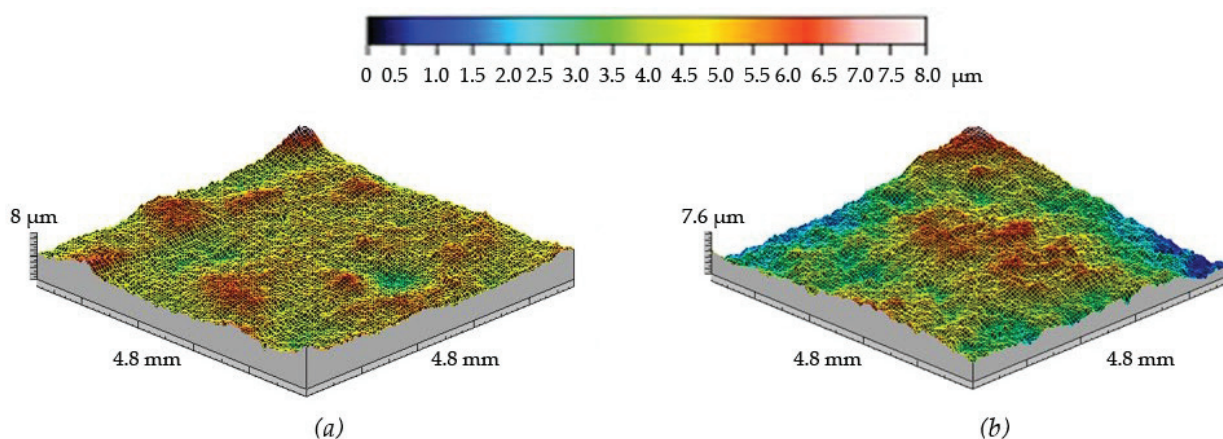


Figure 10. Topographic maps: (a) standard sanitaryware part, (b) SA18 printed part.

Table 5 shows the corresponding roughness values. The R_a value obtained in both parts was identical. However, there was a slight variation in R_z , which remained within acceptable tolerance limits. Figure 11 illustrates both parts and shows that the amount of glaze and engobe applied to achieve the observed roughness was still less than the amount used on the sample, leaving room for improvement in roughness if necessary.

Table 5. Surface roughness values.

Specimen	R _a (μm)	R _z ISO (μm)
Sample	0.11 ± 0.03	0.77 ± 0.18
SA18	0.11 ± 0.03	0.87 ± 0.13

**Figure 11.** (left) Standard glazed sanitaryware part, (right) part printed with SA18, engobed and glazed.

4. Conclusions

The results presented here demonstrate the feasibility of producing full-size ceramic parts using binder jetting for the rapid prototyping and testing of sanitaryware components. The composition that best meets the various requirements is SA18. With the highest green strength, it can support the weight of the powder during printing, maintain dimensional stability, and allow for safe handling during post-processing. The measured pyroplastic deformation of $12.2 \cdot 10^5 \text{ cm}^{-1}$ fell within acceptable limits, confirming its suitability for a conventional firing cycle. Additionally, the application of an engobe facilitated proper glaze adhesion, resulting in a surface roughness comparable to that of industrially manufactured components. This ensured that subsequent testing would meet the technical requirements and certification standards of conventional sanitaryware.

As a final test, a full-size washbasin was printed, sintered, and glazed to prove the feasibility of binder jetting prototyping with ceramics. The positive results can be seen in Figure 12.

**Figure 12.** Different printed and sintered washbasins. **Top left:** real-scale glazed washbasin; **top right:** scaled, glazed washbasin; **bottom right:** scaled sintered washbasin.

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Article

Reduction of Ceramic Wear by Concave Dimples on the Bearing Surface in CoC Hip Implants: A Finite Element Analysis

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Abstract: The wear of hip prostheses represents a significant challenge for the longevity and functionality of joint implants. Recent studies have explored surface texturing of prostheses as a strategy to enhance tribological performance. This study aims to evaluate the impact of textured ceramic surfaces with dimples on wear and friction reduction in ceramic-on-ceramic (CoC) prostheses. **Materials and Methods:** Three-dimensional models of ceramic surfaces with and without dimples were created. Contact pressure was analyzed and wear volume was estimated using Archard's law. Simulations were conducted using finite element methods (FEM) under various loading conditions. **Results:** Numerical simulations demonstrated that the wear rate for the dimpled femoral head was 0.2369 mm³/year, compared to 0.286 mm³/year for the smooth counterpart, highlighting a wear reduction of 17.2%. **Conclusions:** The integration of textured surfaces with dimples in ceramic prostheses can substantially improve their functionality and durability, representing a promising approach to addressing the issues associated with hip prosthesis wear.

Keywords: surface modification; texturing; CoC; FEA; hip joint

1. Introduction

The goal of total hip arthroplasty (THA) is to replace a damaged or compromised joint with an artificial joint [1,2]. This procedure is usually performed for conditions such as arthritis, inflammation, or in more severe cases such as hip fractures [3]. In the United States, more than 285,000 total hip replacements (THA) are performed annually to treat degenerative joint disease [4]. A variety of biomaterials are used in the manufacture of hip implants, including metals, polymers, and ceramics. There are several types of prosthetic joints available, including ceramic-on-ceramic (CoC), ceramic-on-metal (CoM), ceramic-on-polyethylene (CoP), metal-on-metal (MoM), and metal-on-polyethylene (MoP) combinations [5–8]. In 2014, more than half of new hip replacements in the United States were CoP implants (51%), followed by MoP (42%), MoM (4%), and CoC (3%) [9,10]. Major causes of MoP hips failure include wear of the polyethylene liner, caused by interaction with the Co-Cr femoral component, resulting in the generation of particles that can accelerate contact surface degradation. In addition, biological responses to the presence of wear debris can induce periprosthetic osteolysis, which can compromise the stability of the implant [11]. It has been observed that although cross-linked polyethylene reduces wear to some extent, it can still contribute to osteolysis phenomena [11–13]. Minimizing friction and wear rate are essential to increase the longevity of the prosthesis, especially with the use of femoral heads that allow a greater range of motion [14]. The current engineering

approach to addressing wear in implants involves improving the mechanical properties of the polyethylene component and creating ultra-smooth bearing surfaces, along with the development of ceramic-on-polyethylene (CoP) and ceramic-on-ceramic (CoC) prostheses. For example, CoC bearing surfaces have an average roughness of less than 5 nm, allowing them to operate in an (elasto-hydro)dynamic lubrication regime, which helps to reduce friction and wear [15]. In an analysis conducted by Buttaro et al. [16], a retrospective review was performed of 939 cases (880 patients) who underwent primary total hip arthroplasty with CoC bearing surfaces. The results showed an exceptional average survival rate of 99.3% over a period of 2–10 years. In addition, Lee et al. [17] reviewed data on 2.78 million AMC ceramic femoral heads implanted worldwide and found a clinical fracture incidence of only 1 in 100,000 for contemporary AMC ceramic femoral heads. Furthermore, a study by Solarino et al. [18] found that CoC is the ideal choice for younger and more active patients due to its reliability and longevity, highlighted by the lack of material-related complications. CoC implants also allow the use of femoral heads larger than 28 mm without increasing the coefficient of friction, which is not always possible with CoCr heads due to concerns about polyethylene wear [19,20]. In a comparative analysis by Higuch et al. [21], the average wear rate on anteroposterior (AP) radiographs was 0.0037 mm/year for CoC compared to 0.0051 mm/year for MoM. Therefore, the lower wear rates of CoC prostheses could indicate a longer implant life and fewer problems related to osteolysis and revision compared to MoP, MoM, and CoP. However, despite the excellent results observed with CoC, the number of revision surgeries is steadily increasing, especially in younger and adult patients, and is expected to double by 2026 [22–26]. This could have a significant social and economic impact if effective preventive measures are not implemented [27,28]. Various surface modification techniques have been developed to extend the life of joint prostheses. These include surface texturing (dimpling) and the application of surface coatings. These methods are typically applied to the surfaces of the femoral head [29–33]. Surface texturization helps to improve tribological performance by increasing the thickness of the lubricating film between contacting components, acting as a lubricant reservoir.

Increasing the thickness of the lubricant film by creating dimples on the surface of the femoral head allows direct contact between the surfaces to be avoided, reducing the risk of dry friction. This system helps to trap wear particles under mixed lubrication conditions, preventing damage to the bearing surface during movement. Roy et al. [34] documented a significant 22% reduction in friction and 53% reduction in wear on textured surfaces compared to non-textured surfaces. Vaidyanathan et al. [35] found that the use of a textured CoCrMo femoral head in conjunction with a UHMWPE liner resulted in a reduction in coefficient of friction of up to 36% and a reduction in wear of up to 69%. Finite Element Methods (FEM) provide an effective alternative to laboratory testing [36–39]. These methods allow faster and more cost-effective simulations of different loading and kinematic scenarios. However, some studies, such as that of Jamari et al. [40], have used simplified models that do not always accurately reflect physiological conditions. Despite the lack of studies on the wear volume of CoC prostheses, there is a great deal of experimental and numerical research on the textured surfaces of MOP and COP prostheses [41]. The aim of this research is to analyze the contact pressure on the surface of the acetabular cup with and without the addition of dimples in a ceramic-on-ceramic (CoC) configuration. The analysis is performed using 3D dry contact models with simplified loading conditions to obtain immediate results. In addition, the wear rate for both models is estimated using Archard's law to validate the null hypothesis that the introduction of dimples would significantly reduce the wear rate.

2. Materials and Methods

The CoC hip implant has a 32 mm diameter head made of BioloX Delta zirconia matrix [42] with a Young's modulus of 350 GPa and a Poisson's coefficient of 0.26. The acetabular insert has an internal diameter of 32.49 mm, a thickness of 8 mm, and an external diameter of 40 mm. It is made of zirconia with a modulus of elasticity of 210 GPa and a Poisson's coefficient of 0.26. In addition, the distance between the acetabular insert and the femoral head is 0.245 mm (Figure 1). The two components were manufactured and assembled using the 3D modelling software Autodesk Inventor 2024 [43,44].

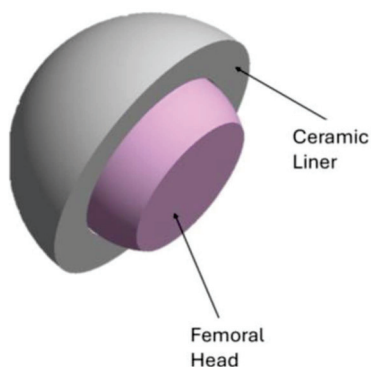


Figure 1. View of femoral head and ceramic liner.

Based on the geometric parameters of dimples reported in the literature [41], a model was created with the addition of circular dimples as shown in Figure 2. Using Autodesk Inventor's geometric modeling commands, dimples were created that are 0.5 mm in diameter and 0.25 mm deep. The industrial technology for creating dimples on ceramic surfaces using lasers is known as laser surface texturing (LST) or laser surface treatment. This process modifies the surface properties of the material, resulting in microstructures that improve tribological properties such as reduced friction and wear.

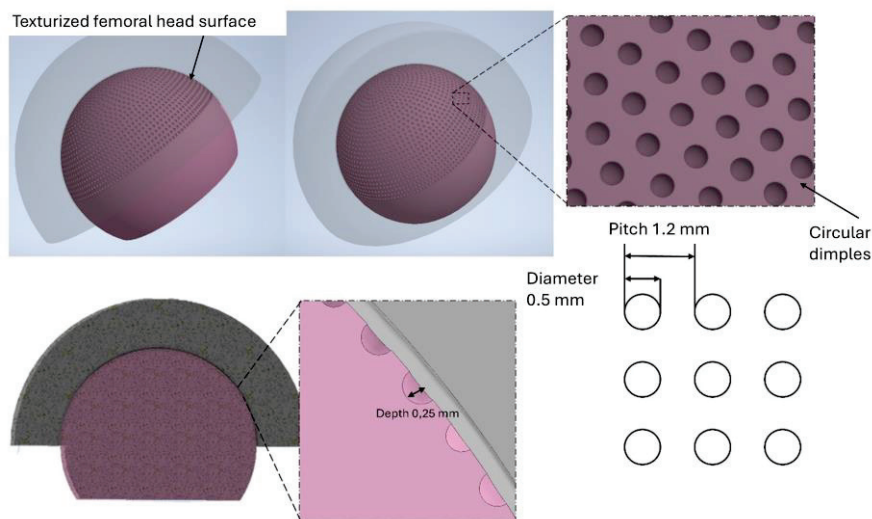


Figure 2. Model of the CoC joint with circular dimples on the surface of the femoral head.

One of the important parameters describing the geometry of textured features is the aspect ratio ε [45]. It is defined as the ratio of the depth (h) to the equivalent diameter (d) of the textured feature. Deep pits with an aspect ratio $\varepsilon > 0.1$ act as lubricant reservoirs, reducing friction and wear in mixed lubrication conditions and providing lubricant to contact surfaces in deficient conditions. They also provide trapping of wear debris that would otherwise scratch the surface. Conversely, for aspect ratios $\varepsilon < 0.1$, there is a

micro-hydrodynamic support effect which increases the pressure and thickness of the lubricant film between the bearing surfaces, reducing contact and, consequently, friction and wear (Figure 3).

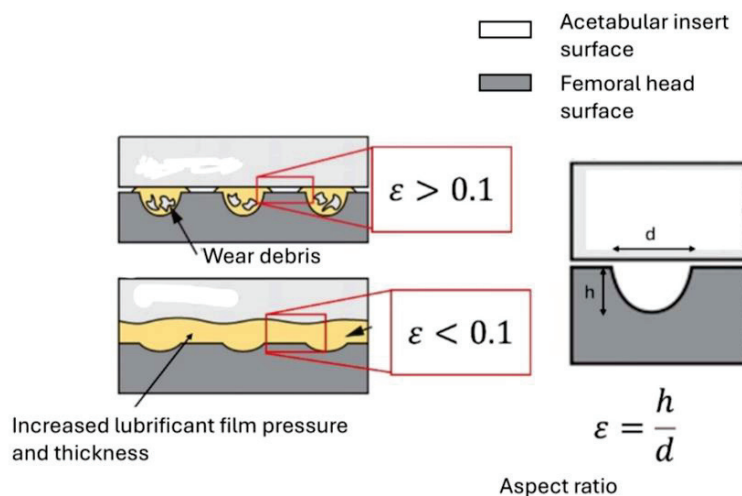


Figure 3. Representation of the tribological behavior of dimples as a function of aspect ratio.

In this study, an aspect ratio of $\varepsilon = 0.5$ was chosen, contributing to a higher load capacity and a reduction in the coefficient of friction. The materials considered in this analysis were modelled with isotropic linear behavior as they are characterized as brittle materials that do not exhibit yielding behavior [43,46–48] (Table 1).

Table 1. Mechanical properties of materials.

Components	Young's Modulus [GPa]	Poisson's Ratio
Femoral head	350	0.26
Liner	210	0.26

2.1. FEA Modeling

The classical workflow for an FEM analysis in (Ansys® R 2024) software consists of four steps: (1) pre-processing (PREP 7); (2) solving (SOLU); (3) post-processing (POST 1 or POST 26); (4) validation. In the pre-processing step, materials are selected, and the geometry of the model is created. During the solution step, boundary conditions are applied, and solution options are set. In the post-processing step, results are obtained, and analysis is performed Figure 4.

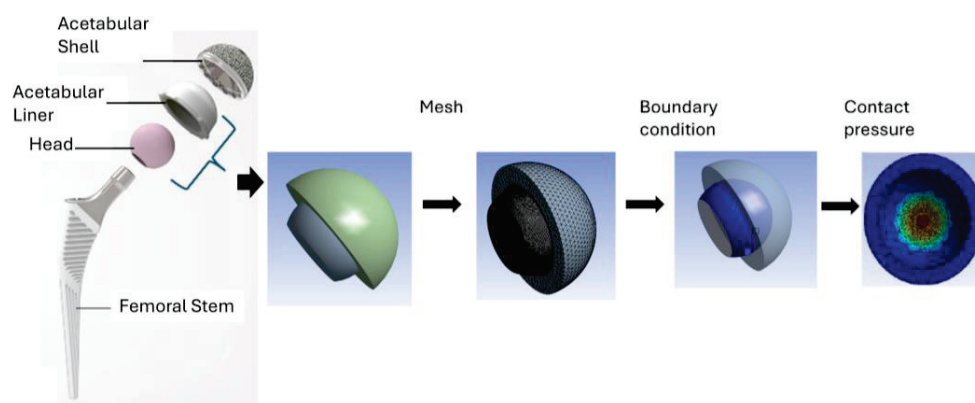


Figure 4. Workflow used in FEM simulation.

While the acetabular insert and the femoral head were discretized with a mesh size of 1 mm, the contact area was refined using the Contact refinement command. A finer mesh of 0.5 mm was used to better represent the stress distribution in this area (Figure 5).

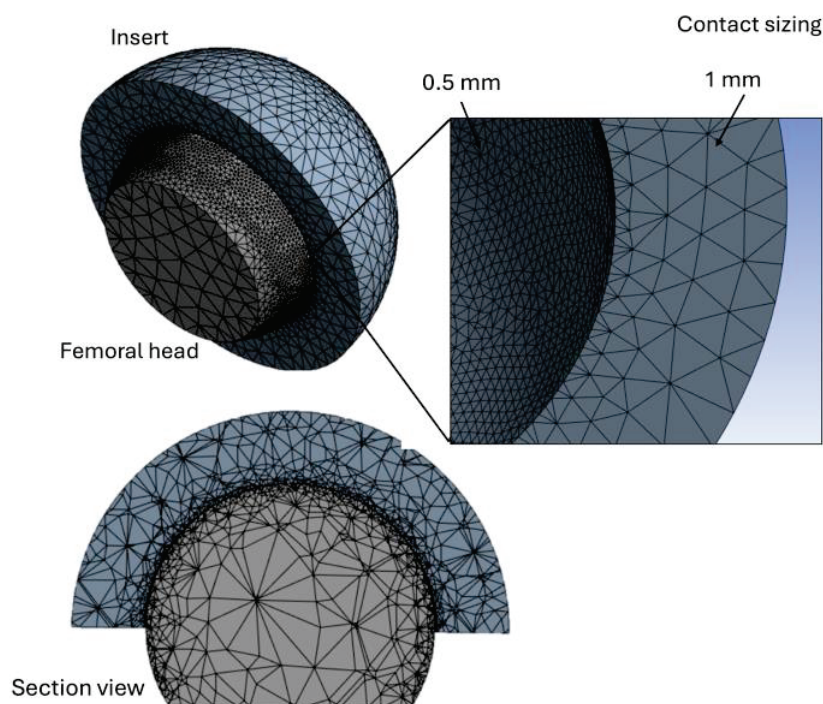


Figure 5. Mesh model of the artificial hip joint.

These parameters were subsequently validated by convergence analysis, which showed an error in the contact pressure results of less than 1% using a mesh of 0.5 mm and 0.6 mm. The element order was set to Quadratic (SOLID 187), and the error limits were set to Standard Mechanical. The most used elements are hexagonal and tetrahedral. Hexagonal elements are generally preferred due to their higher accuracy but are more expensive to calculate [49–52]. The choice between the two types of elements depends on the level of accuracy required. A mesh that is too coarse leads to imprecise solutions but low computational cost, while a fine mesh gives very accurate results, may become computationally impractical. Tetrahedral elements were therefore used in this study because they allow easier meshing, resulting in a total of 15,479 nodes and 9452 elements.

2.2. Boundary Conditions

Regarding contact conditions, the femoral head is modelled as ‘Target Body’, as it is the strongest material, while the acetabular insert is defined as ‘Contact Body’. Eight-node linear 3D elements (CONTA 174) were used for the contact, while four-node linear 3D elements (CONTA 170) were used for the target. A frictional contact between the two surfaces was then assigned using a Ceramic-Ceramic friction coefficient of 0.12 [53,54] (Figure 6).

The calculation is simplified through the study of Bergmann et al. [55] and shows that the resultant force is equivalent to the vertical component. Therefore, only this component is considered in this analysis for an individual weighing 80 kg. In this study, various activities shown in Table 2 were considered. Then, the equivalent forces for the individual activities were applied to the upper surface of the insert.

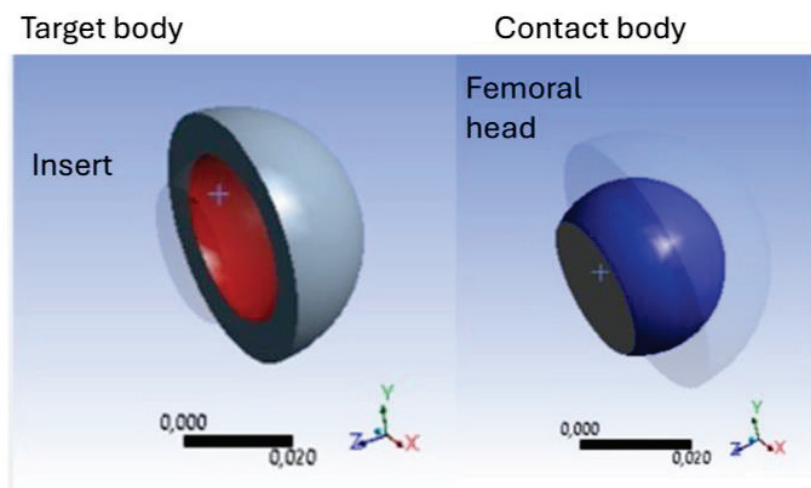


Figure 6. Contact conditions for liner and femoral head.

Table 2. Loads acting on the joint as daily activities vary and as a function of body weight.

Activity	Maximum Contact Force (% of Body Weight) or Activity Factor
Going upstairs	2.6
Going downstairs	2.51
Fast walking	2.5
Slow walking	2.42
Sitting down	1.56

The lower part of the femoral head was fully constrained in all directions, while a vertical load was applied to the upper surface of the insert Figure 7.

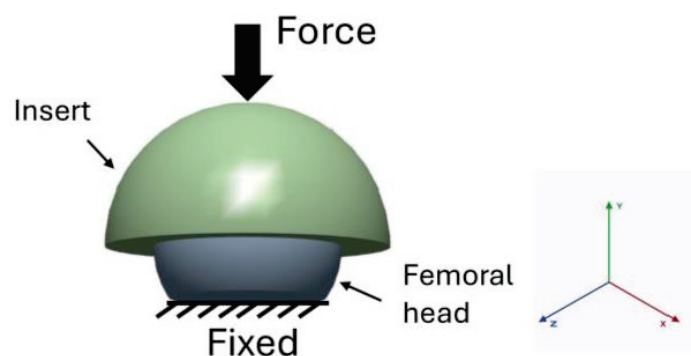


Figure 7. Load and constraint conditions.

In this study, the normal contact case is defined to represent the basic interaction between surfaces, concentrating on axial loading conditions during femoral head articulation within the acetabulum. While rotation plays a critical role in real-life scenarios, more detailed analyses can incorporate rotational dynamics in subsequent studies. Future finite element analyses may explore how dynamic loading and rotational forces impact contact mechanics and wear over time, particularly in the context of dynamic testing conditions.

A total of 10 cases (five model a, five model b) were analyzed for the various activities shown in Table 2.

2.3. Calculation of the Wear Rate

Using Archard's formulation [56,57], wear can be calculated. This assumes that the two contact surfaces are not perfectly smooth but consist of asperities. It is also assumed that only the higher asperities carry the normal load W during the sliding motion.

Given a small sliding section ds and a small load increment dW , we assume that the volume of material removed dV is proportional to these quantities and inversely proportional to the hardness H of the "soft" material:

$$dV = k \frac{dW ds}{H} \quad (1)$$

where k is a dimensionless proportionality constant (incorporating the fraction of asperities broken and transported as wear particles).

Integrating over the total sliding distance S and the total load W gives Archard's volumetric law:

$$V = \int dV = \int_0^W \int_0^S K \frac{dW ds}{H} = \frac{K W S}{H} \quad (2)$$

In the case of the femoral head and insert coupling, where R is the radius of the head with a circumference of length $2\pi R$, Archard's formula can be rewritten as:

$$V_{tot} = \frac{K W S}{H} = \frac{K W (2\pi R)}{H} \quad (3)$$

Equation (3) is scaled to reproduce actual daily loading conditions (10,000 cycles) and then adjusted to an annual period with an additional scaling factor of 365. A factor of 1000 was also applied to convert the results to mm^3 per year. The final equation of Archard's law applied in this study is Equation (4), where the contact area S_l was calculated by subtracting the area of the femoral head from the hemispherical area of the insert, resulting in a contact area of 1608.5 mm^2 .

$$V = k_w * \sigma_c * A * S_l * 1000 * 365 * 10^3 \quad (4)$$

where:

k_w : wear coefficient in mm^3/Nm .

σ_c : contact pressure in MPa

A : contact area in mm^2

S_l : sliding distance in mm.

The wear coefficient k_w can be obtained from experimental studies such as pin-on-disc tests or hip wear simulators [57], considering the surface roughness R_a . In the present study, a k_w value of 1×10^{-8} is used for a ceramic-ceramic contact in a CoC joint. The results of the FEM simulation, such as contact pressure and sliding distance, can then be used to calculate the wear volume during different activities using Equation (4).

3. Results

Numerical simulation of this model was conducted to determine the maximum value of contact pressure and sliding distance, assuming static loading conditions to simplify the analysis. Using Archard's wear rate formulation, it is possible to estimate the volume of wear that occurs on the inner surface of the acetabular liner. The situation involving the maximum load is the activity of climbing stairs, in which the body weight increases by 2.6 percent. Figure 8 shows the contact stress found during stair-climbing activity. From these findings, it can be seen that the maximum stress values are located in the central region of the inner surface of the liner, while the minimum values are located in the circumferential area.

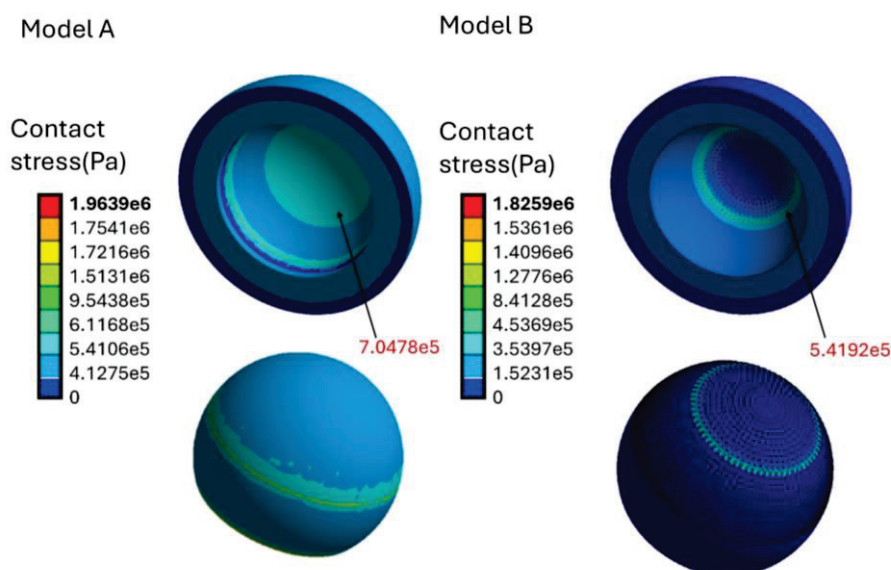


Figure 8. Contact stress distribution during the stair-climbing task in the model without dimples (model A) and with dimples on the femoral head (model B).

For the model without dimples (model A) a maximum contact stress of 0.7047 MPa is reached, whereas for the model with dimples (model B) 0.5419 MPa is reached. Furthermore, the maximum stress observed at the femoral head for model A is 0.5043 MPa, while for model B lower values of 0.3097 MPa reached Figure 9.

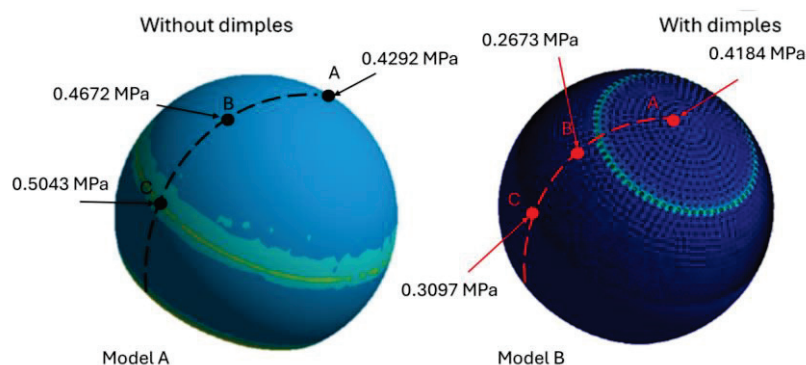


Figure 9. Stress path analysis of the femoral head in the two models with dimples (model B) and without dimples (model A).

From Figure 9 the maximum stress value is reached in the c zone for both models. While the lowest contact stress values are reached in zone a, 0.4292 MPa for model A and 0.4184 MPa for model B. Regarding the sliding distance, the relative values in mm are shown in Table 3.

Table 3. Sliding distance values for model A and model B.

	Sliding Distance (mm)
Without dimples	0.01832
With dimples	0.00874

In the case of a dimpled model, the sliding distance is less than in the case of a model with a smooth femoral head.

Wear Volume

The wear volume (V) of the surface modified femoral head was calculated using the modified Archard wear equation. This method allows the quantitative measurement of material loss from artificial implant components, which is critical in assessing their performance and durability over time. To estimate the annual wear volume, a condition of 10,000 load cycles per day, a femoral head surface roughness of $0.008\text{ }\mu\text{m}$ and a radius of 16 mm was assumed. Figure 10 shows that the wear rate of a femoral head is higher during stair-climbing activities. In this activity, the model with dimples exhibits a lower wear rate ($0.2369\text{ mm}^3/\text{year}$) compared to the smooth head model ($0.286\text{ mm}^3/\text{year}$). Therefore, the dimples may help distribute pressure more evenly across the contact surface between the femoral head and the insert. This contributes to reducing localized stress peaks, which are often responsible for excessive wear. Furthermore, the dimples reduce the contact area, distributing the load over a larger surface. As a result, a smaller contact area can lead to lower wear, as there is less direct material in contact to wear away. The dimples can also act as traps for debris, reducing friction and wear caused by direct contact between surfaces.

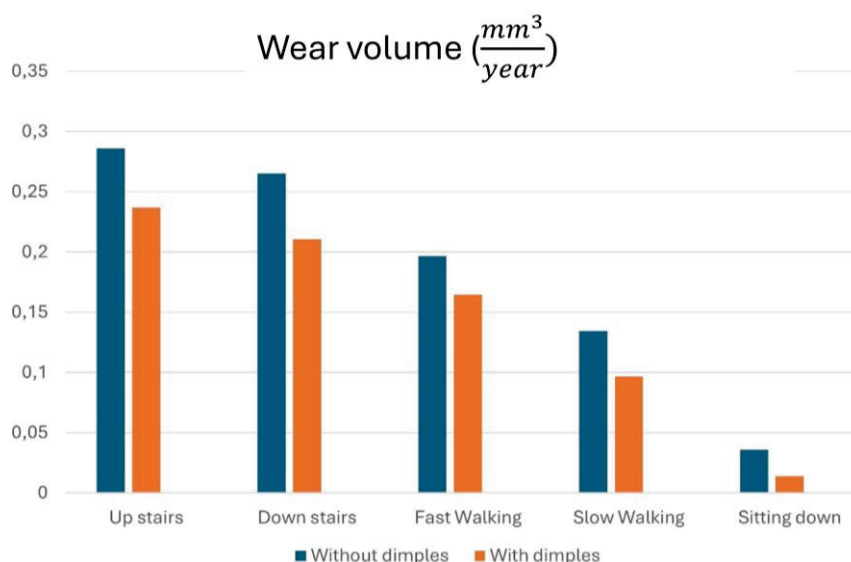


Figure 10. Comparison of the wear rate of the two models for different activities for an 80 kg body weight, 32 mm diameter femoral head with and without dimples.

Sitting is the activity that causes the least wear, with values of 0.0358 mm^3 for the model without dimples and 0.01369 mm^3 for the model with dimples. These results are consistent with previous clinical studies and suggest that the empirical relationships developed may be useful in the design of hip prostheses.

4. Discussion

The prevention of aseptic loosening of artificial joints poses a significant challenge in orthopedic surgery. It is crucial to improve the lubrication properties of friction surfaces and reduce the generation of wear particles [58–60]. This necessity can be justified on three main grounds. First, high friction can generate elevated shear stresses at the bone-implant interface. This mechanism is often responsible for aseptic loosening, which can compromise implant stability [61,62]. Therefore, it is essential to mitigate friction to prevent such events. Second, numerous studies have shown that high molecular weight polyethylene (UHMWPE) liners wear at rates between 0.1 and 0.2 mm per year [63], resulting in a thick reduction of approximately 1–2 mm over a decade. In situations where the liner is thin, increased wear can lead to higher friction with the femoral head. This friction

is associated with conditions such as metallosis, which can lead to osteolysis [64,65]. Finally, wear particles generated during friction serve as stimuli for the immune system, provoking an adverse foreign body response. Histological and biochemical studies conducted on wear particles from UHMWPE and metallic components, collected from surrounding tissues during revision surgeries, have demonstrated how these particles can negatively affect the biological response and longevity of the implant [66–68].

Conversely, the adoption of materials with different mechanical and tribological characteristics in the coupling of femoral heads and acetabular cups has allowed for better control over wear rates and friction [69]. In recent years, the implementation of ceramic-on-ceramic (CoC) prostheses in total hip arthroplasties has shown significant advancements in addressing the previously mentioned issues [70–72]. Ceramic surfaces are characterized by a high level of smoothness, which substantially reduces friction during joint movement. In comparison to traditional materials such as metal and polyethylene, the use of ceramic surfaces in prosthetic devices allows for a reduction in the interaction between surfaces, leading to decreased wear over time and thereby ensuring a longer lifespan of the implant. A particularly crucial aspect is the adoption of femoral heads with a larger diameter (≥ 36 mm), which not only enhances the stability of the implant by reducing the risk of dislocation but also improves the distribution of forces within the joint, minimizing contact and friction between the bearing surfaces [73]. This approach has demonstrated significant improvements compared to lower-diameter prosthetic systems, which are generally associated with higher wear rates [74–76].

Furthermore, recent studies have shown that even under conditions of poor lubrication, ceramic heads can maintain good performance characteristics, limiting both friction and the accumulation of wear debris in the joints [77–79]. An important innovation has been the introduction of laser surface texturing (LST), which allows the creation of microstructures (dimples) on various materials, including metals and ceramics, thereby contributing to the reduction of friction and wear. A study conducted by Joshi et al. [80] showed that LST significantly reduces the coefficient of friction, achieving a reduction of up to 60% in textured samples compared to polished ones. Numerous experiments in total hip arthroplasty have been conducted to optimize the tribological characteristics of joints through texturing techniques [81–83].

One of the main purposes of texturing is to create structures on the surface called dimples, which serve various functions: they act as reservoirs for lubricants; they increase hydrodynamic pressure during movement; they trap wear debris or foreign materials in the concavities; they reduce the contact area; and they minimize friction and wear [84]. However, the effectiveness of wear reduction depends on the optimization of geometric parameters such as the density, pitch, and size of the dimples. Roy et al. [85] demonstrated that a dimple diameter of 400 μm with a density of 15% improves friction and wear performance compared to other geometries. On the other hand, Huang et al. [86] reported enhanced lubrication effects from smaller-sized concavities with a high pore density, due to the uniform distribution of lubricants within the micro-dimples. This also confirms the role of dimples as lubricant reservoirs. The lubricant is expelled from the concavities to minimize contact under load conditions. However, surface roughness may increase with dimple density. Moreover, from a geometric perspective, circular shapes have been commonly used since they can be easily fabricated with high precision. Ito et al. [29] studied the tribological performance of a textured Co–Cr–Mo surface, observing a 17% reduction in friction and a 36% reduction in polyethylene wear. Meanwhile, a study by Shen et al. [87] reported a significant improvement in tribological performance by creating a trapezoidal shape of the dimples. However, few studies have been reported on the application of dimples on ceramic heads. Research in this area is limited compared to other

implant surfaces, such as those made of metal or polyethylene. This could be attributed to the technical challenges associated with creating dimples on ceramic materials, which may influence the tribological performance and durability of the implants. The use of laser technology has made it possible to texture ceramic surfaces in recent years [88]. In this study, the finite element method was employed to investigate the effect of dimples on a ceramic surface in a CoC coupling [89–95]. The results indicated that the addition of dimples led to a significant reduction in wear rate of approximately 17% compared to a model without dimples. Clinically, dimples on ceramic heads improve lubrication and reduce the contact area, mitigating vibrations and resulting in quieter operation with decreased squeaking. These findings align with previous literature. For instance, Tewelde et al. [96] reported a wear volume reduction of up to 87% on smooth metal surfaces using various texture configurations. Similarly, Sagbas et al. [97] demonstrated a 29% decrease in friction coefficient and a 39% reduction in wear volume when comparing smooth CoCrMo pins with textured UHMWPE disks. Concerning ceramic surfaces, only physical experiments have been conducted. For example, an analysis by Min Ji et al. [98] showed that various surface textures reduced the friction coefficient by 24% compared to untextured surfaces during ceramic-ceramic friction tests.

Limitations

Although this study showed a significant improvement in wear rate reduction by introducing textured surfaces with dimples, it is important to consider some relevant limitations of the model used. The simulations performed were carried out under static conditions, which do not reflect the actual behavior of the implants during the physical activity of the patients. This is a crucial issue since the joints are subjected to repeated load cycles and different motion conditions, factors that could significantly affect the tribological performance of the ceramic surfaces. To address these limitations, *in vitro* studies are proposed to validate numerical simulations. In addition, controlled tests under dynamic conditions would provide useful empirical data to better understand how textured surfaces interact with synovial fluid. Another aspect to consider is the strength and fatigue of the material. Textured surfaces may behave differently under cyclic loading over time; therefore, longitudinal studies would be valuable in assessing their durability. It is therefore necessary to develop models that simulate mechanical fatigue over time and to analyze the effect of wear-induced particle accumulation on the integrity of ceramic materials.

5. Conclusions

This study highlighted the importance of dimpled textured surfaces in ceramic hip replacements and demonstrated significant and quantifiable results. A 17.2% reduction in wear rate was observed, with wear values of $0.2369 \text{ mm}^3/\text{year}$ for textured femoral heads compared to $0.286 \text{ mm}^3/\text{year}$ for smooth femoral heads. In addition, during stair-climbing activity analysis, the textured model showed a maximum contact pressure of 0.5419 MPa, which was lower than that of 0.7047 MPa for the smooth model, demonstrating better load distribution. The sliding distance was reduced from 0.01832 mm in the dimpleless model to 0.00874 mm in the dimpled model, indicating better tribological behavior. Finally, the dimples were shown to act as lubricant reservoirs, further reducing friction. These results suggest that the incorporation of dimples into ceramic prostheses represents an innovative approach to improving the durability and function of hip prostheses.

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Article

Optimized Development of High-Porosity Structural and Thermal Insulation Foam Ceramics Based on Local Natural and Technogenic Raw Materials

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Abstract: This study explores the optimization of foam ceramic materials through experimental research and mathematical modeling. The goal was to enhance mechanical strength, thermal insulation, porosity, water absorption, and density by adjusting composition and firing conditions. Regression analysis and response surface methodology were used to assess the effects of loam, fly ash content, and the firing temperature. The optimal composition of 60–65% loam, 10% fly ash, and a firing temperature of 950–1000 °C yielded foam ceramics with a bulk density of 680–700 kg/m³, a compressive strength of 3.5–4 MPa, and a thermal conductivity of 0.135–0.140 W/(m·K). Controlled porosity (70–72%) enhanced insulation while maintaining structural integrity. X-ray diffraction confirmed mullite, quartz, and cristobalite phases, with mullite improving mechanical properties. This research demonstrates the potential of optimized foam ceramics for energy-efficient construction. Mathematical modeling and experimental validation provide a pathway for developing lightweight, high-performance ceramic materials. Future work should refine sintering processes, explore new additives, and evaluate the long-term performance.

Keywords: foam ceramics; optimization; mathematical modeling; thermal insulation; mechanical strength; porosity; water absorption

1. Introduction

The demand for high-performance thermal insulation materials is increasing due to the necessity of improving energy efficiency in residential and industrial construction [1]. The necessity of improving energy efficiency in residential and industrial construction is increasingly evident, with the global energy demand for space heating and cooling accounting for approximately 35% of total building energy consumption. The adoption of advanced thermal insulation materials has been shown to reduce heat loss in buildings by up to 40%, significantly lowering energy costs and carbon emissions. Various materials, including dense and porous concrete, gypsum-based composites, and cellular ceramics, have

been developed to address these requirements. The ceramic industry still predominantly produces dense structural bricks with limited porosity, as evidenced by market reports indicating that over 80% of globally manufactured ceramic bricks fall within the category of dense structural ceramics with a porosity below 10% [1]. This trend highlights the need in construction for innovative porous ceramic materials to improve thermal insulation. However, despite the progress in building materials science, the ceramic industry still predominantly produces dense structural bricks with limited porosity, affecting their insulation properties. Granular foam glass, produced using recycled cullet and ceramic fillers, is an alternative lightweight insulating material. While it offers high compressive strength and resistance to chemical degradation, it has limitations in terms of thermal stability and brittleness compared to foam ceramics. In contrast, foam ceramics provide a more uniform pore structure, superior thermal insulation, and enhanced fire resistance, making them particularly suitable for high-temperature applications in construction. Recent studies have explored the possibility of producing granular foam glass using household and commercial cullet combined with ceramic fillers, demonstrating the feasibility of obtaining eco-friendly thermal insulation materials through controlled foaming techniques. These advancements highlight the potential of both materials in sustainable construction while emphasizing the advantages of foam ceramics in demanding thermal environments [2–7].

The heat-insulating properties of ceramic foams have made them widely applicable in high-temperature industrial settings, such as structural catalyst supports and energy storage systems. Research has shown that the effective thermal conductivity of ceramic foams is strongly influenced by the pore structure, stacking thickness, and temperature conditions [8–14]. Foam ceramics exhibit excellent heat-insulating properties due to their high porosity and low thermal conductivity, typically ranging from 0.05 to 0.15 W/(m·K) depending on the composition and processing conditions. Compared to conventional dense ceramics, these materials can reduce heat transfer by up to 50%, making them highly effective for energy-efficient building applications. These properties make them particularly valuable for applications requiring both thermal resistance and lightweight construction materials. Moreover, mathematical modeling and experimental validation play crucial roles in optimizing the physical and mechanical properties of foam ceramics [15]. Computational fluid dynamics (CFDs) simulations play a crucial role in optimizing the properties of foam ceramics by modeling heat transfer, pore structure evolution, and fluid behavior during foaming. These simulations enable the prediction of thermal conductivity, airflow resistance, and mechanical stability, allowing for the fine-tuning of processing parameters to achieve the desired porosity and insulation performance. By using CFD-based optimization, researchers can enhance the structural integrity and thermal efficiency of foam ceramics before conducting extensive experimental trials, reducing material waste and production costs. For instance, CFDs simulations have been used to evaluate the pressure drop in ceramic foam filters, providing insights into how the material structure influences fluid flow and heat transfer, further refining the design and functional performance of foam ceramics [16–23].

In Kazakhstan, extensive studies have been conducted on the thermal insulation performance of various construction materials, particularly by researchers such as Ibraimbayeva G.B., Orynbekov E.S., and Saduakasov M.D. These studies highlight the importance of developing innovative, eco-friendly insulation materials with enhanced mechanical and thermal properties. Kazakh researchers have actively explored the development of foam ceramics using local natural and industrial raw materials, focusing on optimizing the composition and processing conditions to improve their performance. Their findings align with the present study's focus on sustainable material development by demonstrating the feasibility of incorporating regional resources such as loess and fly ash into foam ceramics.

This synergy reinforces the global effort to create cost-effective, energy-efficient building materials whilst addressing local raw material availability and environmental concerns. Recent advancements in foam ceramic technology have focused on optimizing sintering conditions, where controlled heating rates and sintering times significantly affect the porosity, compressive strength, and water absorption of the final products. For instance, previous studies have shown that increasing the sintering temperature from 900 °C to 1100 °C can reduce the porosity from 85% to 65% whilst simultaneously increasing the compressive strength from 1.2 MPa to 4.5 MPa. Additionally, prolonged sintering times (e.g., from 60 to 180 min) can enhance densification but may lead to a decrease in the water absorption from 40% to 20%, depending on the composition of the ceramic mass [24–28]. Additionally, novel processing techniques for foam ceramics allow for the incorporation of industrial waste, such as coal gangue and phosphorus tailings, into their compositions, contributing to resource conservation and waste recycling.

Despite the progress in foam ceramic development, many conventional insulation materials, such as mineral wool and expanded polystyrene, have significant drawbacks. These include moisture sensitivity, fire hazards, and the release of toxic gases upon combustion. Alternative approaches, such as nanostructured foam ceramics, have demonstrated improved moisture resistance, mechanical strength, and chemical durability, making them a superior choice for long-term thermal insulation applications [29–36]. These materials, which undergo controlled sintering at temperatures between 950 and 1100 °C, exhibit high mechanical stability due to the formation of mullite-based crystal bonds within their microstructure.

Thus, the present study aims to explore the optimization of foam ceramic compositions based on local raw materials to achieve enhanced thermal insulation and mechanical properties. By evaluating the influence of key parameters such as foaming agents, the firing temperature, and the sintering conditions, this research seeks to optimize porosity, thermal conductivity, and compressive strength to improve the suitability of foam ceramics for modern construction applications. Refining the composition and processing conditions allows for an optimal balance between mechanical durability and thermal insulation efficiency. These improvements are particularly relevant for energy-efficient building materials, contributing to reduced heat loss, improved structural integrity, and sustainable resource utilization in construction.

2. Materials and Methods

The primary objective of technological experiments is to establish relationships that link the properties under investigation (such as strength, density, etc.) with a set of independent variables (such as additive content, drying time, and firing temperature). These relationships are used to optimize the process by identifying the best technological parameters.

Experimental planning plays a crucial role in mathematical modeling by minimizing the number of experiments while varying all influencing factors. Applying the principles of experimental theory enhances research efficiency, allowing researchers to construct mathematical models, optimize processes, and test various hypotheses with minimal resource expenditure. The range of tasks that experimental planning can address includes identifying optimal conditions, constructing interpolation formulas, evaluating and refining theoretical model constants, and studying composition–property relationships.

One of the most common scientific and technical challenges is determining the optimal conditions for a process once its feasibility has been established. This can be effectively approached using a cybernetic system model, often referred to as a “black box”, which Figure 1 schematically represents. The arrows on the right denote optimization parameters (y), which are also referred to as optimization criteria, objective functions, or black box outputs.



Figure 1. Black box diagram.

The primary objective of technological experiments is to establish relationships between investigated properties (e.g., strength, density) and independent variables (e.g., additive content, drying time, firing temperature) to optimize the process. Experimental planning plays a crucial role in minimizing the number of trials while systematically varying influencing factors. This approach enhances research efficiency by enabling the construction of mathematical models, the optimization of processes, and hypothesis testing with minimal resource expenditure.

Experimental planning addresses a wide range of tasks, including identifying optimal conditions, constructing interpolation formulas, refining theoretical model constants, and studying composition–property relationships. One of the most common challenges is determining optimal process conditions once feasibility has been established.

The research object can be represented using a cybernetic system model, often referred to as a “black box”, as shown in Figure 1. The arrows denote optimization parameters (y), also known as optimization criteria or objective functions. To solve the research problem, mathematical models will be employed, where the response function links optimization parameters with influencing factors, as expressed in Equation (1) as follows:

$$y = f(x_1; x_2; x_3 \dots x_n), \quad (1)$$

where $f(x)$ represents the response function.

Various methods of mathematical planning are used in technological research, such as full factorial experiments (FfEs), rational planning, and multifactor experimental design. Some of these methods require the use of electronic computing machines (ECMs) for data processing, while others can be applied without computational assistance.

Experimental Design: A full factorial experiment (FFE) was utilized to systematically analyze the influence of multiple factors on the properties of foam ceramics. This approach allows for the evaluation of the combined effects of independent variables while minimizing the total number of experiments.

Materials

Local natural and industrial materials were used in the study to produce highly porous foam ceramics with a density of D600–D700. The primary raw materials included clay from the Koskuduk deposit and loam from the Burunday deposit, both characterized by optimal physicochemical and technological properties. To improve the structure and strength, construction gypsum, sodium silicate, and fly ash from thermal power plants were added [36–39]. Foaming was carried out using two types of foaming agents, “PB-2000” and “IFoamOrganic”, which ensured the formation of a uniform cellular structure in the foam ceramic samples. To stabilize the structure and regulate coagulation processes, polycarboxylate additives SP-1 and KH-5 were used. The study involved analyzing the physical and mechanical properties of the resulting materials and assessing the effects of various additives on the structural stability and the reduction in shrinkage deformations.

IFoamOrganic is a keratin-based foaming agent derived from animal horns and hooves. It is commonly used in the production of thermal insulation blocks. Compared to synthetic foaming agents, keratin-based foam is known for its higher stability—both during the mixing with mineral components and during the setting phase of the molded ceramic mass.

In this study, both IFoamOrganic and PB-2000 were tested to evaluate their impact on foam structure and material performance.

Physical and Mechanical Properties of IFoamOrganic:

- Working solution concentration: 2.5–3.5%,
- Syneresis time: 10 min,
- Physical state: liquid,
- Density: 1.12–1.15 g/cm³,
- pH at 20 °C: 6.5–7.2,
- Expansion ratio (foamability): ≥ 6 ,
- Foam stability: 55 min,
- Shelf life: up to 12 months,
- Color: dark brown,

The PB-2000 foaming agent (TU 2481-185-05744685-01) is a light brown, water-based surfactant solution with a density of 1.0–1.2 g/cm³ at 20 °C and a pH range of 7.0–10.0.

Preparation Method

Step 1. Preparation of Clay Slip

Raw clay is dispersed in water with the addition of electrolytes such as polysilicates and polycarboxylates. This creates a stable, highly fluid suspension (slip). The electrolytes bind with coagulating cations and release bound water by adsorbing anions onto the clay particle surfaces, improving liquefaction.

Step 2. Introduction of Sodium Silicate (Na₂SiO₃)

Adding sodium silicate promotes the exchange of Ca²⁺ cations in the clay's sorbed complex with monovalent Na⁺ ions. This replacement leads to:

- An excess negative surface charge on clay particles, causing repulsion and dispersion into finer grains.
- Released Ca²⁺ cations reacting with silicate anions (SiO₃²⁻) to form insoluble calcium metasilicate (CaSiO₃), further enhancing fluidity.

Step 3. Electrolyte Reaction Mechanism

Adding sodium silicate (Na₂SiO₃) plays a crucial role in modifying the structure of clay during the preparation of the ceramic slip. It promotes the displacement of divalent calcium ions (Ca²⁺) from the sorption complex of clay minerals, replacing them with monovalent sodium ions (Na⁺). This ionic exchange increases the negative surface charge of clay particles, which leads to electrostatic repulsion between them. As a result, aggregated clay particles disintegrate into finer, elementary grains, enhancing the homogeneity and plasticity of the suspension.

Purity and Manufacturer of Sodium Silicate

The sodium silicate used in this study was of industrial grade, with a purity of 98%, and was sourced from Omsk Plant of Industrial and Household Chemistry. This company was established in the 1990s by a group of specialists from aerospace and defense enterprises in Omsk, Russia. The high purity level ensures consistent chemical behavior and reliable performance in the modification of the clay structure during the preparation of the slip.

In aqueous suspension, sodium silicate dissociates into Na⁺, Na⁺, and SiO₃²⁻ ions. The released Na⁺ ions primarily act within the diffusion layer, replacing Ca²⁺ ions that

normally bind clay particles into flocs. The freed Ca^{2+} ions then react with silicate anions (SiO_3^{2-}), forming insoluble calcium metasilicate (CaSiO_3). This is represented as follows:



and this precipitation reaction further contributes to the release of bound water, increasing the amount of free water in the system and enhancing the fluidity and workability of the clay slip.

Step 4. Limiting Electrolyte Concentration

Liquefaction improves only up to a certain electrolyte threshold.

- Excess Na^+ and Ca^{2+} ions form new hydration shells or precipitates.
- Beyond optimal concentrations, free water decreases, suspension viscosity increases, and particles begin to coagulate, reducing fluidity.

Step 5. Role of Electrolytes and Coagulants

Optimized concentrations of electrolytes and coagulants are crucial for:

- Controlling slip fluidity,
- Reducing shrinkage,
- Achieving stable, strong foam ceramic structures.

Step 6. Addition of Fly Ash and Sawdust (Organic Fillers)

For economic and ecological reasons, fly ash is added to reduce clay and fuel consumption:

- It acts as a mineral filler, improving moldability and reducing energy demand,
- The optimal clay-to-ash ratio was determined experimentally (15–50% clay by dry mass).

To reduce shrinkage and enhance drying:

- Sawdust (10–20% by dry mass, ground to 10 μm) is added, improving permeability and reducing drying time,
- Fly ash (10–20% by dry mass) further aids in reducing shrinkage and increasing porosity.

Step 7. Evaluation of Drying Performance

After forming the samples, drying is conducted under controlled conditions.

- Visual inspection (Figure 2) confirms that samples show no visible cracks or shrinkage deformations after drying.

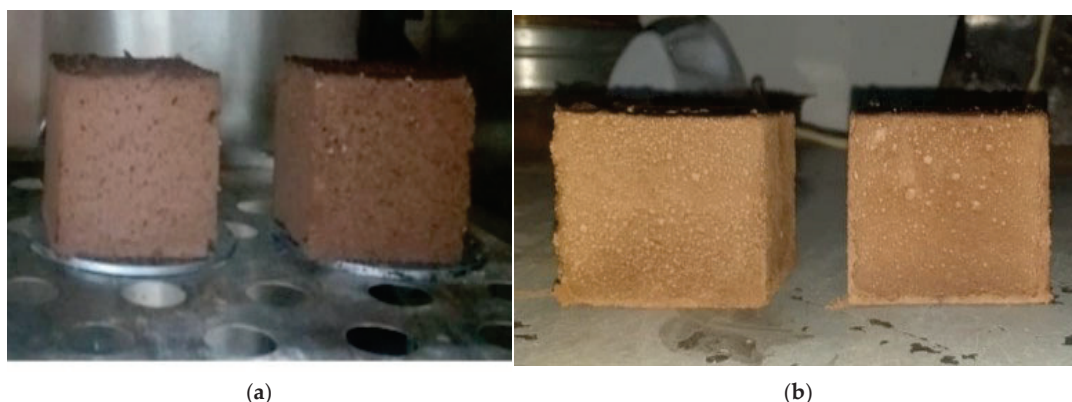


Figure 2. Foam ceramic samples before and after drying: (a) sample before drying; (b) sample after drying.

Step 8. Optimization of Batch Composition and Firing Regime

Once the drying process is optimized, the next stage involves adjusting the raw mix composition and determining the appropriate firing temperature to achieve the desired mechanical and thermal properties in the final foam ceramic products.

Optimization of Foam Ceramics

We have described the technology and composition for preparing foam ceramics. Based on this composition, we will now determine the optimal formulation and plan experiments to assess the following physical and mechanical properties.

Using the developed technology and composition of the foam ceramic mass, component optimization is conducted to achieve superior physical and mechanical properties. Methods of mathematical modeling and experimental design are employed for this purpose. Key parameters for optimization include the clay-to-ash ratio, the concentration of coagulants and electrolytes, as well as the molding and firing conditions.

The experimental planning focuses on determining the physical and mechanical properties of foam ceramic products.

The fired samples undergo the following tests: determination of firing and total shrinkage, bulk density, water absorption, firing quality, and strength limits.

The most important structural and operational properties of foam ceramic products depend on bulk density and true porosity. As demonstrated above, bulk density is determined by the composition of the initial mixture, primarily the surfactant content.

Determination of Air and Firing Shrinkage

Air and firing shrinkage were measured according to GOST 32026–2012 [40], which regulates the procedures for determining the key technological properties of clay raw materials used in expanded ceramic and lightweight aggregate production. This standard provides guidelines for sample preparation, drying, firing, and measurement techniques, ensuring consistency and comparability of results. It is particularly relevant for characterizing shrinkage behavior under thermal treatment in ceramic materials.

The clay raw material was mixed with water to achieve molding moisture and then shaped into samples. After molding, two intersecting diagonal lines were carefully drawn on the tiles using a sharp tool and a ruler. The samples were dried in a SNOL drying oven at 100 °C until a constant mass was achieved. The dried samples were cooled in a desiccator, inspected for defects, and the distance between shrinkage marks was measured with calipers. Air shrinkage was determined by the difference in distances between the marks on molded samples before and after drying.

Firing shrinkage was measured on dried samples. The samples were fired in a laboratory electric muffle furnace (SNOL 6.7/1300). Firing shrinkage was calculated as the difference in distances between the shrinkage marks on the molded, dried, and fired samples.

The raw materials were dried at a temperature of 110 °C and ground until they passed through a 0.63 mm sieve. Then, batch compositions were prepared. The components were mixed in dry form. The prepared batch was moistened to form a slurry with a specified moisture content. Using the casting method, 7 × 7 × 7 cm samples were molded from the slurry.

The samples were then dried at 20 °C for 9.5–10 h, followed by drying at 60 °C in a drying oven until the moisture content reached 1–2%. The dried samples were fired with a holding time of 2 h at a maximum temperature of 1000 °C.

Shrinkage is a critical parameter in foam ceramic production because it directly affects the dimensional stability, mechanical strength, and microstructure of the final product. Excessive shrinkage can lead to cracks, deformation, and poor fit in construction applications, while insufficient shrinkage may indicate incomplete sintering. Accurate control of

shrinkage ensures that the material maintains its intended shape, porosity, and performance characteristics after thermal processing.

Total and linear shrinkage were determined based on changes in linear dimensions. Formulas (3) and (4), which are as follows, were used to calculate volumetric changes in the products after firing:

$$V_{\text{total}} = (V_1 - V_3)100/V_1, \quad (3)$$

$$V_{\text{total}} = (V_2 - V_3)100/V_1, \quad (4)$$

where V_1 is the volume of the product in the freshly molded state (cm^3), V_2 is the volume in the air-dry state (cm^3), and V_3 is the volume after firing (cm^3).

Water Absorption: The water absorption of fired samples characterizes both the porosity and strength of the ceramic body, as well as the sintering process. Water absorption (%) was determined using Formula (5), which is as follows:

$$W = (m_2 - m_1) \times 100/m_1, \quad (5)$$

where m_1 is the mass of the fired sample (g) and m_2 is the mass of the water-saturated sample (g). Water absorption in foam ceramics varies with thermal treatment conditions and mass composition, depending primarily on the bulk density.

Porosity: True porosity was calculated to assess the internal structure of foam ceramics using Formula (6), which is as follows:

$$P_t = (1 - \rho_m/\rho) \times 100, \quad (6)$$

where ρ_m is the bulk density and ρ is the true density.

Open Porosity: Open porosity (%) was derived from water absorption and bulk density using Formula (7), which is as follows:

$$P_a = W \times 100/\rho_m. \quad (7)$$

Closed Porosity: Closed porosity (%) was determined using the following relation (8), which is as follows:

$$P_x = P_t - P_a. \quad (8)$$

The presence of both open and closed porosity plays a crucial role in balancing the mechanical strength and thermal insulation properties of foam ceramics. Open porosity allows for the material to trap air within its structure, significantly improving thermal insulation by reducing heat transfer. However, excessive open porosity can weaken the mechanical strength, making the material more susceptible to deformation under stress. On the other hand, closed porosity, which is not interconnected, contributes to structural integrity by enhancing the material's ability to resist external forces and improving its overall mechanical strength. A balance between open and closed porosity ensures that foam ceramics achieve optimal thermal insulation without compromising mechanical stability.

Thermal Conductivity: The thermal conductivity of porous ceramic samples was measured using an ITP-MG4 electronic thermal conductivity meter. Both the steady-state heat flux density method and the thermal probe method were applied.

The thermal conductivity of porous ceramic samples was determined experimentally using an electronic thermal conductivity meter of the ITP-MG4 type, employing the steady-state heat flow density method and the thermal probe method applied directly to the samples.

Mechanical Strength: Compressive and flexural strength were tested following GOST 7025-78. Foam ceramic cubes were dried to a residual moisture content of 5–6% and fired

at optimal temperatures. Tests were conducted on the PGM-100MG4A press, applying a uniform load at 0.5 MPa/s until failure. The maximum load was recorded for each sample.

The experimental results will support the development of mathematical models to predict the behavior of foam ceramics under varying compositions and processing conditions. This will optimize production, enhancing strength while minimizing energy consumption.

3. Results

The strength of foam ceramic products must meet standards for thermal insulation materials. Based on experiments, the required compressive strength was determined to exceed 1 MPa. Density correlates with thermal conductivity, influencing insulation properties. Products with a density below 0.8–1 g/cm³ show significant insulation performance, while thermal conductivity rises from 0.6 to 1.7 W/(m·°C) between 20 and 1500 °C.

The goal was to develop foam ceramics based on thermal power plant fly ash, ensuring high strength with minimal density and thermal conductivity for optimal insulation. Comparative properties like water absorption and porosity were also evaluated.

We used computer modeling with the STATSOFT program for statistical experimental planning. A full factorial experimental design was applied, enabling a comprehensive assessment of the influence of each variable and their interactions on the properties of the foam ceramic material. This approach allowed for the development of a second-order regression model based on the results of a complete set of combinations of factor levels, including three parallel trials to assess reproducibility, regression coefficients, and model adequacy.

Objective: To optimize the batch composition and firing temperature for foam ceramics using mathematical modeling and experimental design.

Tasks:

- Encode variables.
- Construct a Box–Behnken planning matrix considering paired interactions.
- Calculate regression coefficients and test their significance.
- Optimize batch composition and firing temperature.
- Build a three-factor experimental matrix.
- Analyze results, verify model adequacy, and assess coefficient significance.
- Optimize process parameters and develop a general model linking responses (y) to factors (x1, x2, x3), identifying minima using classical optimization methods.

A full factorial three-factor experiment (2³ orthogonal design) was conducted to study physical–mechanical properties. Key optimization parameters included the physical–mechanical properties of the foam ceramics.

Input Variables:

- x1, x2: Loam and fly ash dosage (%).
- x3: Firing temperature (°C).

Loam and fly ash stabilized the porous structure. Loam was chosen for its alkali oxides (Na₂O, K₂O at 15–16%), promoting early melt formation and sintering. Fly ash improved swelling stability and sintering due to its fine dispersion and unburned carbon content, ensuring uniform firing.

Hydraulic ash from the Almaty Combined Heat and Power Plant (CHP) was used in this study. The plant operates an ash and slag disposal site with a total area of 1300 hectares. The properties of the ash were investigated in accordance with the requirements of GOST 25818–2018.

Based on the type of coal used, the ash belongs to the bituminous coal group (KU), which is formed from the combustion of bituminous coal, excluding lean coal.

According to its chemical composition, the ash is classified as acidic, containing up to 10% CaO by mass. Table 1 presents the chemical composition of the ash.

Table 1. Encoding and variation in input factors.

Factor	Code	Levels of Varying Factors			Variation Interval (Δx_i)	Unit
		−1	0	+1		
Loam	x_1	45	55	65	5.0	%
Fly Ash	x_2	10	15	30	5.0	%
Firing Temperature	x_3	850	925	1000	10.0	°C

The ash consists of black and dark gray particles ranging in size from 10 to 100 microns, has a dense glassy structure, and shows low loss on ignition.

The ash was used as a siliceous component in the experiments. The hydraulic ash from the CHP was characterized by the following properties:

- Specific surface area: 2700–2900 cm²/g.
- Bulk density: 800 kg/m³.
- True density: 2.65 g/cm³.
- Loss on ignition: 4.3%.
- Moisture content: 17%.
- Ash activity: 43.8.

A protein-based foaming agent (0.5–1% of dry mass) was used. The water-to-solid ratio ranged from 0.5 to 0.7.

Response Criteria (y): These are physicalmechanical properties like strength, density, thermal conductivity, water absorption, and porosity. Planning conditions, adjustable factors, levels, and variation intervals are shown in Table 1.

The most convenient tool for gradient estimation is the well-developed and tested method of factorial experiments. A series of experiments can be conducted, where all factors take values within a specified range, and the corresponding value of the function y, known as the target parameter, is determined experimentally. Table 2 presents the results of the experimental study.

The planning matrix was constructed using the Box–Behnken method.

The practical value lies in selecting the composition of the initial mixture that ensures the final product has minimal values for indicators y2 and y5, and maximal values for indicators y1, y3, and y4.

The mathematical foundation of experimental design theory is regression analysis, which aims to establish relationships between the target parameter y and the influencing factors of the studied object $x_1, x_2, \dots, x_j, \dots, x_k$. Typically, the exact analytical expression of the function $y = f(x_1, x_2, \dots, x_j, \dots, x_k)$ remains unknown, requiring its approximation using a polynomial representation (Equation (9)), which is as follows:

$$y = b_0 + b_1 \cdot x_1 + b_2 \cdot x_2 + b_3 \cdot x_3 + b_{12} \cdot x_1 \cdot x_2 + b_{13} \cdot x_1 \cdot x_3 + b_{23} \cdot x_2 \cdot x_3 + b_{123} \cdot x_1 \cdot x_2 \cdot x_3 \quad (9)$$

where b_i, b_j, b_{ij} are the regression coefficients, and x_i, x_j, x_k are the input factors.

The values of the regression coefficients b_i and b_{ij} allow for an assessment of the influence of individual factors and their interactions on the optimization parameter. The greater the numerical value of a coefficient, the stronger the factor's influence. A positive coefficient indicates that an increase in the factor value leads to an increase in the optimization parameter, whereas a negative coefficient signifies a decrease.

Table 2. Planning matrix and experimental results in the study.

#	Input Parameters				Interactions				Optimization Criteria ($y = f(x_1, x_2, x_3)$)					
	x_0	x_1	x_2	x_3	x_2x_1	x_2x_3	x_1x_3	$x_1x_2x_3$	y_1 Strength (MPa)		y_2 Thermal Conductivity		y_5 Density (g/cm ³)	
									Calc.	Avg.	Calc.	Exp.	Calc.	Exp.
1	+	−	−	0	+	0	0	0	1933 1869 1941	1.92	0.149 0.148 0.151	0.15	820 817 819	818,666
2	+	−	+	0	−	0	0	0	2954 2965 3005	2.98	0.152 0.160 0.157	0.156	830 828 827	828,333
3	+	+	−	0	−	0	0	0	2599 2621 2698	6.45	0.135 0.129 0.130	0.131	790 785 787	787,333
4	+	+	+	0	+	0	0	0	4463 4473 4451	4.45	0.141 0.139 0.137	0.139	750 749 747	748,666
5	+	−	0	−	0	0	+	0	3571 3668 3541	3.59	0.138 0.135 0.137	0.136	754 750 753	752,333
6	+	−	0	+	0	0	−	0	2424 2519 2462	2.47	0.139 0.136 0.134	0.136	770 768 767	768,333
7	+	+	0	−	0	0	−	0	3694 3714 3721	3.72	0.140 0.136 0.139	0.138	790 789 786	788,333
8	+	+	0	+	0	0	+	0	3412 3484 3429	3.44	0.132 0.130 0.126	0.129	687 685 683	685

The regression coefficients are determined using Formula (10), which is as follows:

$$b_j = \frac{\sum_{i=1}^N y_i}{N}; b_j = \frac{\sum_{i=1}^N x_{ij} \cdot y_i}{N} \quad (10)$$

where $N = 15$ is the number of experiments, and x_i, x_j, x_i are the input factors.

Following the execution of the experiment and data processing using the least squares method (LSM) through the LSM software version 1, the regression coefficients of the experimental statistical models describing the properties of the foam ceramic samples were calculated. For clarity, a table is constructed to summarize the obtained regression equation coefficients (Table 3).

Table 3. Regression coefficients results.

No	b_0	b_1	b_2	b_3	b_{12}	b_{13}	b_{23}	b_{123}
y_1	3.310	0.36	0.47	0.45	0.2	−0.08	0.16	0.91
y_2	0.146	0.004	0.012	0.028	−0.001	0.003	0.002	0.044
y_3	68.66	3.555	6.34	13.23	0.71	−1.336	−6.81	19.61
y_4	53.22	2.447	5.07	10.54	−0.52	−0.331	−0.323	15.21
y_5	722.2	29.61	77.47	145.5	−11.92	15.42	−4.52	233.02

We formulate the regression equations with respect to the new variables:

Compressive strength (11) is as follows:

$$y_1 = 3.31 + 0.36x_1 + 0.47x_2 + 0.45x_3 + 0.21x_1x_2 - 0.08x_1x_3 + 0.16x_2x_3 + 0.91x_1x_2x_3 \quad (11)$$

Thermal conductivity (12) is as follows:

$$y_2 = 0.146 + 0.004x_1 + 0.012x_2 + 0.028x_3 - 0.001x_1x_2 + 0.003x_1x_3 + 0.002x_2x_3 + 0.044x_1x_2x_3 \quad (12)$$

Porosity (13) is as follows:

$$y_3 = 68.66 + 3.555x_1 + 6.34x_2 + 13.23x_3 + 0.71x_1x_2 - 1.336x_1x_3 - 6.81x_2x_3 + 19.61x_1x_2x_3 \quad (13)$$

Water absorption (14) is as follows:

$$y_4 = 53.22 + 2.447x_1 + 5.07x_2 + 10.54x_3 - 0.52x_1x_2 - 0.331x_1x_3 - 0.323x_2x_3 + 15.21x_1x_2x_3 \quad (14)$$

Density (15) is as follows:

$$y_5 = 722.2 + 29.61x_1 + 77.47x_2 + 145.5x_3 - 11.92x_1x_2 + 15.42x_1x_3 - 4.52x_2x_3 + 223.02x_1x_2x_3 \quad (15)$$

After obtaining the mathematical model, the significance of the regression coefficients (i.e., their deviation from zero) and the adequacy of the model are evaluated. The significance of the coefficients is tested using Student's *t*-test, which is calculated using Equation (16).

For foam ceramics, a threshold *p* value of 0.05 was used to determine the statistical significance of the regression coefficients. Coefficients with *p* values below this threshold were considered to have a significant influence on the response variables such as compressive strength, porosity, and thermal conductivity. This ensured that only the most relevant factors were included in the final model. Equation (16) is as follows:

$$t_i = \frac{|b_i|}{S\{b_i\}} \quad (16)$$

where b_i is the *i*-th regression coefficient, and $S\{b_i\}$ is the standard deviation in the determination of the coefficients.

The standard deviation is determined based on the variance of the reproducibility of results across all conducted experiments and is calculated using Equation (17), which is as follows:

$$S_i^2 = \frac{\sum_1^n (y_i - \bar{y})^2}{n - 1} \quad (17)$$

where $\bar{y}$ is the arithmetic mean value of the optimization parameter obtained from five repeated experiments.

After determining the reproducibility variance, a table is constructed for clarity and convenience to present the response values (y_1 , y_3 , y_4) (Table 1).

The degrees of freedom are calculated using Equation (18), which is as follows:

$$f_1 = N(n - 1) = 20 \cdot (3 - 1) = 40. \quad (18)$$

Since the value of Student's *t*-test for the number of observations $f_1 = 40$ and a 95% confidence level is 2.021 (according to the reference table), the comparison results for the five optimization criteria are presented in Table 2.

The adequacy of the obtained regression equation with the significant coefficients is verified using Fisher's criterion: if $F_{\text{calc}} < F_{\text{tab}}$ the equations are considered adequate.

The calculated Fisher's value is determined using Equation (19), which is as follows:

$$F_{\text{calc}} = \frac{S_{\text{oct}}^2}{S_{\{y\}}^2} \quad (19)$$

After verifying the significance of the obtained coefficients and eliminating insignificant ones, the regression equation describing the physical and mechanical properties of foam ceramics as a function of the loam dosage (x_1), fly ash content (x_2), and firing temperature (x_3) is established.

Next, calculations are performed separately for each response variable, and the adequacy of each model is evaluated. Additionally, a quality assessment of each model must be conducted.

Table 4 summarizes the results of the calculations for the analysis.

Table 4. Results of the performed calculations.

No	$S_{y_1}^2$	$S_{y_2}^2$	$S_{y_3}^2$	$S_{y_4}^2$	$S_{y_5}^2$
1	0.0016055	0.000003	0.0007	0.37	2.333334
2	0.000763	0.0000165	0.0006335	0.043334	2.333335
3	21.784473	0.0000105	0.0002335	0.063334	6.333335
4	0.0003495	0.000004	0.0001	0.7633335	2.333334
5	0.2873745	0.000003	0.0002335	0.2533335	4.333335
6	2.448058	0.1375045	64.877178	57.3304445	770.5559445
7	0.0003565	0.0000045	0.28	0.1733335	4.333335
8	0.0014205	0.0000095	0.01	0.28	4
9	0.001972	0.000009	0.0004335	0.25	4
10	0.010852	0.00001	0.0002335	0.28	154.333334
11	0.0171345	0.0000025	0.01	0.2633335	4.333335
12	0.002623	0.000007	0.012134	0.253334	2.333334
13	0.0025335	0.0000045	0.010134	0.023334	4.333334
14	0.003823	0.000003	0.0004335	0.163334	6.333334
15	0.0000375	0.0000025	0.004134	0.2533335	4.333335
16	0.0002645	0.000003	1.013334	0.10315	1.666667
17	0.000066	0.0000045	0.0028	0.182934	3.3884445
18	0.000129	0.0000025	0.0433335	0.002324	6.111889
19	0.0003575	0.000004	0.043334	0.025644	6.8323335
20	0.0003665	0.000003	1.083334	0.37	2.333334
Total:					
Σ	24.56456	0.137611	67.39272	61.44783	996.8886
$S^2(y^-)$	0.409409	0.002294	1.123212	1.024131	16.61481
σ	0.639851	0.047896	1.059817	1.011994	4.076127
f_1	1.293139	0.096798	2.14189	2.04524	8.237853
SBOCnp	0.909624	0.06809	1.506656	1.438669	5.794699
F	0.450086	0.033684	0.7455	0.71186	2.867243

The significance of the coefficients is analyzed separately for each response variable.

As a result of mathematical modeling using the obtained equation and the identified model parameters, response graphs were generated to illustrate the dependence of response variables on factor values.

Based on the averaged values, graphical dependencies were constructed to show variations in response parameters (strength, density, thermal conductivity, porosity, and water absorption) as a function of each individual factor, while maintaining the averaged values of the remaining factors.

From a practical perspective, the most valuable composition of the initial mixture is the one that results in the lowest values for y_2 and y_5 , while maximizing y_1 , y_3 , and y_4 .

A strength of this is that Student's t -test confirmed that the obtained coefficients are statistically significant.

The Fisher criterion test demonstrated that the regression equation is adequate, as the calculated value is lower than the critical threshold ($F < F_{\text{critical}}$).

Figure 3 presents the strength variation graphs as a function of the slip composition. The obtained determination coefficient of $R^2 = 0.887$, which is sufficiently close to 1, further confirms the adequacy of the developed mathematical model.

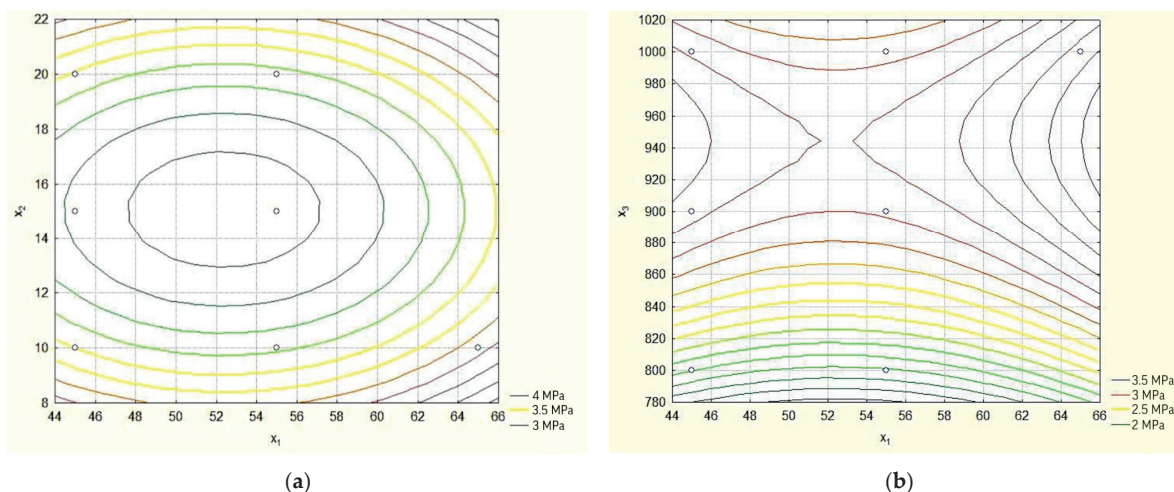


Figure 3. Isoline diagram of the mathematical model for foam ceramic strength: (a) $x_3 = \text{const}$; (b) $x_1 = \text{const}$.

The most significant factors contributing to increased strength are the loam content in the batch and the firing temperature. The fly ash content is the most critical factor influencing the strength of the samples. Fly ash reduces shrinkage in the porous mass, while the development of structural strength occurs more intensively. According to the response graph, this threshold is in the range of 15–20%.

The lowest strength values (1.5–2 MPa) are observed in compositions containing 45–50% loam and 10% fly ash, whereas the highest strength values (4–5 MPa) are achieved in compositions with 55% loam and 15% fly ash. The weakest results are obtained at a firing temperature of 800 °C, while the best results are achieved at 950–1000 °C.

For a visual representation of the samples, refer to Figure 4. The cross-sections of the response surface are shown as vertical lines. In the analysis of foam ceramic strength, the samples were visually categorized based on their compressive strength refer to Figure 5.

Thermal Conductivity: Student's t -test confirmed that the obtained coefficients are statistically significant.

The Fisher criterion test demonstrated that the regression equation is adequate, as the calculated value is lower than the critical threshold ($F < F_{\text{critical}}$).

An increase in firing temperature leads to a rise in thermal conductivity due to densification of the ceramic matrix and a corresponding decrease in total porosity. As the firing temperature increases, pore walls thicken and closed porosity may be partially eliminated, allowing better heat transfer through the solid phase. This effect has been observed in similar studies on foam ceramics, where thermal conductivity increased from 0.09 to 0.15 W/(m·K) as firing temperature rose from 900 °C to 1100 °C. These results are consistent with the trends observed in our regression model.

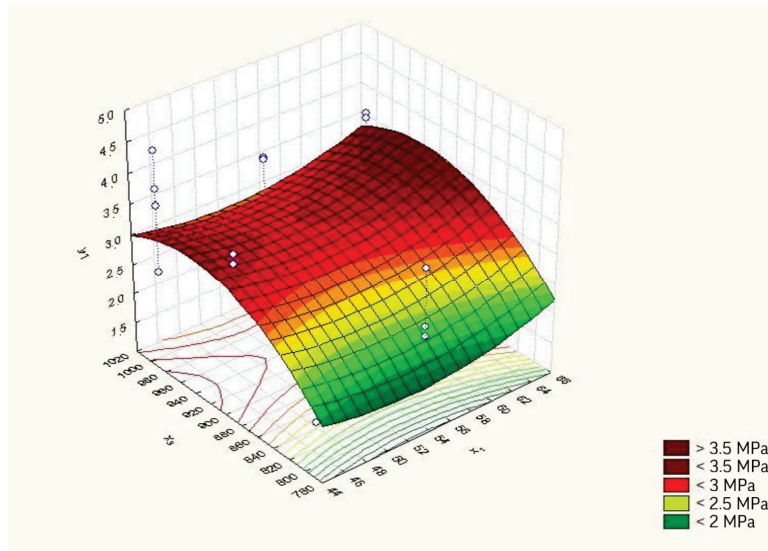


Figure 4. Response surface of y_1 at $x_2 = \text{const.}$

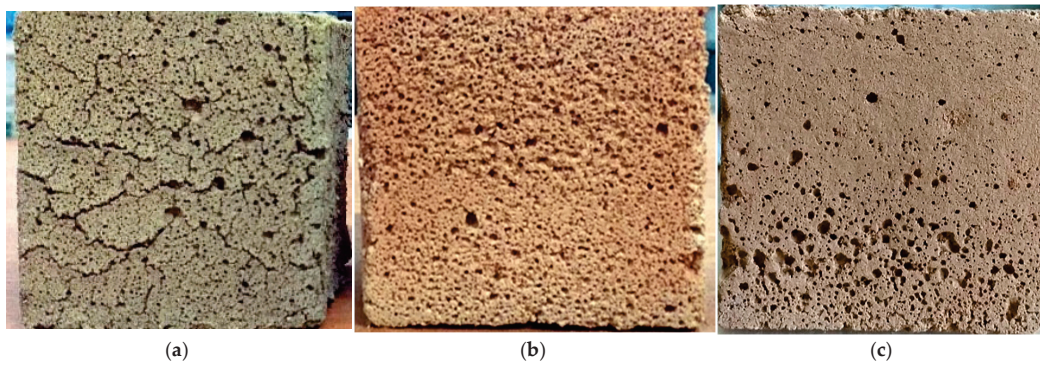


Figure 5. Visual representation of samples with varying strength: (a) 1–1.5 MPa; (b) 2.5–3 MPa; (c) 3.5–4 MPa.

Figures 6 and 7 present the thermal conductivity variation graphs as a function of the slip composition.

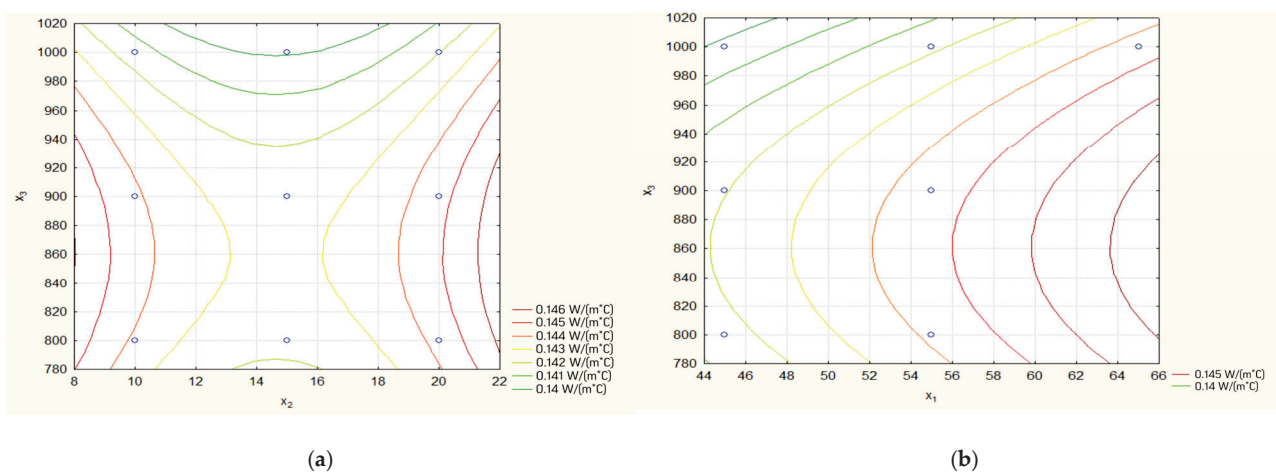


Figure 6. Isoline diagram of the mathematical model for foam ceramic thermal conductivity: (a) $x_1 = \text{const.}$; (b) $x_2 = \text{const.}$

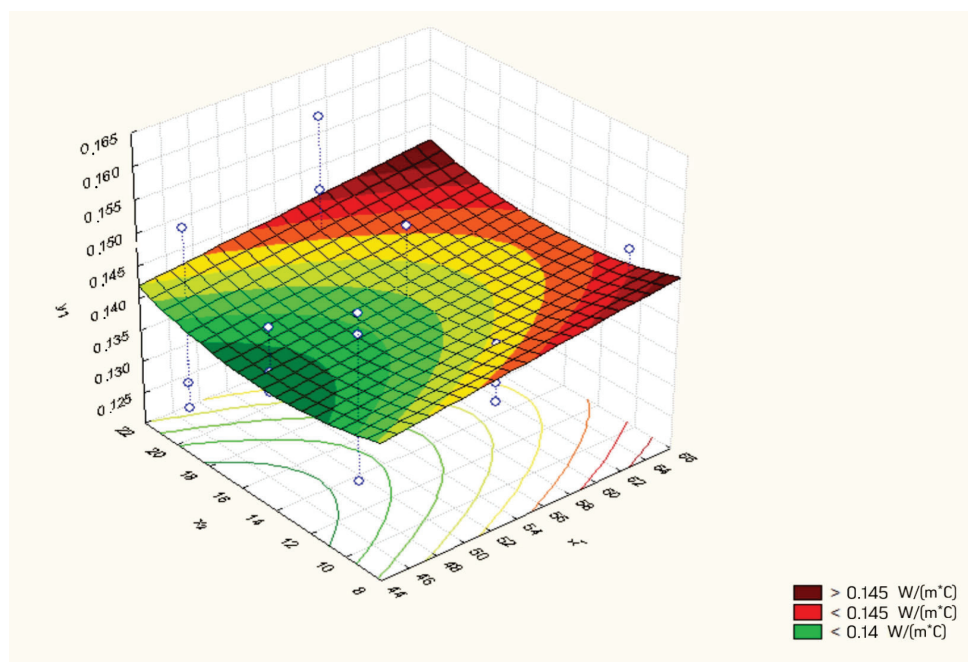


Figure 7. Response surface of y_2 at $x_3 = \text{const.}$

The obtained determination coefficient of $R^2 = 0.781$, which is sufficiently close to 1, further confirms the adequacy of the developed mathematical model describing the dependence of thermal conductivity on the mixture composition.

The most significant factor reducing thermal conductivity is a fly ash content of 15%, along with a loam content of 45% or 60% and a firing temperature of 950–1000 °C. With an increase in the firing temperature, the thermal conductivity coefficient of the samples also increases.

However, by analyzing parallel dosage compositions, it is possible to determine the optimal fly ash content, ensuring the production of samples with high operational performance.

Porosity: Student's *t*-test confirmed that the obtained coefficients are statistically significant.

The Fisher criterion test demonstrated that the regression equation is adequate, as the calculated value is lower than the critical threshold ($F < F_{\text{critical}}$).

The obtained determination coefficient of $R^2 = 0.882$, which is sufficiently close to 1, further confirms the adequacy of the developed mathematical model describing the dependence of porosity on the mixture composition.

The optimal porosity range of 70–72% observed in this study is comparable to or higher than that of many conventional thermal insulation materials, such as lightweight aerated concrete (55–65%) or mineral wool (up to 70%). This high level of porosity contributes to the low thermal conductivity of foam ceramics while maintaining acceptable mechanical strength, making them suitable for energy-efficient construction applications.

Figure 8 presents graphs illustrating the variation in thermal conductivity as a function of mixture composition.

The highest porosity values (70–72%) are observed at 10% fly ash, 55% loam, and a firing temperature of 900 °C. The lowest porosity values (60–65%) are achieved at 15% fly ash, 65% loam, and a firing temperature of 1000 °C.

Figures 8 and 9 illustrate the porosity variation as a function of the slip composition.

For water absorption, Student's *t*-test confirmed that the obtained coefficients are statistically significant.

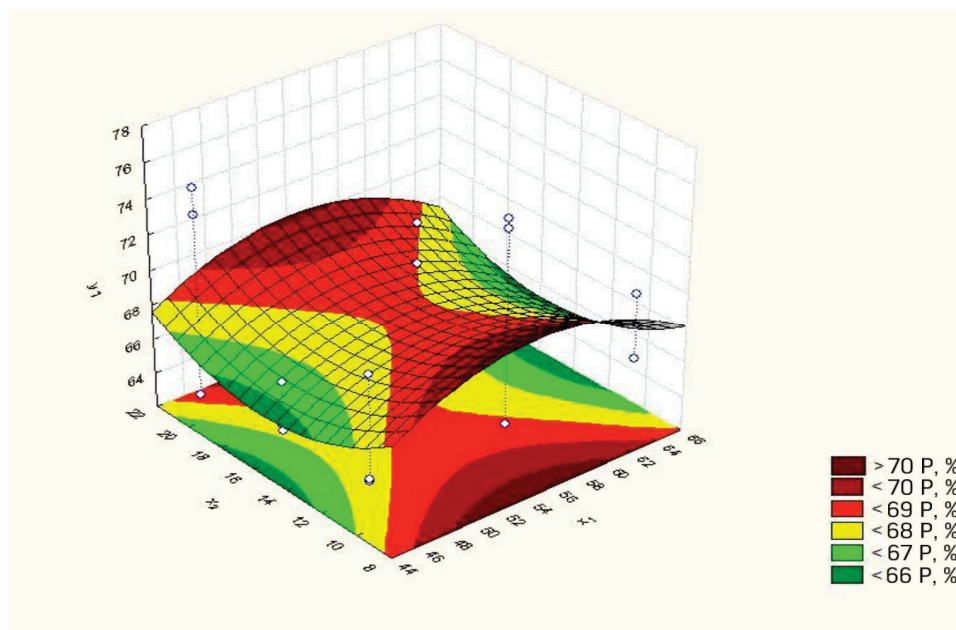


Figure 8. Response surface of y_3 at $x_3 = \text{const.}$

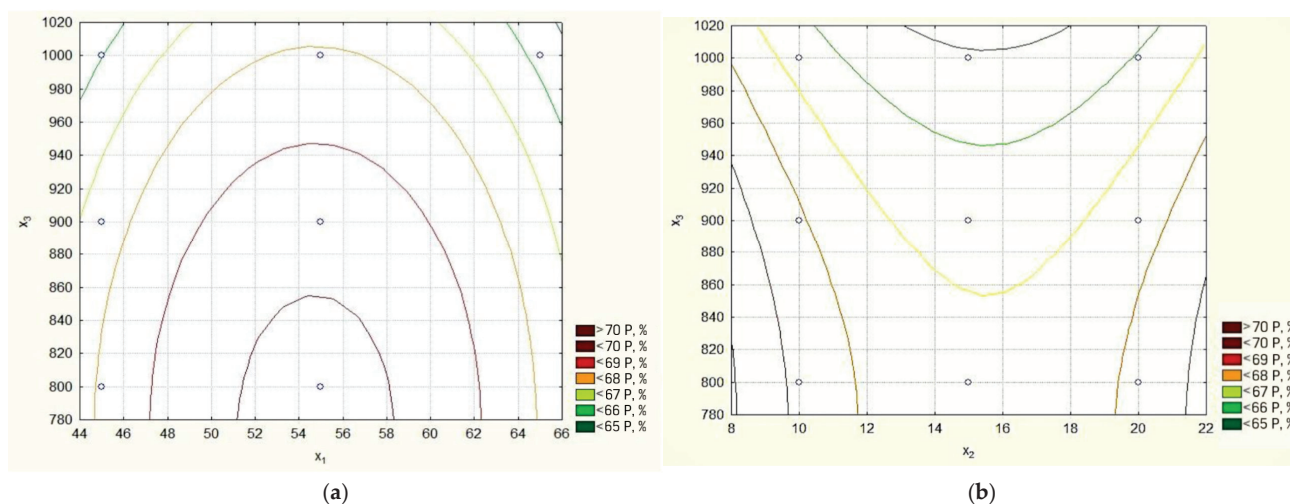


Figure 9. Isoline diagram of the mathematical model for foam ceramic porosity: (a) $x_1 = \text{const.}$; (b) $x_2 = \text{const.}$

The Fisher criterion test demonstrated that the regression equation is adequate, as the calculated value is lower than the critical threshold ($F < F_{\text{critical}}$).

Figures 9 and 10 present the water absorption variation graphs as a function of the slip composition. The cross-sections of the response surface are shown as vertical lines.

The obtained determination coefficient of $R^2 = 0.874$, which is sufficiently close to 1, further confirms the adequacy of the developed mathematical model describing the dependence of water absorption on the mixture composition and firing temperature.

As the fly ash content in the composition increases, the water absorption of the fired samples also increases. However, it is possible to determine the optimal fly ash dosage, ensuring the production of samples with high operational properties.

The lowest water absorption value (53.1%) is observed in a composition of 10% fly ash, 55% loam, and a firing temperature of 1000 °C.

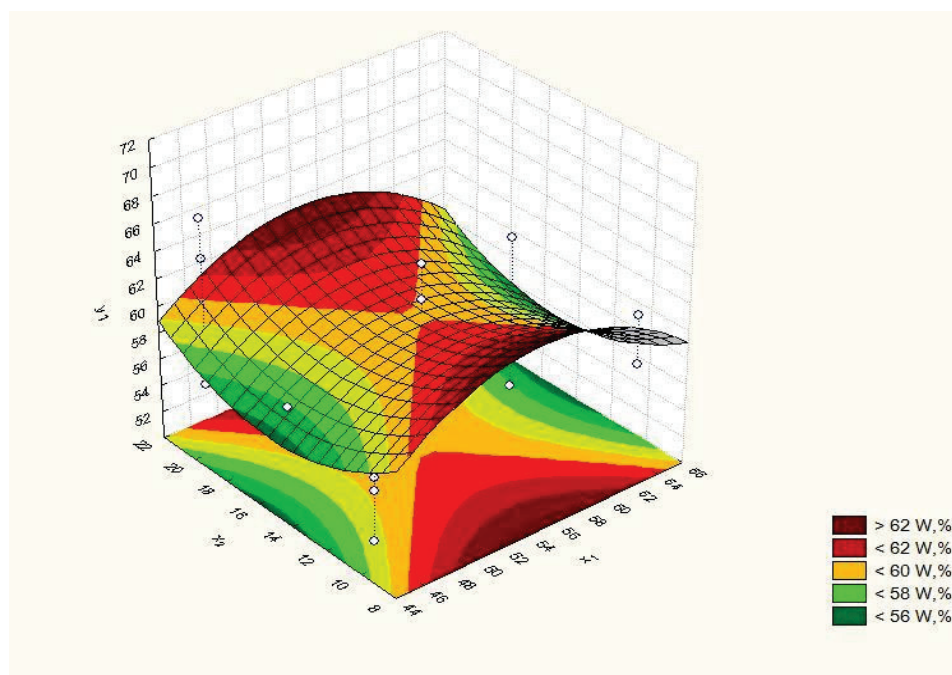


Figure 10. Response surface of y_4 at $x_3 = \text{const.}$

The highest water absorption value (55.6%) is observed in a composition of 20% fly ash, 60% loam, and a firing temperature of 900 °C.

Figure 11 illustrates the isoline diagram of the mathematical model for foam ceramic water absorption at constant values of x_1 and x_2 . The cross-sections of the response surface are shown as vertical lines.

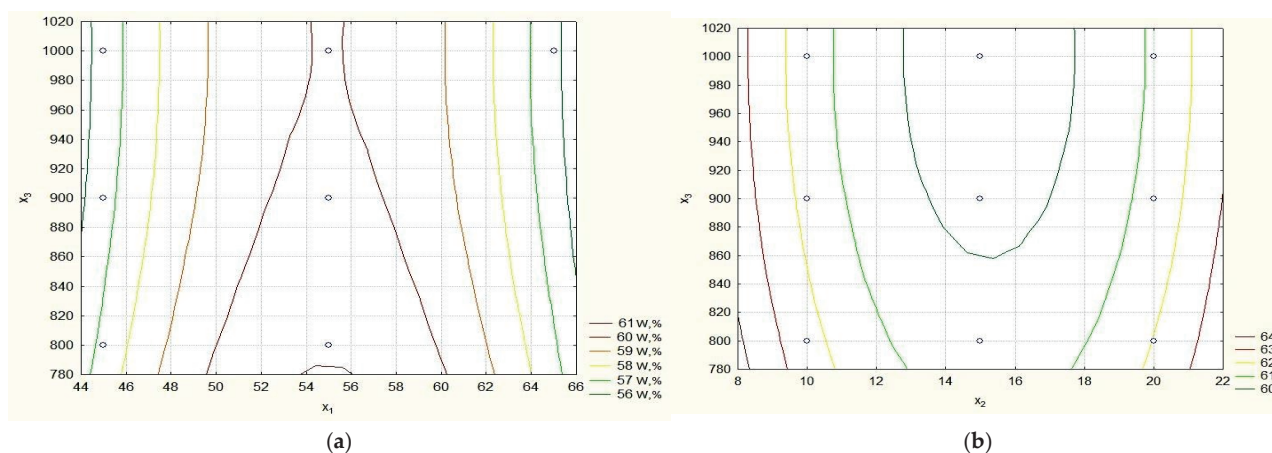


Figure 11. Isolines diagram of the mathematical model for foam ceramic water absorption: (a) $x_1 = \text{const}$; (b) $x_2 = \text{const}$.

Density: Student's t -test confirmed that the obtained coefficients are statistically significant.

The Fisher criterion test demonstrated that the regression equation is adequate, as the calculated value is lower than the critical threshold ($F < F_{\text{critical}}$).

Figure 12 shows the response surface of the average density y_5 of foam ceramics at constant x_3 , illustrating the influence of ash content and firing temperature on density. The cross-sections of the response surface are shown as vertical lines.

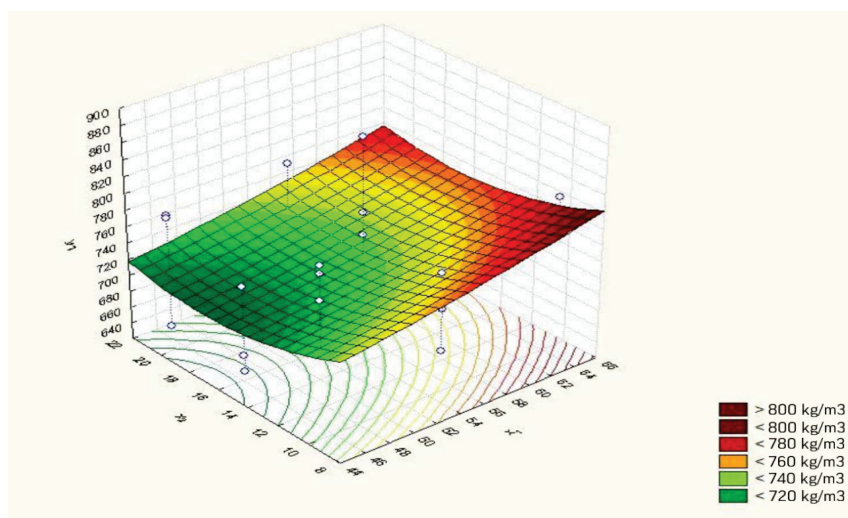


Figure 12. Response surface of y_5 at $x_3 = \text{const}$.

Figures 13 and 14 present the density variation graphs as a function of the slip composition.

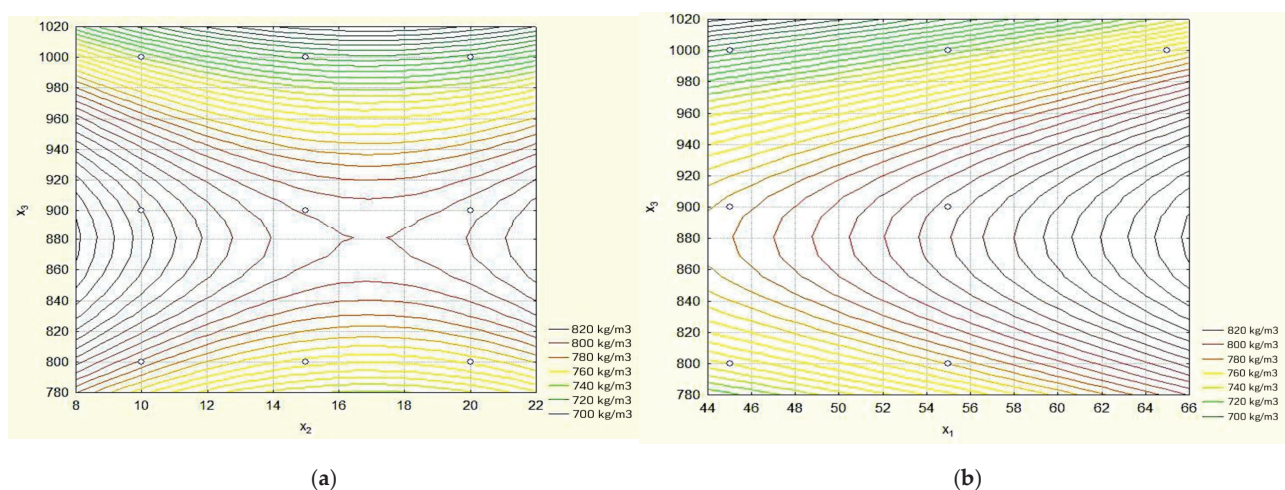


Figure 13. Isoline diagram of the mathematical model for foam ceramic density: (a) $x_1 = \text{const}$; (b) $x_2 = \text{const}$.

The optimal average density of foam ceramics (650 kg/m^3) is significantly influenced by the fly ash content in the slip and the firing temperature. Adjusting the slip composition with an optimal fly ash content contributes to reducing the density of the foam ceramic product. However, an excess of fly ash is detrimental as it can negate the positive effects. The optimal fly ash content is 10%.

With an increase in the firing temperature from 900°C to 1000°C the average density increases. The optimal firing temperature is considered to be 900°C as further temperature increases lead to clay melting.

The loam content also affects density; as the loam percentage increases the average density decreases. The optimal loam content is 65%.

A higher average density of 850 kg/m^3 is observed at 20% fly ash, 45% loam, and a firing temperature of 800°C .

The density range of $650\text{--}700 \text{ kg/m}^3$ is considered ideal for foam ceramics because it provides an optimal balance between thermal insulation performance and mechanical strength. In comparison, lightweight aerated concrete has a typical density of $400\text{--}700 \text{ kg/m}^3$, while mineral wool ranges from 30 to 200 kg/m^3 . Foam ceramics with

densities in this range exhibit lower thermal conductivity than denser materials and yet are mechanically more robust than low-density fibrous insulators. This makes them particularly suitable for structural thermal insulation in energy-efficient buildings.

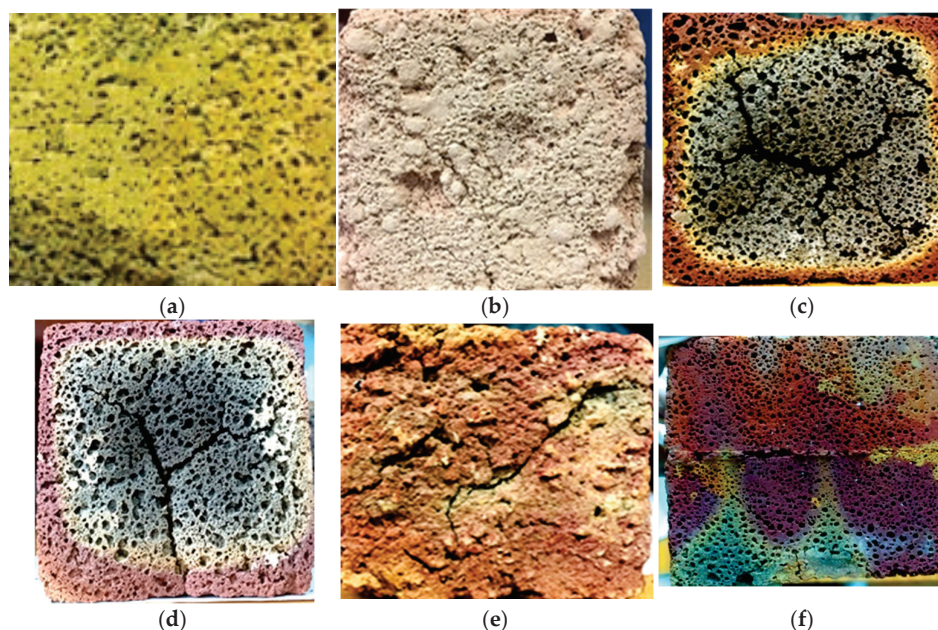


Figure 14. Image of foam ceramic samples with a non-optimal composition (containing gypsum binder). (a) Uniform firing without significant defects; (b) under-firing; (c) uneven firing and over-firing with cracks; (d) uneven firing and over-firing with cracks; (e) uneven firing with cracks; (f) uneven firing.

Optimization of Foam Ceramic Batch Composition

Based on the obtained experimental data and mathematical models, the following conclusions can be drawn. For clarity, a table summarizing the optimal compositions for each response variable is presented (Table 5).

Table 5. Optimal compositions for each response variable.

Optimization Criteria	Loam	Fly Ash	Firing Temperature (°C)	W/S Ratio	Surfactant	Sodium Silicate	Clay	Sawdust
y_1	65	10	1000	0.55	0.5	10	15	10
y_2	55	10	800	0.55	0.5	10	25	10
y_3	55	10	900	0.55	0.5	10	25	10
y_4	60	10	900	0.55	0.5	10	20	10
y_5	55	10	1000	0.55	0.5	10	25	10

It should be noted that foam ceramics with the addition of gypsum binder were completely excluded from consideration. The foam ceramic mass failed to maintain structural integrity, making it impossible to determine the physical and mechanical properties of the samples.

Additionally, samples containing gypsum exhibited uneven firing, further affecting their quality. Visual representations of the foam ceramic samples with a gypsum binder are shown in Figure 15.

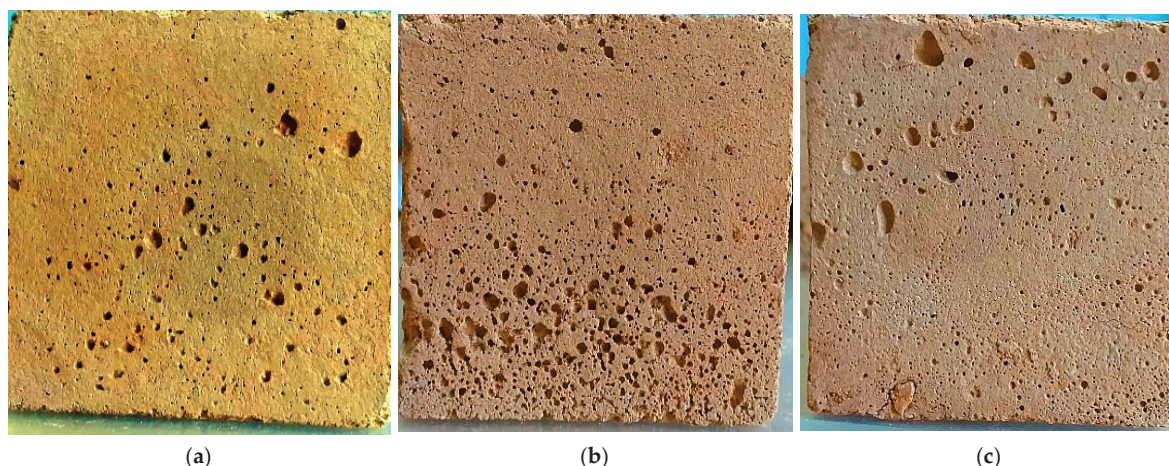


Figure 15. Visual representation of foam ceramic samples with optimal compositions. (a) 55% loam; (b) 60% loam; (c) 65% loam.

Additionally, the use of gypsum is currently environmentally unacceptable as it leads to intensive air pollution with sulfurous gases.

For each sample, the same amounts of water, surfactant, sodium silicate, and sawdust were selected. The table also summarizes the results for each composition.

From the table, it can be observed that the optimal fly ash content for all responses is 10%, and the optimal firing temperature is 900 °C. However, for a more precise selection, the response values must be further analyzed.

Table 6 presents the experimental results for foam ceramic samples with varying loam content and firing temperature, showing their corresponding compressive strength, thermal conductivity, porosity, water absorption, and density.

Table 6. Response values of the optimal composition.

Loam/Firing Temperature	y_1 , MPa	y_2 , W/(m·°C)	y_3 , % Porosity	y_4 , % Water Absorption	y_5 , kg/m ³
55/1000	3	0.14	60	60	700
60/1000	3.5	0.143	70	65	740
65/1000	4	0.145	69	56	720

Based on the given data, it can be concluded that the optimal composition of foam ceramics is as follows: loam 60–65%, fly ash 10%, clay 15–20%, and a firing temperature of 950–1000 °C.

A visual representation of foam ceramic samples with optimal compositions is shown in Figure 14.

Investigation of the properties of fired foam ceramic products. Fired samples underwent the following tests: determination of fire and total shrinkage, bulk density, water absorption, firing quality, and strength limits.

The most important structural and operational properties of foam ceramic products depend on their bulk density and true porosity. Bulk density is primarily determined by the composition of the initial mixture, particularly the surfactant content.

Total and Fire Shrinkage: The total and linear shrinkage were determined based on changes in linear dimensions.

Table 7 summarizes the results obtained for the total and linear shrinkage of the samples.

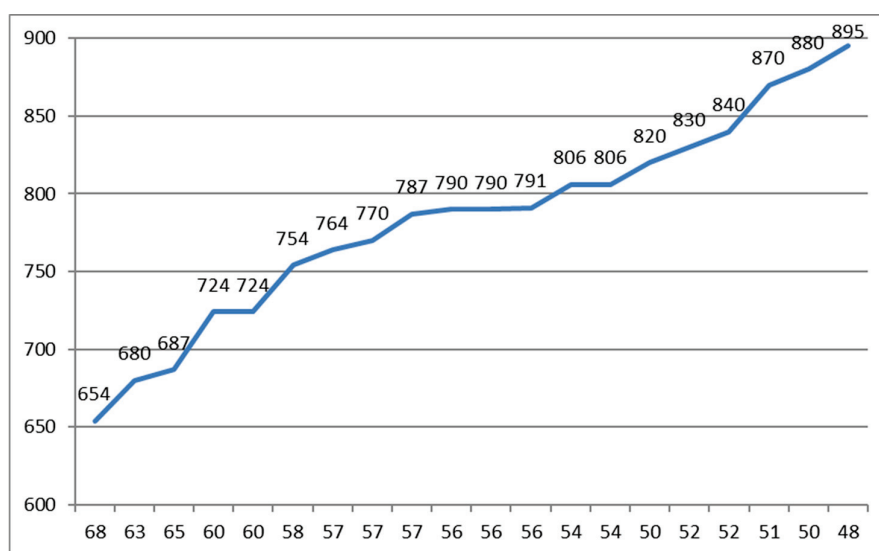
Table 7. Shrinkage properties of foam ceramics.

No.	Air Shrinkage, %	Fire Shrinkage, %	Total Shrinkage, %	Volumetric Air Shrinkage, %	Volumetric Fire Shrinkage, %
1	9.6	1.7	10.7	20.5	14.2
2	11.8	2.4	10.9	21.2	15.1
3	10.7	1.5	9.3	20.32	14.1
4	14.1	2	10.5	20.1	13.2

Water Absorption: The water absorption of fired samples serves as an independent characteristic of the ceramic body, defining its porosity, strength, and the sintering process of the material.

The water absorption of foam ceramic products, under slight variations in thermal treatment regimes and mixture composition, primarily depends on their bulk density.

Figure 16 illustrates the influence of the bulk density of foam ceramic products on the W_m and W_y parameters.

**Figure 16.** Water absorption of foam ceramic products as a function of bulk density.

Porosity

For foam ceramics, true density has an auxiliary role and is used in the calculation of material porosity.

Based on experimental data, Table 8 summarizes the porosity values.

Table 8. Porosity values of foam ceramic products.

No.	Total Porosity (P_t), %	Open Porosity (P_o), %	Closed Porosity (P_x), %
1	60	8.1	51.9
2	70	9.02	60.9
3	69	9.58	59.4

Mechanical strength is one of the key technical characteristics of ceramic materials. High strength enables their use in load-bearing structures, reduces wall thickness, and allows for increased building height.

The compressive strength of foam ceramic materials, under otherwise equal conditions, depends on their bulk density. Figure 17 presents the results of compressive strength tests

on foam ceramic products. The horizontal axis represents the compressive strength, while the vertical axis shows the density.

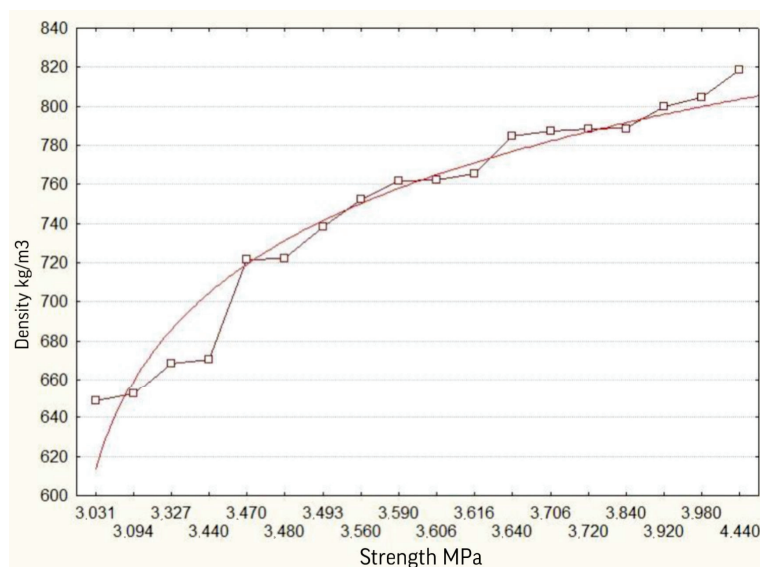


Figure 17. Compressive strength limit of foam ceramic products as a function of bulk density.

The highest strength values were obtained for materials produced from foam ceramic mixtures containing fly ash. However, the addition of more than 10% sawdust to the ceramic mass reduces the strength of the fired products. This effect is less pronounced in certain cases (as indicated by the trend lines in the figure).

Experimental results indicate that the bulk density of foam ceramic products can vary within the range of 800–650 kg/m³, depending on the raw material composition.

The thermal conductivity of the material depends on bulk density, true porosity, pore size and shape, the type of solid phase, and thermal–moisture influences, among other factors.

Figure 18 presents the relationship between the thermal conductivity of foam ceramic materials and their bulk density.

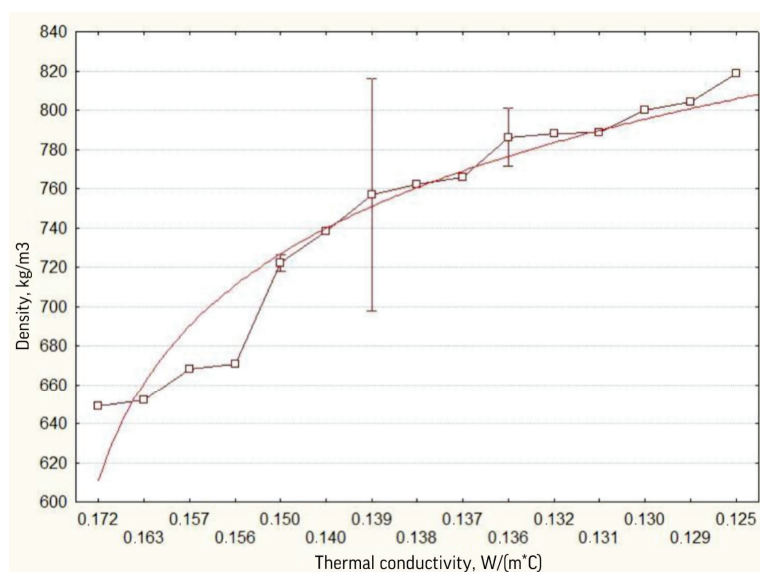


Figure 18. Thermal conductivity of foam ceramic products as a function of bulk density.

Thus, the key properties of fired foam ceramic materials are significantly influenced by the bulk density, porosity, pore size, and pore distribution characteristics.

Following is an investigation and analysis of the phase composition of the optimal foam ceramic sample. As previously described, during the firing process, foam ceramic products undergo various volumetric and linear changes (expansion, shrinkage) as a result of physicochemical transformations. Dilatometric studies allow for determining the sintering onset temperature of foam ceramic materials, analyzing the effect of temperature on dimensional changes, and obtaining essential data for designing and optimizing the firing regime. Figures 19 and 20 present X-ray diffraction patterns of foam ceramic products.

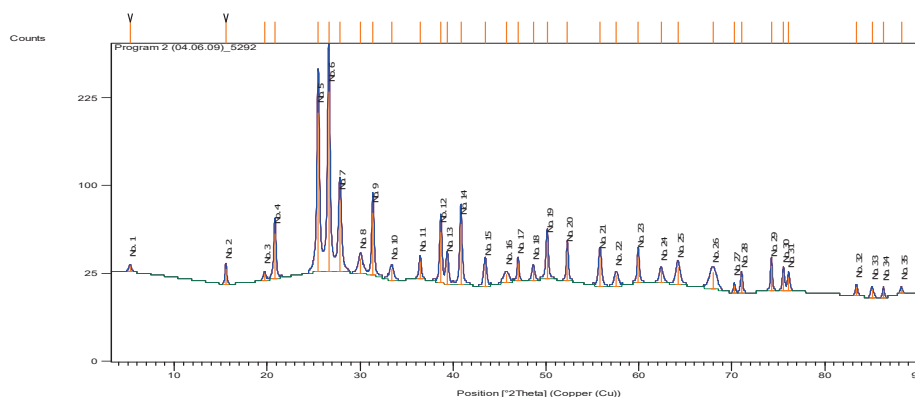


Figure 19. X-ray diffraction patterns of foam ceramic products fired at 900 and 1000 °C, lines from No. 2 to No. 35.

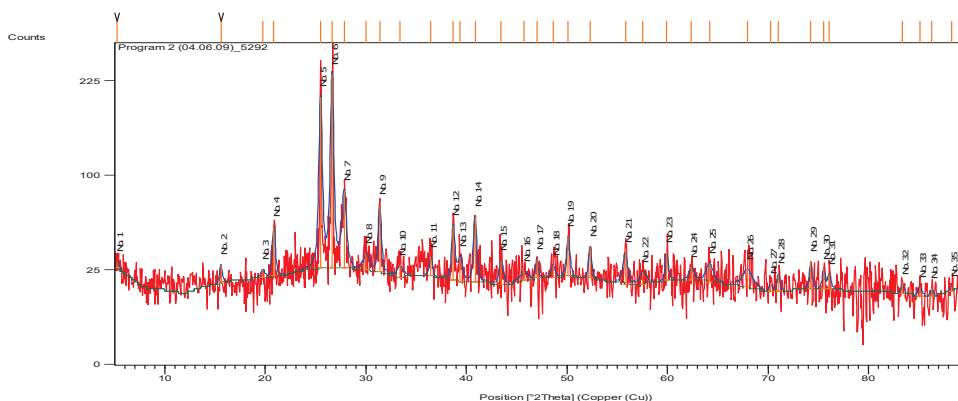


Figure 20. X-ray diffraction patterns of foam ceramic products fired at 950 and 1000 °C.

X-ray phase analysis of the raw material and fired products was performed on a DRON-4 X-ray diffractometer with Cu radiation and a Ni filter, operating at 40 kV and 20 mA using a NaI(Tl) scintillation detector. The interplanar distances were evaluated based on the angle values from the tables of Ya.D. Giller, and the mineral composition was deciphered using the X-ray references from V.I. Mikheev.

The accessories included with the instrument allow for the study of the structure of crystalline and amorphous materials, such as the following:

- Accurate determination of the lattice parameters of crystalline substances;
- Determination of crystallite sizes;
- Study of the material's stress state (first- and second-order stresses);
- Study of textures;
- Qualitative and quantitative phase analysis;
- Investigation of structural changes occurring in deformed metals upon heating.

For the macroscopic characterization of foam ceramic materials, an MBI-1 microscope was used.

X-ray phase analysis confirmed that the phase composition of the synthesized materials is primarily represented by mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), quartz ($\alpha\text{-SiO}_2$), and cristobalite (SiO_2). The effect of firing temperature on the phase composition of optimized samples was examined.

Increasing the firing temperature from 900 °C to 1000 °C leads to a decrease in the intensity of diffraction maxima characteristic of α -quartz, while the intensity of cristobalite diffraction maxima increases, which indirectly suggests changes in their respective quantities.

At the same time, the intensity of peaks corresponding to the crystalline mullite phase remains nearly unchanged. The presence of a mullite crystalline phase in the material structure provides the required strength characteristics.

Phase composition analysis revealed that upon firing foam ceramic masses at 950 °C and 1000 °C, diffraction reflections of clay minerals (lines from No. 2 to No. 35) were absent. This confirms derivatographic analysis data indicating their decomposition.

Furthermore, although cristobalite is known for its high thermal expansion coefficient (CTE), which can lead to reduced thermal shock resistance, its impact in this study was mitigated by the foam ceramics' high porosity. The porous structure absorbs thermal stress and prevents crack propagation during heating and cooling cycles. Thus, despite the presence of cristobalite, the overall thermal performance and structural integrity of the foam ceramics remained acceptable for typical building insulation applications.

As a result of the conducted research, it was established that the macrostructure of foam ceramic products with a bulk density of 650–700 kg/m³ is characterized by a high number of pores with diameters ranging from 0.2 to 1.5 mm (Figure 21).

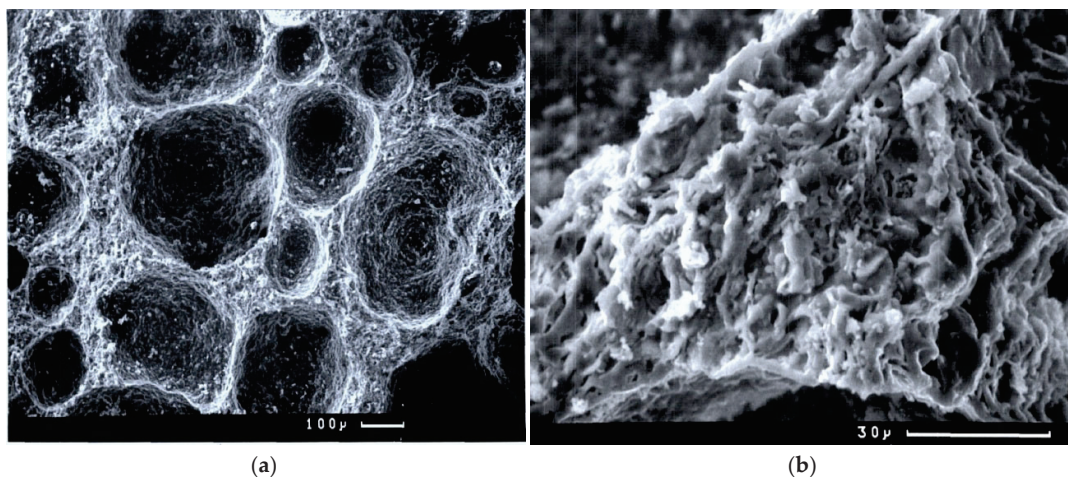


Figure 21. The macrostructure of foam ceramic products: (a) at 100× magnification; (b) at 30× magnification.

Notably, the highest pore distribution in these products falls within the 0.2–0.6 mm range, which is significantly different from raw material-based products.

This suggests enhanced structural and operational properties of the foam ceramic materials. Figure 21 presents photographs of the macrostructure of foam ceramic products.

Analysis of the obtained micro-photographs confirmed that the material exhibits significant porosity. The evenly distributed pores throughout the material have an isometric shape and an average size of 750 μm.

The pore size range (0.2–1.5 mm) was measured using optical microscopy with digital image analysis software, version 1. Micrographs were taken using a ZEISS Axio Imager

optical microscope, and pore dimensions were determined by processing the images with calibrated scale bars and averaging across multiple fields of view.

On the fracture surfaces, crystalline formations in the form of elongated prisms were observed. Based on their habit, these crystals can be identified as mullite. Aggregations of crystals of various shapes and sizes are present both on the surface and within the internal pore cavities and are consistent across all tested compositions.

In certain areas, chamotte grains with residual amorphized clay material were also identified.

4. Discussion

The results of this study provide significant insights into the optimization of foam ceramic materials, particularly concerning their mechanical strength, thermal conductivity, porosity, water absorption, and density. The primary objective of this research was to enhance the structural integrity and thermal insulation properties of foam ceramics by optimizing their composition and firing temperature through mathematical modeling and experimental validation.

One of the key findings of this study is the substantial influence of loam and fly ash content on the mechanical strength of foam ceramics. The experiments demonstrated that an optimal composition, consisting of 60–65% loam, 10% fly ash, and a firing temperature of 950–1000 °C, resulted in foam ceramic samples with the highest compressive strength (3.5–4 MPa) and superior thermal insulation properties. This confirms the role of controlled porosity and well-distributed fine pores in enhancing both strength and insulation performance. The optimization of the clay-to-ash ratio plays a critical role in controlling the formation and stability of the porous structure. A balanced clay-to-ash ratio ensures that the material has sufficient binder properties, enhancing the structural integrity of the foam while also maintaining the desired porosity for thermal insulation. Increasing the fly ash content too much leads to higher porosity, which can negatively affect the mechanical properties by weakening the structure.

Additionally, the concentration of coagulants and electrolytes affects the stability and distribution of the pores. Coagulants help regulate the coagulation process, ensuring uniformity in the pore structure, while electrolytes help in dispersing the particles and improving the fluidity of the suspension. The optimized levels of these additives contribute to a stable, well-distributed pore structure that enhances the material's mechanical properties and thermal performance.

Excessive fly ash content was found to negatively impact mechanical properties by increasing porosity beyond optimal levels, leading to reduced structural integrity.

Furthermore, the analysis of thermal conductivity revealed that it is primarily dependent on density and porosity. The obtained regression model ($R^2 = 0.781$) confirmed the adequacy of the mathematical approach used to predict thermal conductivity. The experimental data showed that increasing the firing temperature from 900 °C to 1000 °C led to an increase in the thermal conductivity due to enhanced densification and reduced air voids. However, an excessive increase in temperature beyond 1000 °C resulted in partial melting of the clay matrix, which could compromise the structural stability of the material.

The study also investigated the impact of porosity on the overall performance of foam ceramics. The experimental results indicated that porosity values between 70 and 72% were optimal for achieving a balance between mechanical strength and thermal insulation. At lower porosity levels (<60%) the density increased significantly, leading to higher thermal conductivity and reduced insulation efficiency. Conversely, at excessively high porosity levels (>75%) mechanical strength deteriorated, making the material less suitable for structural applications.

Water absorption, another critical factor influencing the durability of foam ceramics, was found to be strongly correlated with porosity and bulk density. The regression model ($R^2 = 0.874$) accurately described the dependence of water absorption on the composition and the firing parameters. The lowest water absorption values (53.1%) were achieved at 10% fly ash, 55% loam, and a firing temperature of 1000 °C. Higher fly ash content increased water absorption due to the formation of interconnected pore networks, which facilitated capillary water uptake.

The density optimization experiments demonstrated that the most suitable compositions yielded foam ceramics with a bulk density of 650–700 kg/m³, which aligns with the target specifications for lightweight thermal insulation materials. The regression model ($R^2 = 0.882$) confirmed that the combination of 10% fly ash and 65% loam provided the most favorable balance between density and insulation properties. Increasing the firing temperature from 900 °C to 1000 °C led to higher densification, whereas exceeding this temperature threshold resulted in unwanted vitrification effects.

X-ray diffraction analysis further supported these findings by revealing that the primary crystalline phases in the optimized foam ceramics included mullite, quartz, and cristobalite. The formation of mullite at higher temperatures contributed to improved mechanical properties, while the presence of cristobalite indicated potential trade-offs in the thermal expansion behavior. The phase composition analysis also confirmed that all clay minerals decomposed during firing, ensuring the stability of the final material.

The macroscopic and microscopic structural analysis revealed that the optimized foam ceramics possessed a highly uniform pore distribution, with dominant pore sizes ranging between 0.2 mm and 0.6 mm. This structure contributed to improved thermal insulation performance while maintaining adequate mechanical strength. The microstructural observations also confirmed the presence of mullite crystallites, which reinforced the structural framework of the material.

The percentage of the mullite phase in the final structure is around 20–25%. This proportion is consistent with other ceramic materials used for similar applications, where mullite is typically present at similar levels to enhance strength and thermal stability. In comparison to conventional insulating ceramics, where mullite content may vary, the 20–25% range in foam ceramics provides a balance between mechanical strength and thermal insulation efficiency.

The persistence of the mullite phase across the examined temperature range significantly contributes to the mechanical stability of the foam ceramics, particularly in terms of thermal shock resistance. Mullite's high thermal stability and low thermal expansion coefficient help to mitigate the stresses induced by temperature changes, improving the material's ability to withstand thermal cycling without cracking or degradation. This makes mullite a crucial phase for ensuring the durability of foam ceramics in environments with frequent temperature fluctuations.

Overall, this study demonstrates that mathematical modeling and experimental validation can be effectively combined to optimize the composition and processing conditions of foam ceramics. The findings highlight the potential for producing high-performance, lightweight, and thermally insulating materials suitable for construction and energy-efficient applications. Future research should focus on refining the sintering process, exploring alternative additives for enhanced durability, and investigating the long-term performance of foam ceramics under real-world environmental conditions.

5. Conclusions

The drying and firing processes of foam ceramic materials exhibit several distinct characteristics, influenced by the manufacturing method, the physicochemical and tech-

nological properties of clay raw materials and additives, and the nature of the porous structure. The coagulation ability of clay raw materials enhances the structural strength of the green body in the initial drying stage, allowing for demolding within 2–3 h after forming, which accelerates the drying process. The introduction of 10% sawdust reduces air shrinkage, improving the dimensional stability of the material.

Through mathematical modeling, an optimized method for producing ceramic products was developed with the following composition: loam (60–65%), fly ash (10%), and clay (15–20%), fired at 950–1000 °C. The resulting material has a bulk density of 680–700 kg/m³, a compressive strength of 3.5–4 MPa, and a thermal conductivity of 0.135–0.140 W/(m·K). The high-porosity structure of foam ceramics allows for the intensification of the firing process, leading to energy savings and improved efficiency.

Achieving high-strength foam ceramic materials is possible by creating a fine-pore structure with densely packed pore walls, which minimizes the formation of cracks and defects. The coagulation ability of clay raw materials plays a crucial role in determining the physical and technical properties of the final product, particularly its bulk density, porosity, pore size, and pore distribution.

The optimization of drying and firing conditions using mathematical modeling and predictive analysis has identified the optimal drying time as 9.5 h at a temperature of 90 °C. This drying time is relatively shorter than conventional drying times for similar materials, which typically range from 12 to 24 h, depending on the material and environmental conditions. The optimized drying process significantly improves energy efficiency and production time, contributing to the overall performance of foam ceramics. These optimized parameters contribute to improving the structural integrity and performance of foam ceramic products.

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Article

Impact Resistance of Yttria- and Ceria-Doped Zirconia Ceramics in Relation to Their Tetragonal-to-Monoclinic Transformation Ability

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Abstract: In this work, the impact resistance of three zirconia ceramics was investigated: two yttria-stabilized zirconia (3Y-TZP and 1.5Y-TZP) and a ceria-stabilized-zirconia (Ce-TZP) composite. The impact resistance was evaluated through drop-ball impact tests on disk-shaped samples. The results are discussed in terms of the materials' transformability, which was correlated to the size of tetragonal-to-monoclinic (t-m) transformation zones observed after the impact tests and to the volume fraction of the monoclinic content on fractured surfaces. The findings show that impact resistance increases with the ability of the material to undergo t-m transformation. The Ce-TZP composite exhibited the highest transformability and consequently the highest impact resistance, followed by 1.5Y-TZP, and then 3Y-TZP.

Keywords: impact resistance; zirconia ceramics; transformability

1. Introduction

Zirconia ceramics are widely used in various industrial and biomedical applications due to their remarkable mechanical properties, biocompatibility, and wear resistance. The high toughness of zirconia, when compared to other oxide ceramics, is largely attributed to its stress-induced phase transformation from the tetragonal (t) to monoclinic (m) phase. This t-m phase transformation is accompanied by a volume expansion (~5%), resulting in compressive stresses, which lead to crack shielding from applied tensile stresses. Consequently, this contributes to the toughening of zirconia ceramics by increasing their toughness or crack propagation resistance [1–3].

Ce-TZP and Y-TZP are zirconia ceramics stabilized in the tetragonal phase by the addition of CeO₂ and Y₂O₃, respectively. In the biomedical field, Y-TZP is favored for its aesthetic qualities and high mechanical strength, which may exceed 1 GPa, typically for ceramics containing 3 mol.% of yttria. However, this material exhibits moderate fracture toughness, ranging from 4 to 6 MPa√m [4–6]. In contrast, Ce-TZP ceramics offer higher toughness but lower strength (~500 MPa for zirconia stabilized with 12 mol.% ceria) [7–10] due to grain coarsening during sintering.

Numerous studies have explored strategies to achieve a better balance between strength and toughness in TZP ceramics [3,6,10–25]. Certain approaches involve the development of finer-grained Ce-TZP composites to enhance strength [3,6,9,15,19,21,26]. Another approach focuses on reducing Y₂O₃ content in Y-TZP ceramics to increase the

material's ability to undergo t-m transformation, thereby improving toughness without significantly compromising strength [27–32].

While the strength-toughness relationship in zirconia ceramics is well documented, less emphasis has been placed on impact resistance and energy absorption capacity. These properties, which are important for ballistic or shock-resistance applications, have been understudied and most previous investigations were focused on resistance to impact at very high speeds, known as ballistic impact loading [33–40]. In this study, we present a comparative analysis of the impact resistance of three TZP-based zirconia ceramics with increasing degrees of transformability: a standard 3Y-TZP zirconia, which exhibits transformation toughening but a quite modest crack-tip transformation zone size; a newly developed yttria-doped zirconia with less yttria content (1.5Y-TZP, doped with 1.5 mol.% yttria), which offers an attractive combination of toughness and strength [41]; and a Ce-TZP composite, showing a high transformation ability, a large transformation zone size, and, to a certain extent, some transformation-induced plasticity and ductility [9]. The aim of this work was also to clarify the question: 'Is strength or toughness the most relevant figure of merit when designing a shock-resistant ceramic?'

2. Materials and Methods

Three zirconia-based ceramic materials were used in this study: 1.5 mol.% and 3 mol.% yttria-stabilized zirconia, denoted by 1.5Y-TZP and 3Y-TZP, respectively, and a Ce-TZP composite consisting of 84 vol.% 11Ce-TZP, 8 vol.% Al_2O_3 , and 8 vol.% $\text{SrAl}_{12}\text{O}_{19}$ aluminate platelets. The 1.5Y-TZP material was supplied by TOSOH (Zgaia 1.5Y-HT, Tokyo, Japan) and contained 0.25 wt.% Al_2O_3 ; the two other materials were provided by DOCERAM (Dortmund, Germany). All the samples were received in the shape of sintered disks with a diameter of 20 mm and a thickness of 1 mm. They were mirror-polished using diamond pastes (in the following order of grades: 6, 3, and 1 μm) and a colloidal silica suspension (0.03 μm). Density was measured using the Archimedes method in water [42] and the percentage of theoretical density (TD, from rule of mixture) was reported. The microstructure of the studied ceramics was investigated using Scanning Electron Microscopy (SEM; Zeiss SUPRA VP55, Oberkochen, Germany) at 1 kV on fractured surfaces. The zirconia grain size was estimated from the SEM micrographs from a minimum of 150 grains using ImageJ software (Version 1.54). Vickers hardness was measured by Vickers indentation (FV-700 tester, Future-Tech, Kanagawa, Japan) on mirror-polished samples with a load of 1 kgf applied for 10s (Hv_1).

To evaluate the impact resistance of the studied materials, drop-ball impact tests were performed using a device developed in a laboratory, a schematic representation of which is shown in Figure 1. The mirror-polished surface of the disk-shape samples was placed on three balls equidistant from its center, arranged in a circle of 16 mm in diameter (as would be the case in biaxial bending tests). A tungsten carbide ball of 26.5 g weight and 15 mm in diameter was then dropped onto the center of the disk. The drop heights were chosen between 10 cm and 40 cm (with increments of 5 cm or 2.5 cm for more precision) to include, for all three ceramics, heights where no failure was observed towards heights for which all samples broke. For each material, six samples were tested at each drop height. The results were then analyzed in terms of failure probability, calculated as the ratio of the number of fractured samples to the number of tested samples under the same conditions (i.e., six samples), versus height. For each material, a critical height (H_C)—corresponding to the drop height at which at least one sample among the six fractured (non-null failure probability)—was determined.

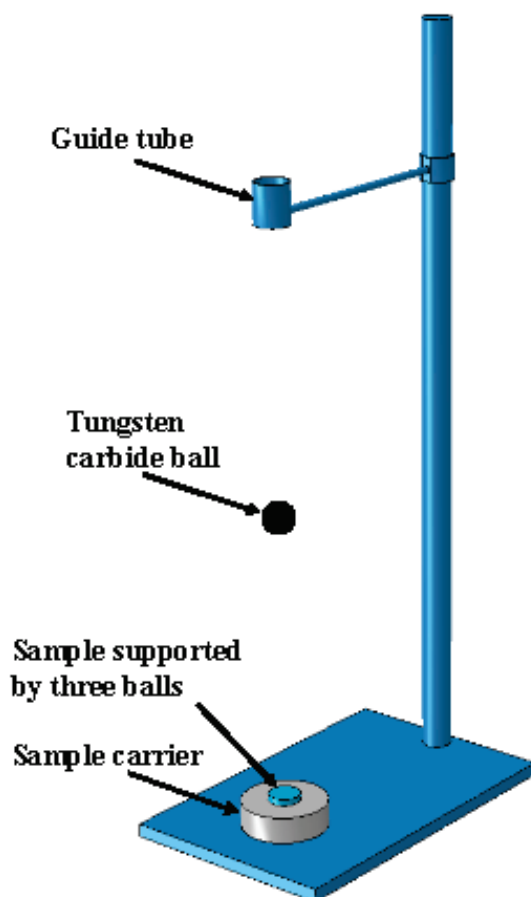


Figure 1. Schematic representation of the impact resistance testing device.

The impact energy, E_{imp} , was calculated considering only the potential energy, i.e., ignoring the loss due to air resistance, as follows:

$$E_{\text{imp}} = mgH \quad (1)$$

where m is the mass of the tungsten carbide drop ball (26.5 g), g is the gravitational acceleration (9.8 m/s^2), and H is the drop height.

The absorbed energy, E_a , during impact tests was calculated, as follows:

$$E_a = mg(H - H_B) \quad (2)$$

where H_B is the bounce height, which was measured using a high-speed camera.

To determine the phase composition and assess the transformability of the studied materials, X-ray Diffraction (XRD) analysis was conducted on mirror-polished and fractured surfaces using $\text{CuK}\alpha$ radiation ($1.5418\text{\AA}$) in the angular domain 2θ ranging from 27 to 33° (D8 Advance Bruker AXS diffractometer, Billerica, MA, USA). The mass fraction of the monoclinic phase (X_m) was calculated according to the following expression [43]:

$$X_m = \frac{I_m(\bar{1}11) + I_m(111)}{I_m(\bar{1}11) + I_m(111) + I_t(101)} \quad (3)$$

where $I_m(hkl)$ denotes the area of the peak generated by the hkl plane in the monoclinic (m) or the tetragonal (t) phase.

The volume fraction of the monoclinic phase (V_m) was then calculated according to [44]:

$$V_m = \frac{1.311X_m}{1 + 0.311X_m} \quad (4)$$

The bottom (tensile) side of the samples was observed for signs of t-m phase transformation zones induced by impact tests using optical microscopy (ZEISS Axiophot, Oberkochen, Germany) as well as 3D confocal microscopy, employing a S-Neox (Sensofar, Barcelona, Spain) 3D non-contact optical profiler machine, which combines confocal and interferometry techniques with a lateral resolution of 0.26 μm . The acquired data were processed using Mountains Map Universal software® (Digital Surf, Besançon, France).

3. Results

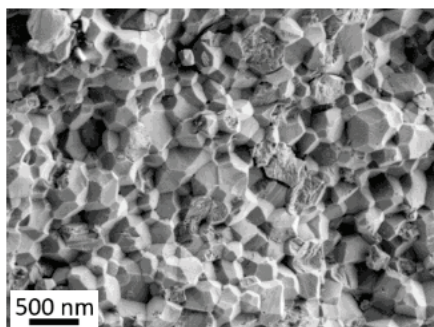
3.1. Microstructure and Properties

The density, Vickers hardness, and the zirconia grain size are presented in Table 1. SEM micrographs of fractured surfaces are shown in Figure 2. All materials exceeded 99% of the theoretical density, indicating almost full densification. The Vickers hardness falls within the typical range for Y-TZP and Ce-TZP composites [45–47], with a lower value for the latter. The initial monoclinic phase content on polished surfaces was less than 5 vol.% for all studied materials.

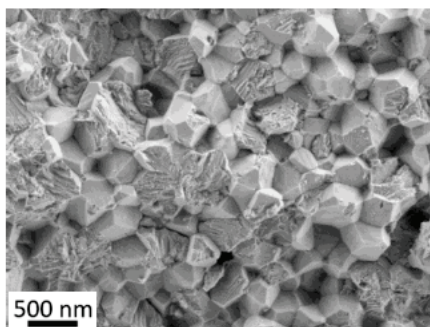
Table 1. Summary of density, hardness, and zirconia grain size of sintered disks.

Sample	1.5Y-TZP	3Y-TZP	Ce-TZP Composite
Density (% TD)	99.7	99.7	99.7
Hardness (Hv ₁)	1180	1305	1000
Zirconia grain size ($\mu\text{m} \pm \text{Sd}$)	0.4 ± 0.1	0.7 ± 0.1	0.9 ± 0.4

1.5Y-TZP



3Y-TZP



Ce-TZP Composite

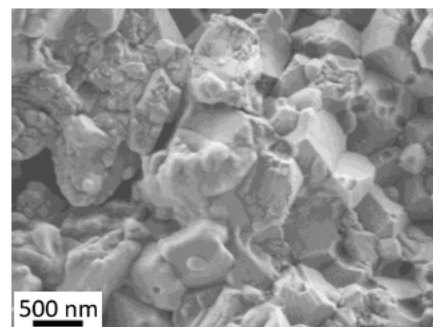


Figure 2. SEM micrographs of fractured surfaces of tested samples for each material.

3.2. Critical Drop Height

Figure 3 summarizes the results of the impact tests in terms of failure probability as a function of drop height. It can be observed that the range of drop heights over which the risk of fracture under impact is 100% is higher for 1.5Y-TZP and Ce-TZP composite (35 cm) compared to 3Y-TZP (25 cm). Both 1.5Y-TZP and Ce-TZP composite show similar drop heights for failure probabilities of 0.5 (30 cm), whereas this height is significantly lower for 3Y-TZP (~17.5 cm). Figure 4 shows the critical drop heights, H_C , determined for the studied materials. The Ce-TZP composite exhibited the highest H_C value of 30 cm. An intermediate value of 22.5 cm was observed for the 1.5Y-TZP zirconia, whereas the lowest value of 17.5 cm was observed for the 3Y-TZP zirconia.

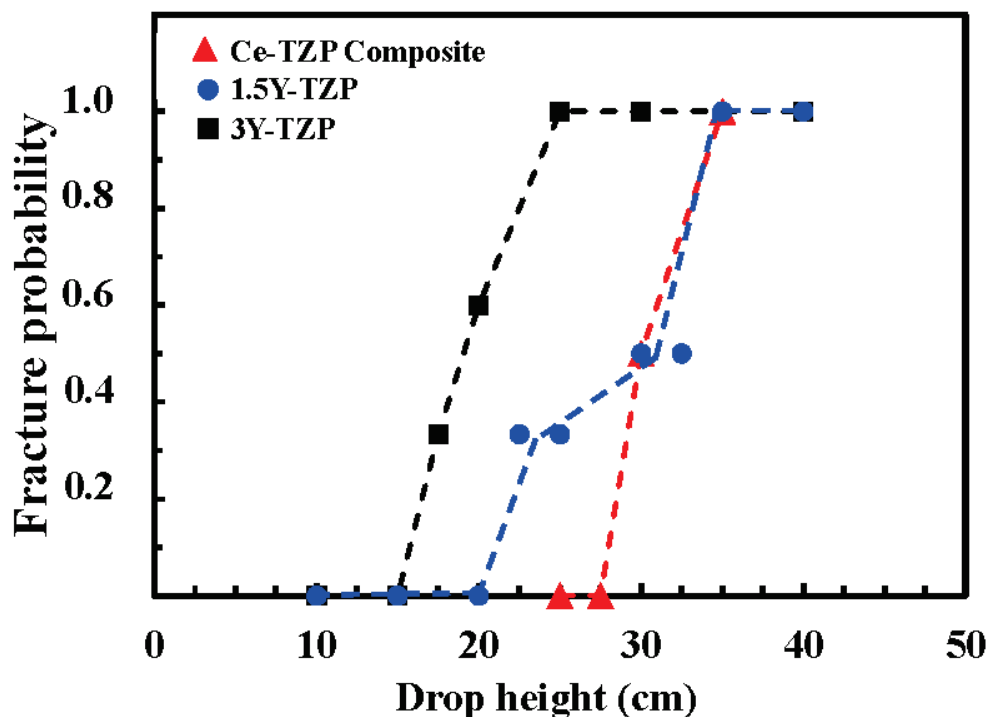


Figure 3. Fracture probability versus drop height for the three materials.

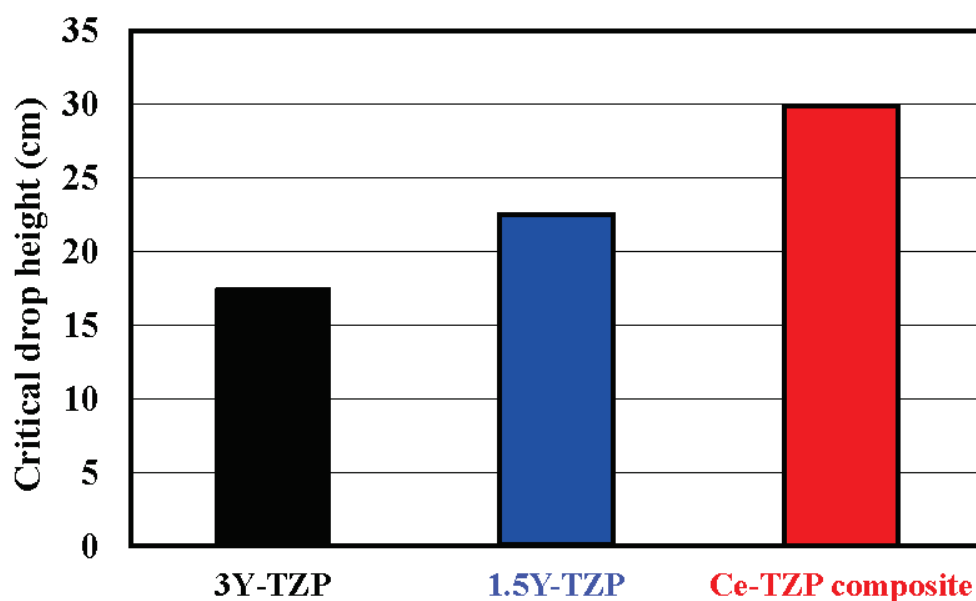


Figure 4. Critical drop heights (H_C) for the three materials.

3.3. Absorbed Energy

Figure 5 shows the absorbed energy, E_a , during impact testing at drop heights of 10, 15, 20, and 25 cm. For the 1.5Y-TZP and 3Y-TZP materials, only rebound measurements performed below their respective critical drop heights were considered for E_a calculations. For all the materials, the absorbed energy increased as drop height increased. At the smaller drop heights of 10 cm and 15 cm, 1.5Y-TZP and 3Y-TZP absorbed roughly the same amount of energy, whereas the Ce-TZP composite absorbed significantly more energy at all drop heights.

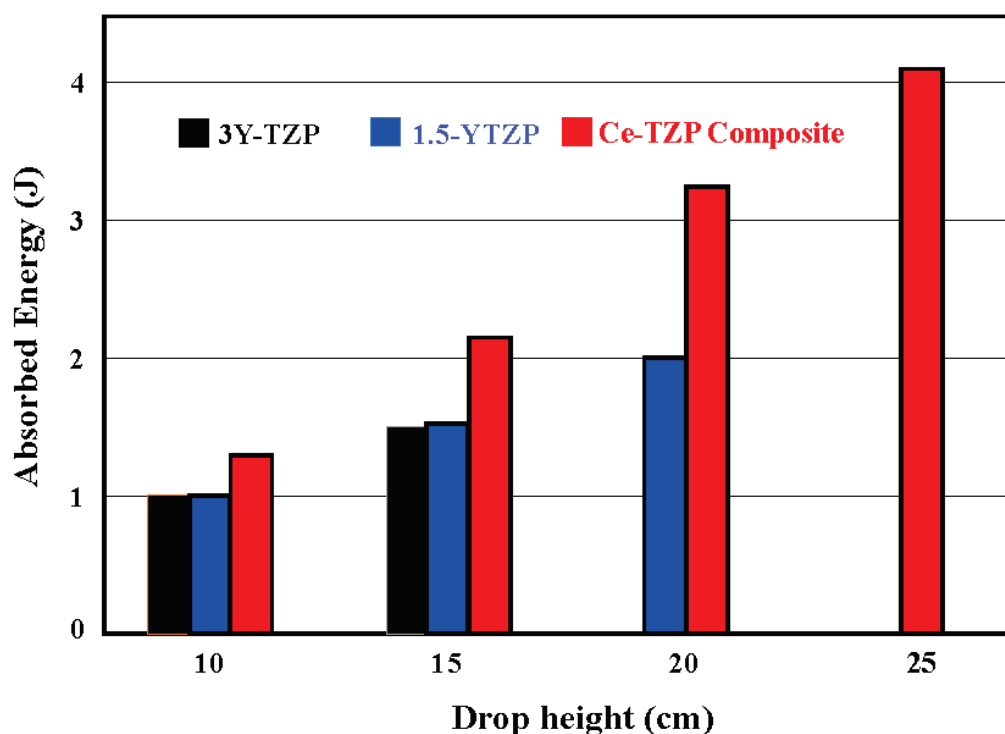


Figure 5. Absorbed energy (E_a) during impact testing at drop heights of 10, 15, 20, and 25 cm.

3.4. Impact-Induced Phase Transformation

Optical observations of the tensile side of impacted and unbroken samples revealed the presence of t-m transformation zones in 1.5Y-TZP and the Ce-TZP composite, while no phase transformation was detected in the impacted 3Y-TZP zirconia. Figure 6 shows typical optical micrographs of the impact-induced t-m phase transformation zones for different drop heights. For heights above H_C , only unbroken tested samples were observed. The transformation zones exhibited a star-shaped geometry, with a circular central transformed region from which radial bands extended towards the edge of the disk. The area of the transformation zone was evaluated by considering the transformed area within a circle corresponding to the effective surface in biaxial tests, as in [48]. Figure 7 shows the evolution of the impact-induced transformation zone area with drop height for the 1.5Y-TZP and the Ce-TZP composite. For both materials, the size of the transformation zone increases linearly with drop height (Figure 7), with consistently higher transformed areas for the Ce-TZP composite, which reached almost five times that of 1.5Y-TZP at a drop height of 30 cm (i.e., around 2.5 and 0.5 mm², respectively).

3D confocal microscopy observations confirmed the t-m phase transformation during impact testing and allowed quantitative analysis of the topography of impacted areas. Volume increase related to the t-m transformation (i.e., around 5 vol.%) was evidenced by circular dome-shaped zones, typical images of which are shown in Figure 8, where radial roughness profiles are also displayed. The effect of the impact on the t-m transformation extended over the sample (at least 5 mm in diameter around the impact point), as evidenced by the absence of a flat area in the 3D confocal images and analyses. For 1.5Y-TZP, roughness profiles revealed an increase of 2.4 μm in the maximum height of the transformation zone from 15 to 25 cm drop heights (1 and 3.4 μm , respectively). Similarly, for the Ce-TZP composite, the maximum height of the transformation zone increased by 9 μm over the same range of drop heights (i.e., from 9 μm at 15 cm to 18 μm at 25 cm).

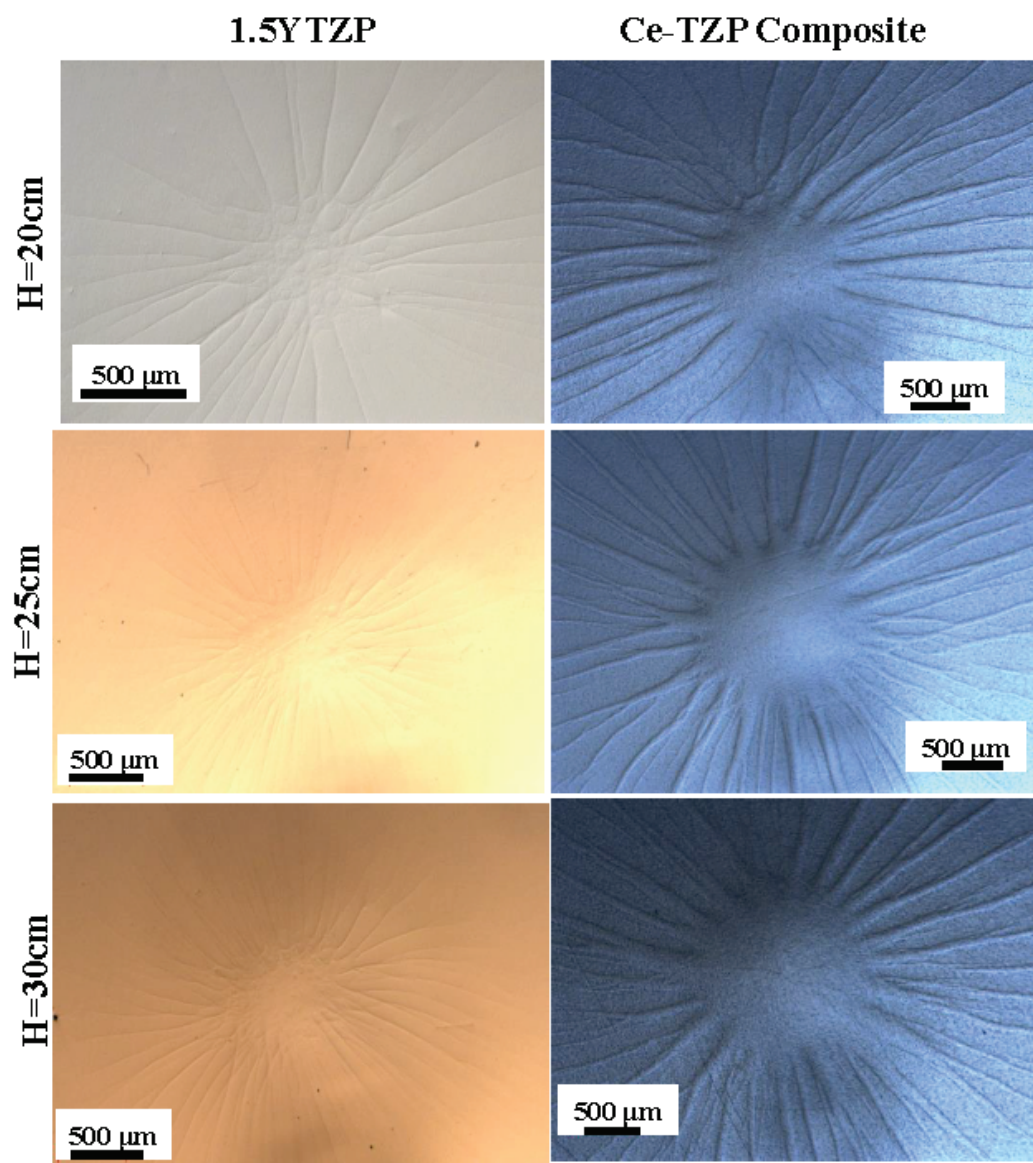


Figure 6. Optical micrographs (Nomarski contrast) of t-m transformation zones observed in 1.5Y-TZP and Ce-TZP composite after impact tests at drop heights of 20, 25, and 30 cm.

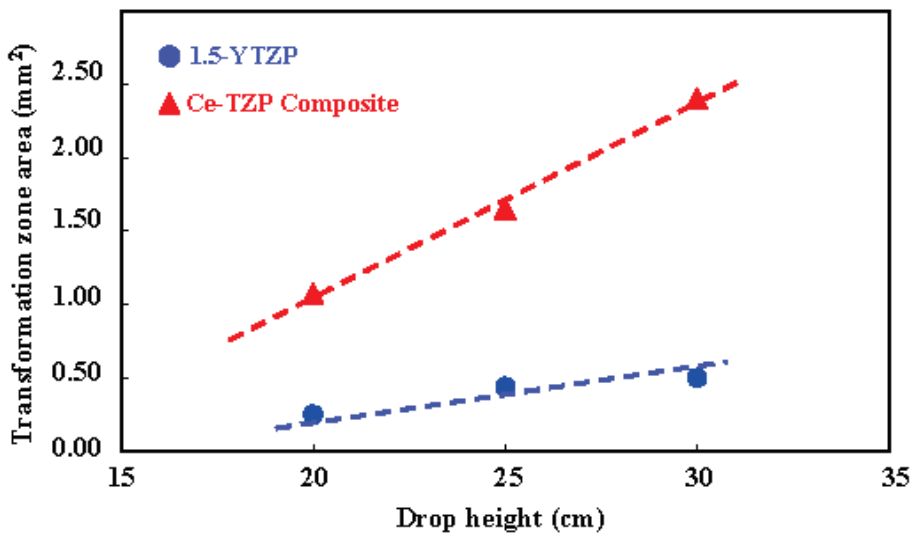


Figure 7. Evolution of the impact-induced t-m transformation zone size with the drop height.

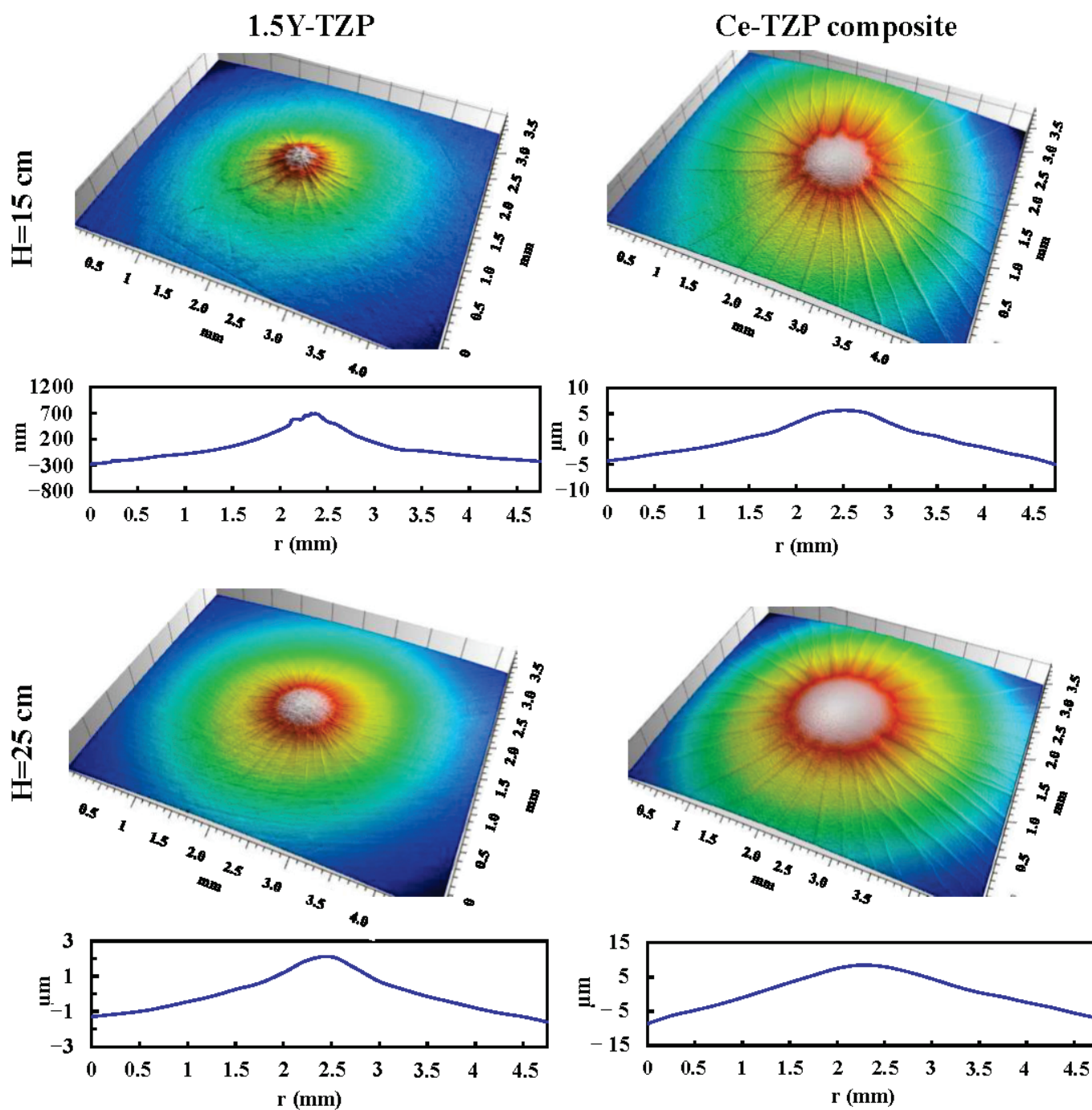


Figure 8. 3D confocal images of the transformation zones developed under impact testing for 1.5Y-TZP and Ce-TZP composite samples with drop heights of 15 and 25 cm, along with their radial topography profile curves as a function of the distance, r .

Evidence of t-m phase transformation in the studied materials during impact tests was also provided by XRD analysis of polished and fractured surfaces, as shown in Figure 9. The monoclinic phase content, (V_m), estimated on fractured surfaces after impact testing, was 80% for 1.5Y-TZP zirconia and the Ce-TZP composite, and 30% for 3Y-TZP zirconia.

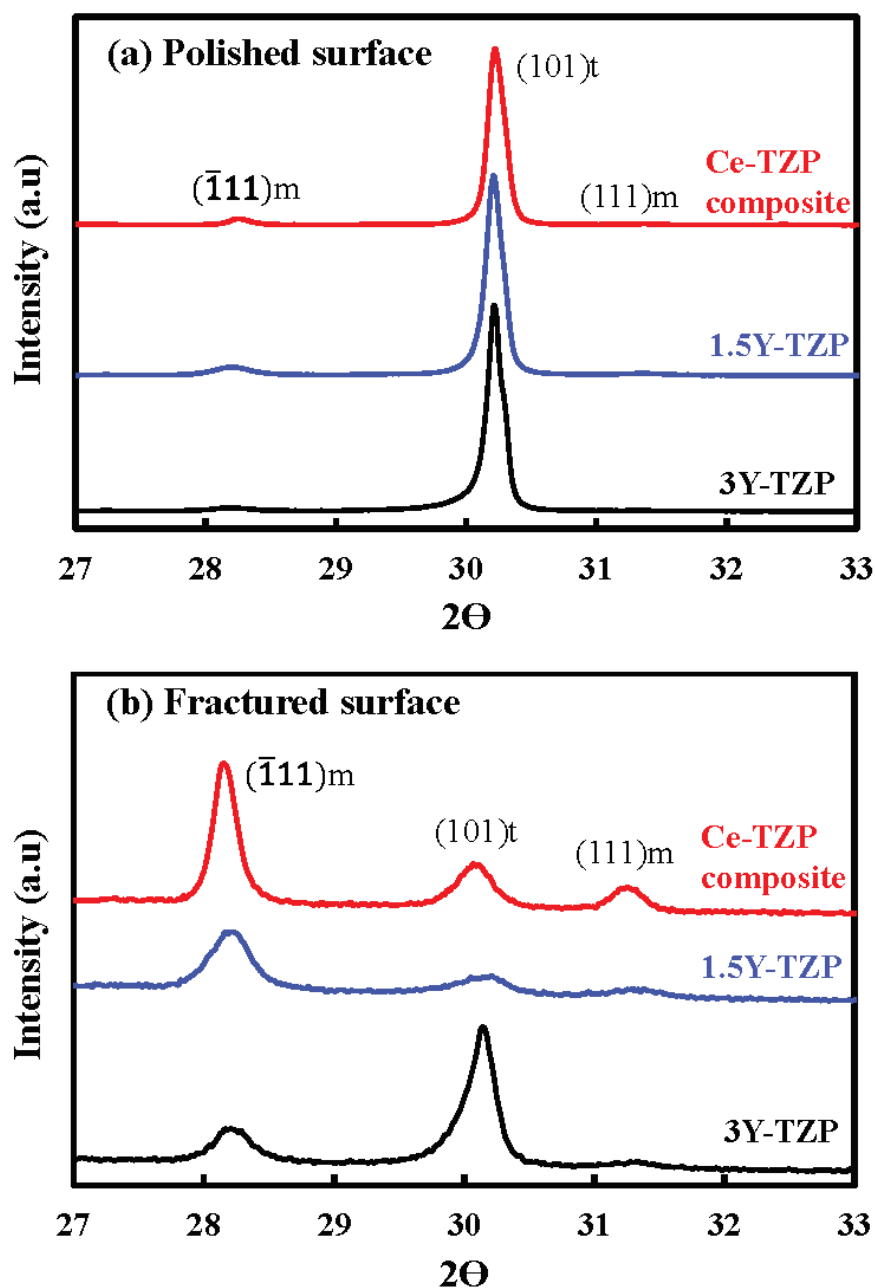


Figure 9. XRD patterns of polished (a) and fractured (b) surfaces of the studied materials.

4. Discussion

The phase transformation observed after impact testing of 1.5Y-TZP and Ce-TZP composite disks was induced by the stresses generated by the highly localized contact force between the ceramic surface and the WC drop ball, which is harder ($H_v \sim 2400$) and stiffer ($E = 500\text{--}700$ MPa). The star-shaped transformation zones induced during impact tests (Figure 6) are similar to those previously observed for these materials on the tensile side of biaxial piston-on-three-ball test samples (i.e., in the center of the disk, over the piston, where the stresses are the highest) or three-ball-on-three-ball tests (i.e., under the three closest balls in contact with the surface under compression, but on the side under tension) [9,41,48,49].

The results revealed a strong correlation between impact resistance, expressed either by the critical drop height (H_C) or the absorbed energy (E_a), and the stress-induced t-m phase transformation of the materials. The Ce-TZP composite, with the largest impact-induced

transformation zones (Figures 6 and 8), exhibited the highest critical drop height compared to the Y-TZP materials (Figure 4). Among the latter, the under-stabilized 1.5Y-TZP, for which impact-induced t-m phase transformation occurred, exhibited a higher critical drop height than 3Y-TZP, for which no transformation was observed on impacted surfaces.

The significantly high energy absorption of the Ce-TZP composite, even at low drop heights (Figure 5), can also be attributed to the high transformability of this material, which is known to provide a ductile-like behavior to these composite ceramics under quasi-static bending and tensile testing [48]. In previous works [10,48], it has been shown that this material and other similar composites [6,9,10,50] exhibited low critical t-m transformation stresses, $\sigma_c^{(t-m)}$, compared to their flexural strengths, allowing t-m phase transformation to occur at relatively low stresses (e.g., $\sigma_c^{(t-m)} \sim 300\text{--}400$ MPa) before any crack propagation, inducing nonlinear behavior ($\sim 0.4\%$ plastic strain at failure) and high energy dissipation before fracture. The plasticity in these Ce-TZP composites is exclusively linked to the stress-induced t-m zirconia phase transformation, as no microcracking and/or damage occurred during plastic deformation under flexural loading [10]. At low drop heights (10–20 cm), no significant difference was observed between the energy absorption in 3Y-TZP and 1.5Y-TZP, as the t-m phase transformation zone was not sufficiently developed in the latter under such conditions. This agrees with the high critical t-m transformation stress of 1.5Y-TZP, which is of the same order as its flexural strength, σ_R (i.e., $\sigma_c^{(t-m)} = \sigma_R \sim 1000$ MPa), placing it at the transition between brittle and ductile behavior [41]. This characteristic also explains the wider range of drop heights over which the risk of fracture under impact increases from 0 to 100% for 1.5Y-TZP (Figure 3). At low drop heights, the transformation zones in this material were not sufficiently developed, and its behavior was close to that of 3Y-TZP (brittle-like). However, it then becomes similar to that of the Ce-TZP composite at high drop heights (ductile-like), at which its t-m transformation becomes important.

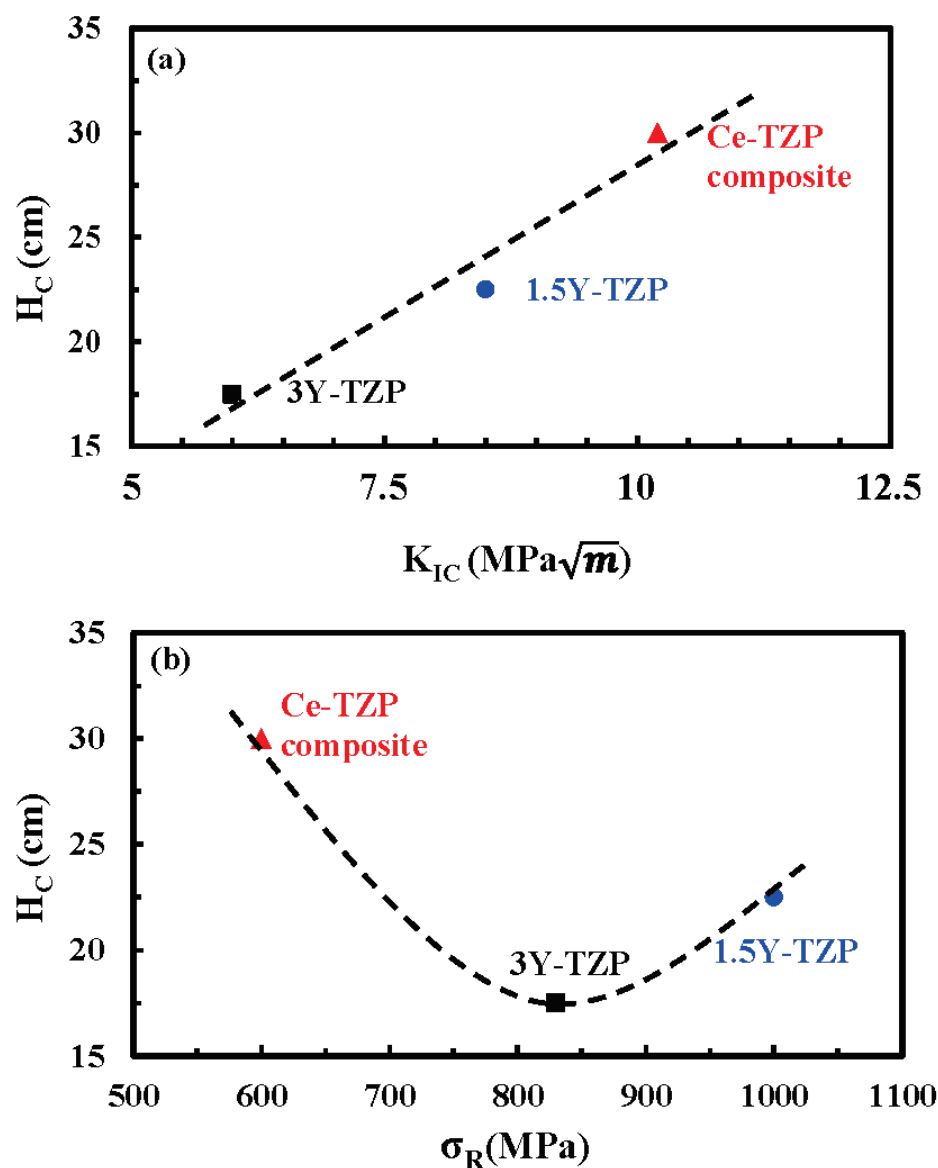
After sintering and polishing, mainly tetragonal zirconia was detected by XRD (Figure 9a). The volume fraction of the monoclinic phase was estimated to be 3% for 3Y-TZP and 5% for both 1.5Y-TZP and the Ce-TZP composite, related to transformation at the surface of the ceramics due to applied polishing stresses. The ability to undergo t-m phase transformation under stress, estimated from XRD performed on as-fractured surfaces (Figure 9b), was much higher for 1.5Y-TZP and the Ce-TZP composite (80 vol.% monoclinic phase) compared to the less impact-resistant material, 3Y-TZP (only 30 vol.%). It is worth noting, however, that the amount of monoclinic phase on fractured surfaces reached the same value for 1.5Y-TZP and Ce-TZP composite materials (80%), despite the higher impact resistance of the Ce-TZP composite. This is due to the limitations of XRD in assessing the extent of monoclinic phase transformation in zirconia, as X-rays only penetrate to a depth of ~ 5 μm [51]. Microstructural analysis of cross-sections should be carried out to better characterize the volume affected by t-m phase transformation under impact, but the transformability is already well described and quantified from topography analyses of the transformation areas.

As outlined by several authors [52–58], the fracture toughness (K_{IC}) is a key material parameter affecting the ballistic resistance of ceramic materials, as it measures the resistance to crack initiation. For the studied materials (Table 2), the higher the fracture toughness, the higher the impact resistance, following a linear trend, as shown in Figure 10a. In contrast, no direct relationship was observed between H_C and strength, (σ_R), previously determined from four-point bending tests (Figure 10b) [41,48,59]. In particular, the material most resistant to impact (i.e., the Ce-TZP composite) displayed the lowest value of strength, indicating that strength has a weaker correlation with impact resistance than fracture toughness under the conditions of this study.

Table 2. Impact resistance parameters (H_C and absorbed energy at H_C , E_{ac}), strength (σ_R), and fracture toughness (K_{IC}) of the studied materials.

Material	H_C (cm)	E_{ac} (J)	σ_R^* (MPa)	K_{IC}^* (MPa $\sqrt{m}$)
3Y-TZP	17.5	1.64	830	6.1
1.5Y-TZP	22.5	2.21	1000	8.5
Ce-TZP composite	30	5.02	600	10.2

* Determined using the Single Edge V-Notched Beam (SEVNB) method in previous works [41,48,59].

**Figure 10.** Variation of the critical drop high, H_C , with toughness, K_{IC} , (a), and with strength, σ_R , (b) for the studied materials.

The correlation between K_{IC} and impact resistance can be understood by considering the positive influence of stress-induced t-m phase transformation on both properties. On one hand, crack shielding due to this transformation decreases the effective applied stress at the crack front, likely to propagate, which leads to improved fracture toughness. The size of the transformation zone around the crack (h) and the volume fraction of the monoclinic transformed phase are key parameters for transformation toughening, as

previously verified for the studied materials during crack propagation under flexural loading [41,48]. It has been shown that h , typically about 5 μm for 3Y-TZP (known for its brittle behavior), reaches 20 μm for 1.5Y-TZP and 100 μm for the ductile Ce-TZP composite, which exhibited a significant crack growth resistance (rising R-curve behavior). On the other hand, the effect of t-m phase transformation on impact resistance can be attributed to the increased energy dissipation associated with the material's ability to exhibit t-m phase transformation and ductile behavior. This finding is consistent with the impact-induced t-m phase transformation results, which highlight the intermediate behavior of 1.5Y-TZP, allowing it to perform relatively well in terms of impact resistance, though not as effectively as the ductile Ce-TZP composite. It would be interesting to better characterize the t-m transformed zones induced by impact to verify whether, as observed during biaxial flexural tests performed on Ce-TZP composites, the t-m transformation takes place without microcracking. If this is the case, strategies for “regenerating” impacted ceramics could be explored by inverse m-t phase transformation, which would be achieved by increasing the temperature of the material.

5. Conclusions

Our work clearly highlights the role of stress-induced t-m zirconia phase transformation in the impact resistance of zirconia ceramics. The higher the transformability, the higher the ability to absorb energy upon impact and the higher the critical height for failure. The highest transformability was observed in the Ce-TZP composite, which had the highest critical height (30 cm), followed by 1.5Y-TZP (22.5 cm) and 3Y-TZP (17.5 cm). A linear relationship between the fracture toughness and critical drop height was observed in these zirconia-transformable materials. However, further studies on other zirconia-based compositions and/or composites are needed to validate this dependence. Conversely, strength measured in bending is not a relevant figure of merit for shock resistance, at least under the conditions of this study. These findings show the positive influence of stress-induced t-m zirconia phase transformation on the impact resistance of zirconia materials, suggesting the potential use of highly transformable materials in applications where shock resistance is of prime importance.

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Article

Experimental and Theoretical Study of the Thermal Shock Behavior of Insulating Refractory Materials

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Abstract: This study investigates the thermal shock behavior of three Al₂O₃-SiO₂ commercial insulating refractory materials (JM23, JM26, and JM28) used in high-temperature industries (>1000 °C). Thermal shock resistance was evaluated through experimental tests and compared with theoretical parameters (R , R''' , R_{st}) based on thermoelastic and thermomechanical models. The tests revealed that JM23 did not withstand thermal shock due to its fragility when in contact with water at room temperature, resulting in its immediate collapse. In contrast, JM26 and JM28 maintained their mechanical strength after several thermal shock cycles, although JM28 experienced a more significant decrease in compressive strength. The mechanical behavior under compression changed from semi-fragile to apparently plastic after severe heat treatments. Porosity analysis showed that JM26 had a lower pore size distribution, which contributed to its better thermal shock performance. Theoretical parameters were calculated, confirming that JM26 exhibited the highest resistance to thermal shock. These findings suggest that controlled porosity and microstructure are key factors in improving the thermal performance and durability of insulating refractory materials in high-temperature applications.

Keywords: porous ceramic; insulating bricks; thermomechanical properties; thermal shock resistance

1. Introduction

Refractory bricks, a specific type of ceramic material, are critical components in high-temperature applications, such as furnaces, kilns, and reactors, where they must withstand extreme thermal stresses [1–3]. To enhance energy efficiency in industrial processes, insulating refractory materials play a key role by minimizing heat loss, lowering energy consumption, and reducing costs [4–7]. Effective thermal insulation is vital to maintain optimal operating temperatures, improving process efficiency and reducing environmental impact.

The study of thermal shock resistance in ceramic materials is of importance due to their widespread use in various industrial applications. Thermal shock occurs when a material undergoes a rapid temperature change that causes it to expand or contract. This can result in the development of internal stresses, which can result in cracking or failure of the material [8,9]. Understanding the thermal shock resistance of ceramics can lead

to the development of more durable and reliable materials, which is essential for the optimization of industrial processes [10,11]. The theoretical parameters that define thermal shock resistance depend on the mechanical properties of the materials. They involve assessing the material's ability to withstand thermal gradients without fracturing. The key parameters are the strength, elasticity, thermal conductivity, and specific heat capacity of the material. These properties determine how the material absorbs and dissipates thermal energy, and how it tolerates induced stresses.

To comprehensively understand the behavior of ceramics under thermal shock, both thermoelastic and thermomechanical models are employed [12–14]. The thermoelastic model considers the elastic response of the material to thermal stresses, focusing on reversible deformations and the development of stress due to temperature gradients. The thermomechanical model, on the other hand, considers both elastic and plastic deformations, as well as the potential for crack initiation and propagation under thermal cycling. These models provide a framework for predicting the performance of materials under thermal shock conditions.

There are several precedents for systematic studies of the thermal shock behavior of refractory ceramic materials in high-temperature applications in general [15–17]. Likewise, there are studies on porous ceramic materials [18–20]. However, to the best of the authors' knowledge, in the literature there is no research on industrial insulating ceramics that involves experimental tests coupled with studies based on the theoretical parameters of thermal shock resistance for this type of ceramic.

Considering all the above, this study aims to evaluate the thermal shock behavior of $\text{Al}_2\text{O}_3\text{-SiO}_2$ commercial insulating refractory materials used in high-temperature industries ($>1000^\circ\text{C}$). The differences in their performance are analyzed based on physical, chemical, textural, microstructural, mechanical, and fracture properties. In addition, this work evaluates the theoretical parameters of merit of the thermoelastic and thermostatic models (R , R'''' , and R_{st}) in order to assess their validity for the studied materials. The results contribute to a better description and understanding of this important class of refractories, allowing extrapolation to materials with similar composition and microstructure.

2. Materials and Methods

2.1. Materials

Three insulating commercial refractory bricks, which are commonly used in high-temperature industries ($>1000^\circ\text{C}$), were studied in this work. The materials used in this study are JM23, JM26, and JM28. In a recent work, a deep textural, mineralogical, and mechanical characterization was carried out by the authors [21]. Table 1 summarizes the properties of these materials. The main components are alumina (Al_2O_3) and silica (SiO_2) for the three materials, and in the case of JM23, calcite (CaO) is also present in a significant quantity. This difference in chemical composition is also observed in the mineralogical composition. The main crystalline phase in JM23 is plagioclase (80.6 wt.%), with around 11 wt.% of mullite. Meanwhile, for JM26 and JM28, mullite is their main crystalline phase, with both also presenting alumina as a secondary phase. The porosity percentage of the three materials is similar, between 64 and 69%, and the difference in density values is associated with the aforementioned mineralogical composition. The pore size distribution, measured by mercury intrusion, shows that JM26 presents the narrowest distribution.

In addition, mechanical fracture parameters show differences between JM23, JM26, and JM28; materials with mullite as the main crystalline phase present the major values of K_{IC} and γ_{WOF} . This implies that the main difference between the three materials is their mineralogical composition, as well as the pore size distributions that are implied by the difference in mechanical properties [21].

Table 1. Chemical and mineralogical composition, mechanical fractures, and physical properties of material data taken from [21].

Material	JM23	JM26	JM28
Chemical composition (wt. %)			
Al ₂ O ₃	37.0	58.0	67.1
SiO ₂	44.4	38.8	30.0
Fe ₂ O ₃	0.8	0.8	0.6
TiO ₂	1.2	0.3	0.5
CaO	15.2	0.1	0.1
MgO + Na ₂ O + K ₂ O	1.4	1.9	1.0
Crystalline and non-crystalline composition (wt. %)			
Mullite (3Al ₂ O ₃ ·2SiO ₂)	11.4	48.8	55.0
Alumina (α-Al ₂ O ₃)	trace	27.5	27.1
Plagioclase (Na,Ca)(Si,Al) ₃ O ₈	80.6	-	-
Non-crystalline phase *	7.0	23.5	17.9
Density (g/cm ³)	0.48	0.80	0.92
Porosity (%)	64	68	69
Pore size distribution (nm)			
<i>d</i> ₁₀	5360	2320	4550
<i>d</i> ₅₀	4150	1720	2360
<i>d</i> ₉₀	340	90	800
Mechanical fracture parameters			
<i>K</i> _{IC} (MPa mm ^{1/2})	0.45	1.2	1.2
γ _{WOF} (J m ⁻²)	3.9	14.4	16.7

* Calculated with Le Bail method [22].

2.2. Methodology

The dilatometric behavior of the materials was studied using thermos mechanical analysis (TMA), which was performed at up to 1100 °C and was carried out at a 10 °C min⁻¹ heating rate in an air atmosphere (Rigaku Evo plus II, Rigaku, Tokyo, Japan).

A total of 10 specimens of dimensions 50 × 50 × 50 mm³ of each material were subjected to thermal shock from room temperature to the temperature studied, which in this work were 800 and 1000 °C. A cycle of the thermal shock (TS) consisted of putting a specimen into a furnace set at the desirable temperature, and after thirty minutes, removing it and quenching it in water at 20 °C for ten minutes. The samples were evaluated by compressive strength after one and five cycles in a universal testing machine (Instron 5985, Instron, Norwood, MA, USA) with steel plates, at a constant rate of 0.5 mm·min⁻¹. The mechanical parameters measured after thermal shock cycles were the apparent Young's modulus (*E*) and the cold crushing strength (CCS, *σ*). *E* was measured as the slope of the first linear part of the stress–strain curve (strain = *ε* < 0.003), and *σ* was measured considering the maximum stress as the failure criterion [23,24].

After TS, the pore size distribution was measured by mercury intrusion porosimetry (Thermo Scientific Pascal 440, Thermo Fisher Scientific, Monza, Italy), from which the apparent pore size at 10%, 50%, and 90% of the distribution (diameters *d*₁₀, *d*₅₀, and *d*₉₀, respectively) and the size span (*d*₉₀ − *d*₁₀)/*d*₅₀ were determined.

The theoretical thermal shock resistance (TSR) parameters for brittle material were calculated according to the thermo-elastic approximation, the energy balance criteria, and the unified theory [25]. The parameters calculated are defined as the following:

$$R = \frac{\sigma_0(1 - \nu)}{E_0\alpha} \quad (1)$$

$$R''' = \left(\frac{K_{IC}}{\sigma_0} \right)^2 \quad (2)$$

$$R_{st} = \left(\frac{\gamma_{WOF}}{E_0 \alpha^2} \right)^{1/2} \quad (3)$$

where E_0 and σ_0 are Young's modulus and CCS, respectively, before the thermal test; α is the coefficient of thermal expansion, ν is the Poisson's ratio, K_{IC} is fracture toughness, and γ_{WOF} is the work of fracture. K_{IC} was measured by single-edge notched beam (SENB) and γ_{WOF} was determined considering the area (energy) under load-displacement curve, obtained in the SENB test, divided by twice the fracture surface area; these parameters were reported by the authors [21] and are presented in Table 1. The thermal expansion coefficients measured during heating in the temperature range of 25–1000 °C were used for the calculations of the TSR parameters, assuming $\nu = 0.25$ [4,26].

3. Results and Discussion

The TMA curves of the studied insulating materials from room temperature to 1100 °C are shown in Figure 1. In general, the fit of the dilatometry curves was linear up to 1000 °C, and after this temperature JM23 started a sintering process reflected by the sudden drop in its curve. The other two samples present higher refractoriness and shrinkage is not observed in the studied temperature range. These results establish a recommended temperature range from room temperature to 1000 °C for the three samples and from room temperature to 1100 °C for JM26 and JM28. The different behavior is attributed to the crystalline composition of the materials (Table 1). While JM26 and JM28 present mullite as the main crystalline phase, which is well known for its refractory properties [27], JM23 presents plagioclase as the main crystalline phase, a silicoaluminate with calcium sodium cations of lower refractoriness and that start a glassy formation process at 1000 °C [28].

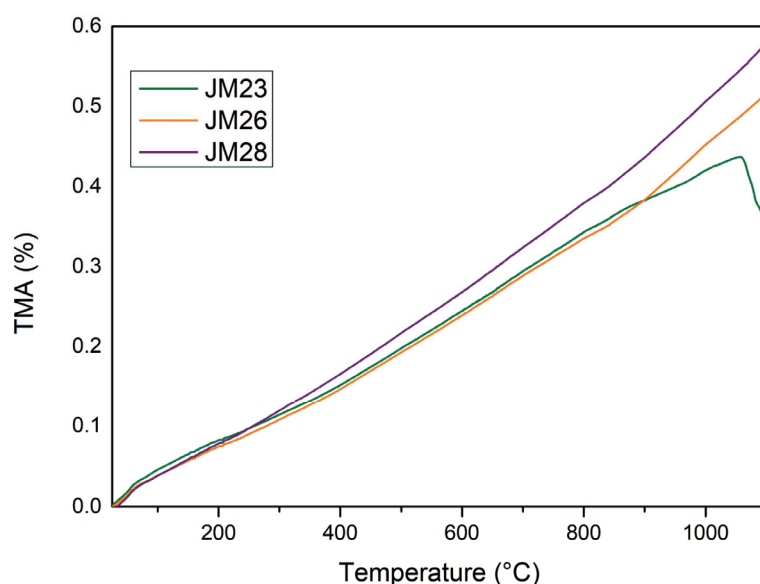


Figure 1. Dilatometric curves of studied materials.

From each TMA curve of Figure 1 the coefficient of thermal expansion (CTE) was determined, considering the temperature range of 25–1000 °C and the values obtained are presented in Table 2. As expected, the CTE is larger in the materials with higher mullite fraction, due to the CTE of mullite being $5.3 \times 10^{-6} \text{ C}^{-1}$ [29]. It should be noted that, although a difference is observed, it does not exceed 20% in relative value.

Table 2. CTE in temperature range of 25–1000 °C.

Material	CTE ($10^{-6} \text{ }^{\circ}\text{C}^{-1}$)
JM23	4.40
JM26	4.64
JM28	5.23

The specimens of JM23 did not withstand the thermal shock at 800 °C because when cooling, immersed in water, they suddenly ruptured. Consequently, this rupture did not allow for testing mechanical resistance in JM23 samples. On the other hand, the other two samples maintained their microstructural integrity after these severe treatments and the mechanical characterization after TS could be carried out. For this reason, it can be argued that the thermal shock resistance of JM26 and JM28 is greater than that of JM23.

Figure 2 presents typical curves of compressive stress versus strain. In both samples, a change in the shape of the curve is observed (Figure 2a). While the original material presents a semi-stable-type fracture curve, after thermal shock, the curves become stable. This “plastic” behavior was reported in the literature for materials with no breaking point in stress–strain curves [30].

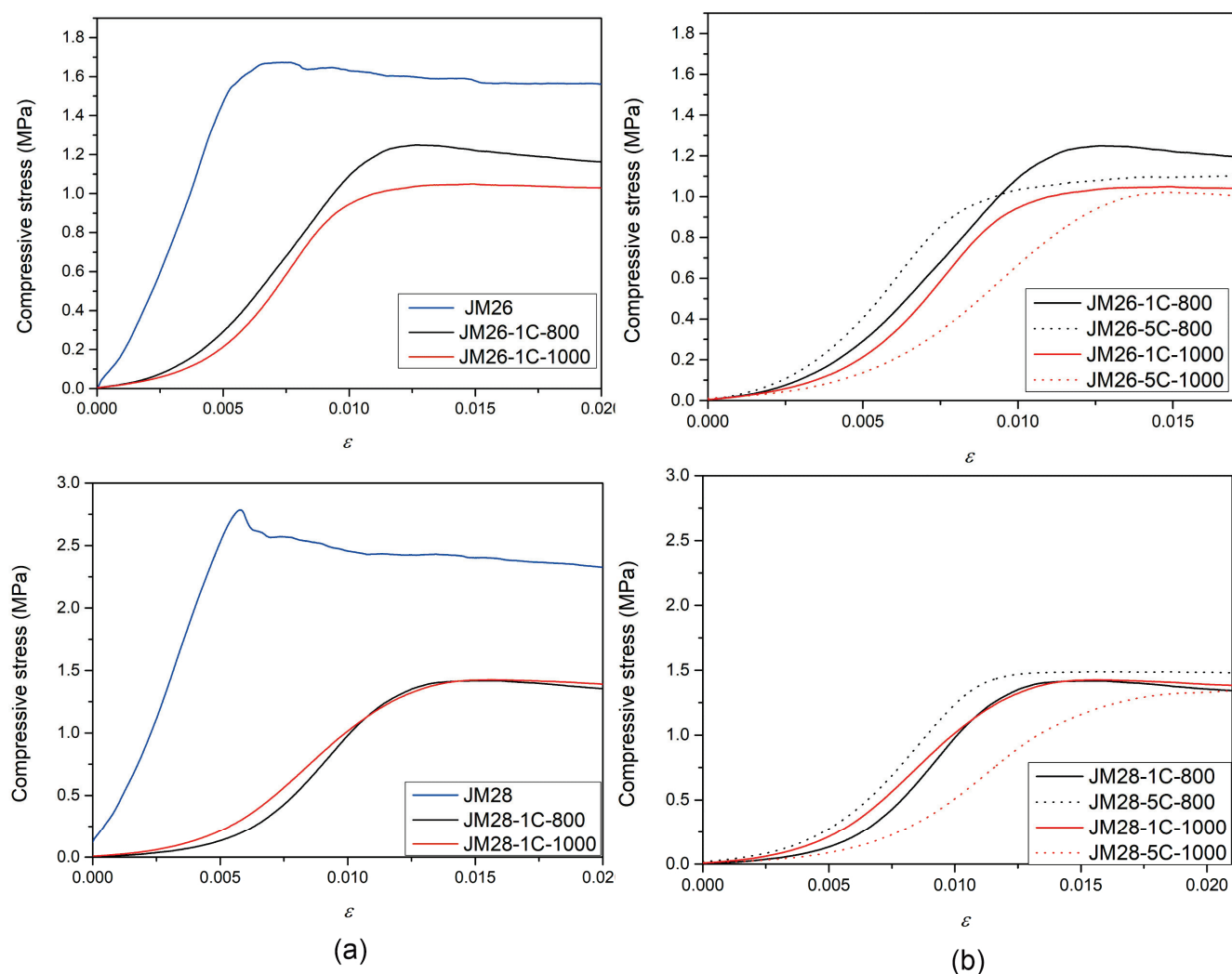
**Figure 2.** Compressive stress–strain curves of samples with and without TS (a) and samples with different cycles of TS (b).

Figure 2b shows the compressive curves after thermal shock at the two temperatures analyzed and for the different cycles. In general, all these curves present a linear zone first and a slight drop in load after fracture, followed by an extended region where strain increases continuously and stress remains almost constant [31]. There are no big differences in the shape and the maximum σ value between the curves comparing the different cycles and the different shock temperatures.

The mechanical parameters determined from the compressive curves are summarized in Table 3. The relative standard deviation of parameters σ and E were in the range of 5–26%, in agreement with those reported in the literature [32]. JM28 presents the highest σ value before and after TS, and its mechanical resistance decreases abruptly after TS (40% after one cycle). Meanwhile, JM26 approximately constantly maintains its compressive strength after different thermal shock cycles at both temperatures evaluated. The behavior of the σ of the materials after different thermal shock cycles is also graphically presented in Figure 3. The decrease in σ after the first TS is higher for JM28 than JM26, ~40% and 20%, respectively; meanwhile, for this parameter no significant differences were observed at one and five cycles. The decrease in σ after TS is between 8 and 23% and is comparable with others reported in the literature [4,33].

Table 3. Mechanical parameters values for materials after and before TS.

	Temperature (°C)	N° of Cycles	E (MPa)	σ (MPa)	$(A_1 + A_2)/2$	X_0
JM23	-	-	138	0.83		0.003
	800	1	-----failure-----			
	1000	1	-----failure-----			
JM26	-	-	217	1.4	0.7	0.003
	800	1	134	1.2	0.6	0.006
		5	124	1.1	0.5	0.007
		1	116	1.1	0.5	0.007
	1000	5	97	0.9	0.7	0.009
JM28	-	-	369	2.4	1.2	0.003
	800	1	170	1.5	0.7	0.01
		5	181	1.5	0.8	0.02
		1	185	1.4	0.7	0.009
	1000	5	142	1.4	0.7	0.011

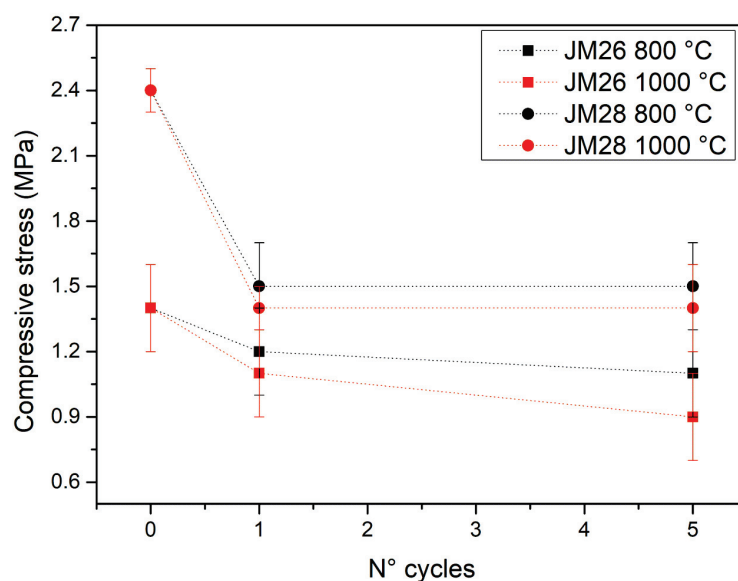


Figure 3. Cold compressive strength (CCS) versus the number of thermal shock cycles.

The linear zone of the compressive stress–strain curves was fitted with A_1 , A_2 , and X_0 parameters, where A_1 is the minimum and A_2 is the maximum value of compressive stress, respectively, and the point $(X_0; A_1 + A_2/2)$ could be assigned to be the limit of a reversible zone of work that the material can withstand without damage. This point could be helpful in the design and selection of materials that will be under thermal and load stress.

In both the JM26 and JM28 materials, the extension X_0 after thermal shock increases by up to three times, which should be attributed to changes in microstructure, since the Al_2O_3 – SiO_2 phase diagram indicates that the mineralogical composition is not altered and remains unchanged at the temperatures used in the thermal shock test [34].

The σ/σ_0 and E/E_0 ratio were plotted for the different TS tests in Figure 4. These ratios allow for estimating, as observed experimentally, the capacity of the material when subjected to a rapid temperature change. As expected, the greater the temperature difference in the test, the greater the loss of strength, indicating that the severity of thermal shock damage in the specimens increases as the quenching temperature difference increases. This was also observed as the number of cycles increased. In general, when comparing the same temperature and an equal number of cycles, JM26 presents higher ratio values for both properties.

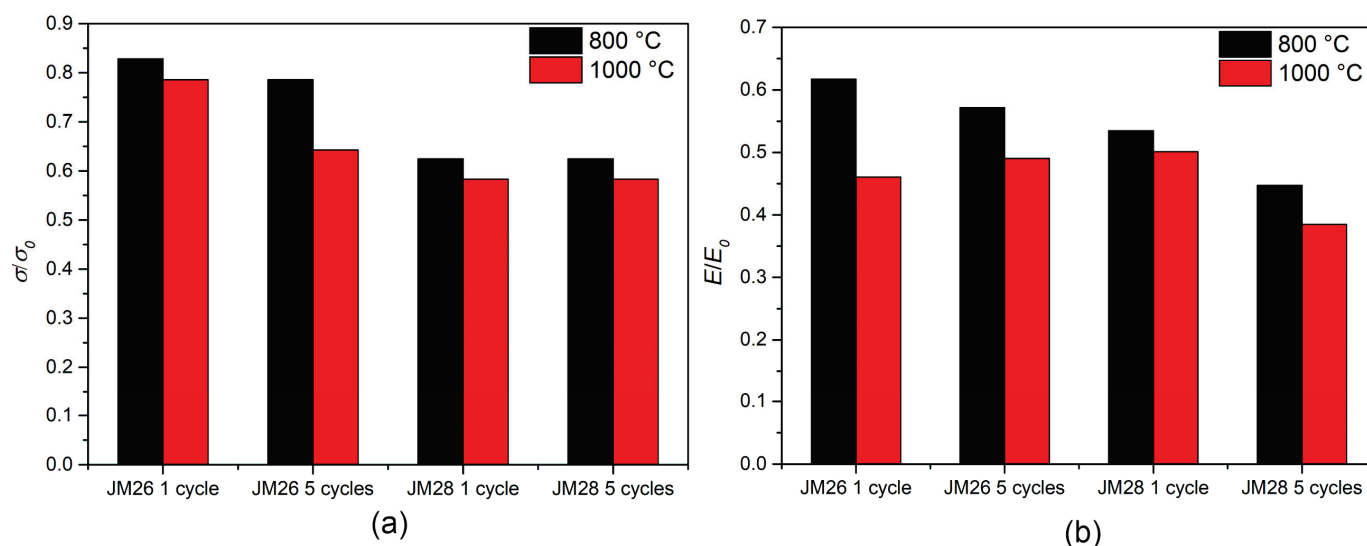


Figure 4. Effect of number of thermal cycling in σ/σ_0 (a) and E/E_0 (b) ratio.

Considering everything described above, it could be concluded that JM26 presents better thermal shock performance. It was observed that this material stabilizes its mechanical behavior after the first thermal shock.

The mercury intrusion porosimetry technique was used to study the pore sizes in the obtained samples before and after TS. Figure 5 presents the open pore size distribution results. For JM26, a bimodal distribution is observed; meanwhile, in JM28, a monomodal distribution is observed. From the comparison between pore distributions, it can be seen that after TS the pore size shifts toward larger values. The cumulative plots allow for determining the diameters d_{10} , d_{50} , and d_{90} , and size span $(d_{90} - d_{10})/d_{50}$, which characterize the distributions. The values are presented in Table 4. Samples after TS present pore sizes around twice or three times higher than before TS, and the size span also increases. This indicates that thermal shock has a significant influence on the microstructure of the material, as was observed in the mechanical behavior (Figure 2). Comparing both samples, JM26 presents lower diameters than JM28. When the heated sample is introduced into water at room temperature, the smaller pores could be useful to keep the structure stable to the stresses generated by the sudden change in temperature plus the violent

evaporation of the water. This phenomenon is clearly observed in Figures 3 and 4, where JM26 presents the lowest decrease in σ after TS and the highest σ/σ_0 and E/E_0 ratios. Clearly, a controlled porosity and microstructure allow for obtaining materials with good thermal stress performance [35].

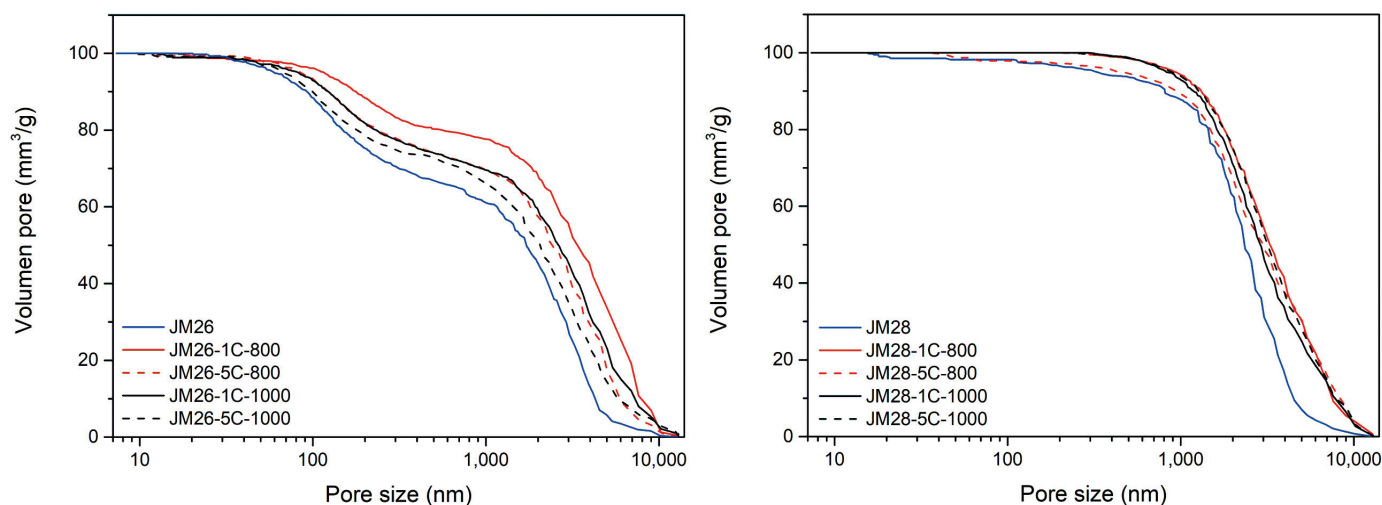


Figure 5. Mercury intrusion porosimetry results for normalized cumulative open pore distribution.

Table 4. Diameters d_{10} , d_{50} , and d_{90} (in μm) and size span.

Material	Temperature ($^{\circ}\text{C}$)	N $^{\circ}$ of Cycles	d_{10} (nm)	d_{50} (nm)	d_{90} (nm)	Size Span
JM26	-	-	4.15	1.72	0.90	2.4
		1	7.62	3.48	0.17	2.1
	800	5	6.05	2.36	0.13	2.5
		1	6.90	2.66	0.12	2.5
		5	5.80	2.06	0.10	2.8
JM28	-	-	4.53	2.36	0.81	1.6
		1	7.60	3.25	1.30	1.9
	800	5	7.61	2.92	0.94	2.3
		1	7.60	2.92	1.16	2.2
		5	7.64	3.05	1.25	2.1

The theoretical TSR parameters R , R''' , and R_{st} were calculated according to Equations (1), (2), and (3), respectively, using the thermal expansion values presented above. The K_{IC} values used were 0.45, 1.2, and 1.2 $\text{MPa mm}^{1/2}$ for JM23, JM26, and JM28, respectively, and the γ_{WOF} values used were 3.9, 14.4, and 16.7 Jm^{-2} for JM23, JM26, and JM28, respectively [21]. The corresponding results are presented in Table 5.

Table 5. Theoretical thermal shock resistance parameters.

	JM23	JM26	JM28
R ($^{\circ}\text{C}$)	1020	1040	930
R''' (mm)	0.3	0.7	0.3
R_{st} ($\text{m}^{1/2} ^{\circ}\text{C}$)	1214	1755	1286

The R parameter expresses the tendency toward crack formation and, therefore, to the loss of strength due to fracture initiation caused by thermal stresses. All the materials present a similar value of R that it is around 1000 $^{\circ}\text{C}$. High values of R can be achieved in materials with a low Young's modulus, low thermal expansion, and high strength, but these properties can lead to very rapid and catastrophic crack propagation due to the

high-level elastic strain energy achieved [36]. Therefore, a high R value does not imply a high resistance to thermal shock [37]. This could be the case for JM23, which presents the lowest values of thermal expansion and Young's modulus, but in the thermal shock test, when the material is put in contact with water at room temperature, it collapses. In addition, considering that good performance of mullite under thermal shock is well known and that JM26 and JM28 have mullite, almost 50 wt. % in contrast with JM23, which contains only 11.4 wt. % (see Table 1), the calculated values of R do not reflect this difference. It could be said that this parameter is not illustrative for these kinds of porous materials, in which microstructure plays an important role.

The R''' parameter gives information on the minimum extent of crack propagation at the initiation of thermal stress fracture, and R_{st} is a parameter of the damage resistance that is proportional to the critical temperature for quasi-static crack propagation [38].

The R''' value for JM26 is almost three times higher than for the other samples, and JM28 and JM23 present equal values. The calculation of this parameter is directly related to fracture toughness and crack growth, so the experimental difference between JM23 and JM28 could be related to the crystalline composition mentioned above.

The values of the R_{st} parameter allow for ordering the materials according to the increased damage resistance: JM26 > JM28 > JM23, corresponding to the observed in the experimental test.

The three parameters suggest that the JM26 specimen displays the greatest resistance to thermal shock damage, a result that corresponds with observations in the experimental tests. Considering the difference between the theoretical results and those observed experimentally, it can be concluded that R_{st} is advisable to use for these types of porous materials.

4. Conclusions

In this study, the thermal shock resistance of three commercial insulating refractory materials was investigated using destructive tests. The thermal damage associated with differences in crystalline phases, porosity, and mechanical and fracture properties was analyzed.

The experimental conditions used were severe enough to observe different performances. While one collapsed, the other samples showed a microstructural deterioration, which was indirectly measurable through the changes in the values of the technological properties strongly linked to the microstructure.

Sample JM23 collapsed drastically upon contact with water at room temperature. Sample JM26 presented the best performance after TS, with the highest TSR indexes. Moreover, it was observed that JM26, after the first cycle of thermal shock, stabilized its mechanical behavior.

Some changes in microstructure occur after TS, as was observed through the increase in pore size in JM26 and JM28, JM26 being the one with smaller pores. Considering that both materials present similar mineralogical composition and total porosity, it can be stated that microstructure has a direct relationship with thermal shock resistance. These results indicate that control of porosity, and thus microstructure, is a key factor in improving the thermal performance and durability of insulating refractory materials for high-temperature applications.

In addition, different theoretical thermal shock resistance parameters were analyzed (R , R''' , and R_{st}). From the comparison of the theoretical parameters with the experimental results, it is concluded that the parameter R_{st} is adequate for the composition, and especially the microstructure, of the porous ceramic materials studied in this work.

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Article

Scratch-Induced Wear Behavior of Multi-Component Ultra-High-Temperature Ceramics

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Abstract: Multi-component ultra-high-temperature ceramics (MC-UHTCs) are promising for high-temperature applications due to exceptional thermo-mechanical properties, yet their wear characteristics remain unexplored. Herein, the wear behavior of binary (Ta, Nb)C, ternary (Ta, Nb, Hf)C, and quaternary (Ta, Nb, Hf, Ti)C UHTCs synthesized via spark plasma sintering (SPS) is investigated. Gradual addition of equimolar UHTC components improves the wear resistance of MC-UHTCs, respectively, by ~29% in ternary UHTCs and ~49% in quaternary UHTCs when compared to binary UHTCs. Similarly, the penetration depth decreased from 115.14 mm in binary UHTCs to 73.48 mm in ternary UHTCs and 44.41 mm in quaternary UHTCs. This has been attributed to the complete solid solutioning, near-full densification and higher hardness (~up to 30%) in quaternary UHTCs. Analysis of the worn-out surface suggests pull-out, radial, and edge micro-cracking and delamination as the dominant wear mechanisms in binary and ternary UHTCs. However, grain deformation and minor delamination are the dominant wear mechanisms in quaternary UHTCs. This study underscores the potential of MC-UHTCs for tribological applications where material experiences removal and inelastic deformation under high mechanical loading.

Keywords: multi-component ultra-high-temperature ceramics (MC-UHTCs); solid solution; spark plasma sintering (SPS); wear resistance; penetration depth

1. Introduction

Ultra-high-temperature ceramics (UHTCs) have gained significant attention due to their excellent mechanical properties, oxidation resistance, and melting temperatures $> 3000\text{ }^{\circ}\text{C}$ [1]. UHTCs are classified as borides, carbides, and nitrides of transition metal elements from groups IV and V [1,2]. Among them, transition metal carbides such as TaC, NbC, HfC, ZrC, and TiC are widely utilized UHTC carbides known for their outstanding thermo-mechanical properties. The literature on UHTCs and their possible application in nuclear reactors, hypersonic vehicles, and rockets' nose cones to support melting conditions has been studied for decades [1–4]. However, none of the unary UHTC components have been able to accommodate all the demanding requirements of extreme environments. To counter this, one approach is the reinforcement of the second phase, such as Si and carbon-based additives (carbon nanotubes, graphene), in UHTCs to enhance oxidation resistance and fracture toughness [5–8].

Another approach is adapted from the recent development by applying the concept of high-entropy alloys (HEA) to a wide range of ceramics [9–11] such as oxides [12], borides [13–15], carbides [13,14,16], and nitrides [10,17,18]. By employing HEA concepts in UHTCs, high-entropy UHTCs (HE-UHTCs) are obtained by adding equimolar compositions of four or more UHTCs. Because of their mutual solubility [11,19], these materials tend to favor the formation of complete solid-solution single phases. Their mutual solubility does not necessitate the entropy to be “high entropy”; hence, authors are in favor

of referring to HE-UHTCs as multi-component UHTCs (MC-UHTCs) [11]. Even though the entropy remains medium, these materials are characterized by a higher degree of disorder in the atomic level, leading to unique material properties such as high mechanical strength, thermal stability, and resistance to oxidation even at extreme temperatures [11]. MC-UHTCs have garnered significant interest as appealing materials for thermal protection systems (TPSs) in structural components, such as hot structures and pointed leading edges found in re-entry vehicles. These materials have attracted rapid attention due to their impressive attributes, which encompass enhanced mechanical characteristics [6,20], increased fracture toughness [21,22], resistance to creep [23], and low thermal conductivity [24,25]. However, to date, there are only a few studies investigating the wear behavior of MC-UHTCs [26–29].

Predicting the safe service life of engineering components requires accounting for wear from dynamic loads caused by atmospheric debris. Micro-particles in the atmosphere can cause plastic deformation of UHTCs [30]. Therefore, studying the abrasion resistance and damage behavior of MC-UHTCs is essential. The micro-scratch test has been widely recognized as a reliable alternative to conventional wear tests, especially for hard ceramics [31–33]. Sun et al. [26] achieved a uniform composition in (Hf–Mo–Nb–Ta–Ti)C ceramics via SPS, reporting outstanding wear resistance due to a synergistic effect of tribo-film formation and enhanced mechanical properties. Dusza et al. [29] developed (Hf–Zr–Ta–Nb–Ti)C high-entropy carbide with high density. These materials displayed high hardness and good tribological properties, primarily attributed to mechanical wear with limited grain pullout and localized tribolayer formation.

Recently, authors have reported the processing, mechanical, and oxidation behavior of binary (Ta, Nb)C, ternary (Ta, Nb, Hf)C, and quaternary (Ta, Nb, Hf, Ti)C UHTCs processed via SPS [34–36]; therefore, it is imperative to look into the wear behavior of these materials. This study reveals that MC-UHTCs (ternary and quaternary) have remarkable thermo-mechanical properties compared to unary and binary UHTC. The results showed that the mechanical properties improved considerably up to 72% for quaternary UHTCs. Moreover, the oxidation rate for binary UHTCs was 0.97 mm/s, while it was negligible in MC-UHTCs, attributed to mixed complex oxide-phase formation with $\text{Hf}_6\text{Ta}_2\text{O}_{17}$ as a major phase in the MC-UHTC system [34,35]. Herein, scratch-induced tribological characteristics and wear mechanisms of these materials are investigated. An effort is made to establish a correlation between the microstructure and mechanical and wear properties with the gradual addition of UHTC components in MC-UHTCs.

2. Materials and Methods

2.1. Solid-Solution Synthesis of MC-UHTCs

The starting materials employed in this study included commercially available UHTC powders. These powders consisted of a binary system; (Ta, Nb)C (a pre-allowed powder of 20 wt.% NbC, 80 wt.% TaC with a particle size of $\sim 0.80\ \mu\text{m}$; Inframat Advanced Materials, LLC, Manchester, CT, USA) was procured. Additionally, unary UHTC powders of HfC ($>99.5\%$ purity, particle size $\sim 0.33\ \mu\text{m}$; Materion LLC, Cleveland, OH, USA) and TiC ($>99.9\%$ purity, particle size $< 3\ \mu\text{m}$, Inframat Advanced Materials, LLC) were procured. For ternary and quaternary UHTC systems, an equimolar concentration of each powder was utilized. The powder mixtures were ball-milled (Across International LLC, Livingston, NJ, USA) in a WC jar using WC balls (6 mm diameter) with a ball-to-powder weight ratio of 1:3 for 60 min. Further, the composite powders were consolidated using the spark plasma sintering (SPS, Model 104; Thermal Technologies, Santa Rosa, CA, USA) process with a heating rate of $100\ ^\circ\text{C}/\text{min}$ at $1850\ ^\circ\text{C}$ and 60 MPa for 10 min. Post sintering, a single solid-solution phase was achieved, with a relative densification of $\sim 86\%$ for binary UHTC and $\sim 100\%$ for ternary and quaternary UHTCs. Information regarding the initial powders, ball-milled powders, sintering processes, and their thermo-mechanical properties can be referenced in the authors' recent publications [34–36].

2.2. Scratch Testing and Characterization of Worn Surface

SPS pellets were sectioned using a high-speed saw (Techcut 5X precision, Allied High-Tech Products, Inc., Compton, CA, USA). After mounting, the samples underwent a grinding process using diamond grit until a surface roughness of up to 6 μm was achieved. Subsequently, cloth polishing was employed with alumina suspension to attain a surface finish of $\leq 1 \mu\text{m}$. The scratch tests were performed using a micro-scratch tester (Revtest scratch tester RST³, Anton Paar, Inc. Houston, TX, USA) with a Rockwell indenter (tip radius: 50 μm) under progressive load conditions. The load varied from 1 N to 50 N with a speed of 2 mm/min and a scratch length of 3 mm. During the test, data on acoustic emission (AE), coefficient of friction (CoF), penetration depth, and residual depths were recorded. Moreover, it generates a panoramic image of the scratch using its integrated optical microscope. Three scratches were made on each sample and the scratch paths were analyzed using FESEM (FESEM, JEOL-F100 FESEM JEOL Ltd., Akishima, Tokyo, Japan) to gain insights into the positions of cracks, delamination, and the various types of deformation that occurred on the samples during the scratching process. Optical profilometry (Nanovea, Irvine, CA, USA) was utilized to assess the surface roughness and wear track profile of the tested samples. To calculate the wear volume of the scratches, the top-view scratch image obtained from optical profilometry was analyzed using Mountains Lab Premium 10 software (Digital Surf, Besancon, France).

3. Results and Discussion

3.1. Microstructural Analysis of MC-UHTCs

The typical fractured microstructure and corresponding elemental composition of the investigated MC-UHTC samples are illustrated in Figure 1 via EDS spectra. The porosity observed in the microstructure aligns well with the densification values, being ~86% for binary (Figure 1a; Table 1) and ~100% for ternary and quaternary UHTCs (Figure 1b,c; Table 1). Consistent with the previous finding [34], segregation of HfC particles is evident in the fractured micrograph of ternary UHTCs (Figure 1b). It is important to mention here that binary and ternary UHTCs have segregation of secondary phases of NbC and HfC, while the quaternary UHTC showed complete single solid-solution phase formation, revealed from the high-resolution microscopy [36]. The presence of closely spaced intense slip lines is evident in ternary and quaternary UHTCs. These slip lines in UHTCs and MC-UHTCs are associated with a material's ability to resist deformation under higher loading conditions [37].

Table 1. Relative densification, elastic modulus, hardness, CoF, and maximum penetration depth of binary, ternary and quaternary UHTCs.

Samples	Densification (%) [34]	Elastic modulus, E (GPa) [34]	Hardness, H (GPa) [34]	CoF	Max. Penetration Depth (μm)
Binary	84	307.52 ± 36.07	15.23 ± 4.51	0.741–0.198	115.14 ± 5.23
Ternary	100	403.66 ± 9.93	33.67 ± 1.69	0.635–0.155	73.48 ± 6.02
Quaternary	100	381.16 ± 9.82	34.82 ± 2.27	0.615–0.113	44.41 ± 4.82

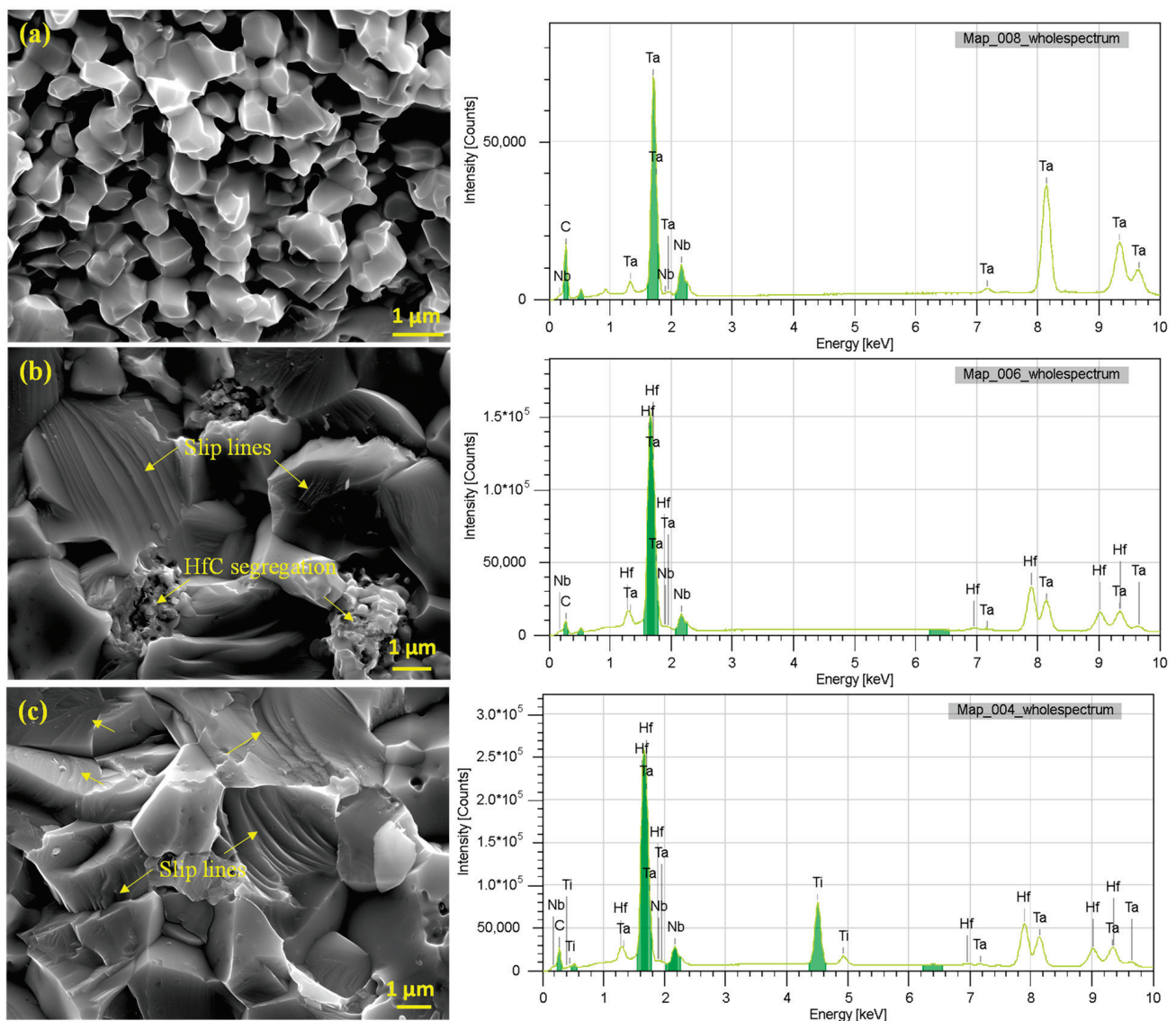


Figure 1. Fractured micrographs and corresponding EDS spectra showing the elemental composition of (a) binary, (b) ternary, and (c) quaternary UHTCs.

3.2. Wear Behavior of MC-UHTCs

The scratch-induced wear behavior test under progressive loading from 1 N to 50 N was conducted on the polished surfaces of binary, ternary and quaternary UHTCs. Figure 2 shows the variation in the coefficient of friction (CoF) and penetration depth with scratch distance in MC-UHTCs. Both CoF and penetration depth were found to increase with the progressive loading in all the samples. Table 1 shows the comparative densification, mechanical properties and wear parameters of binary, ternary and quaternary UHTCs. Based on the three tests carried out on these samples, the average CoFs (Figure 2a, Table 1) for binary, ternary and quaternary UHTCs are 0.43, 0.41, and 0.34, respectively. Similarly, the penetration depth decreased from ~115.14 mm in binary to 73.48 mm in ternary and 44.41 mm in quaternary UHTCs. The decreasing trend in CoF as well as the penetration depth has been attributed to the reduction in deformation under the applied load elicited from the higher densification and hardness in quaternary UHTCs (see Table 1) [34].

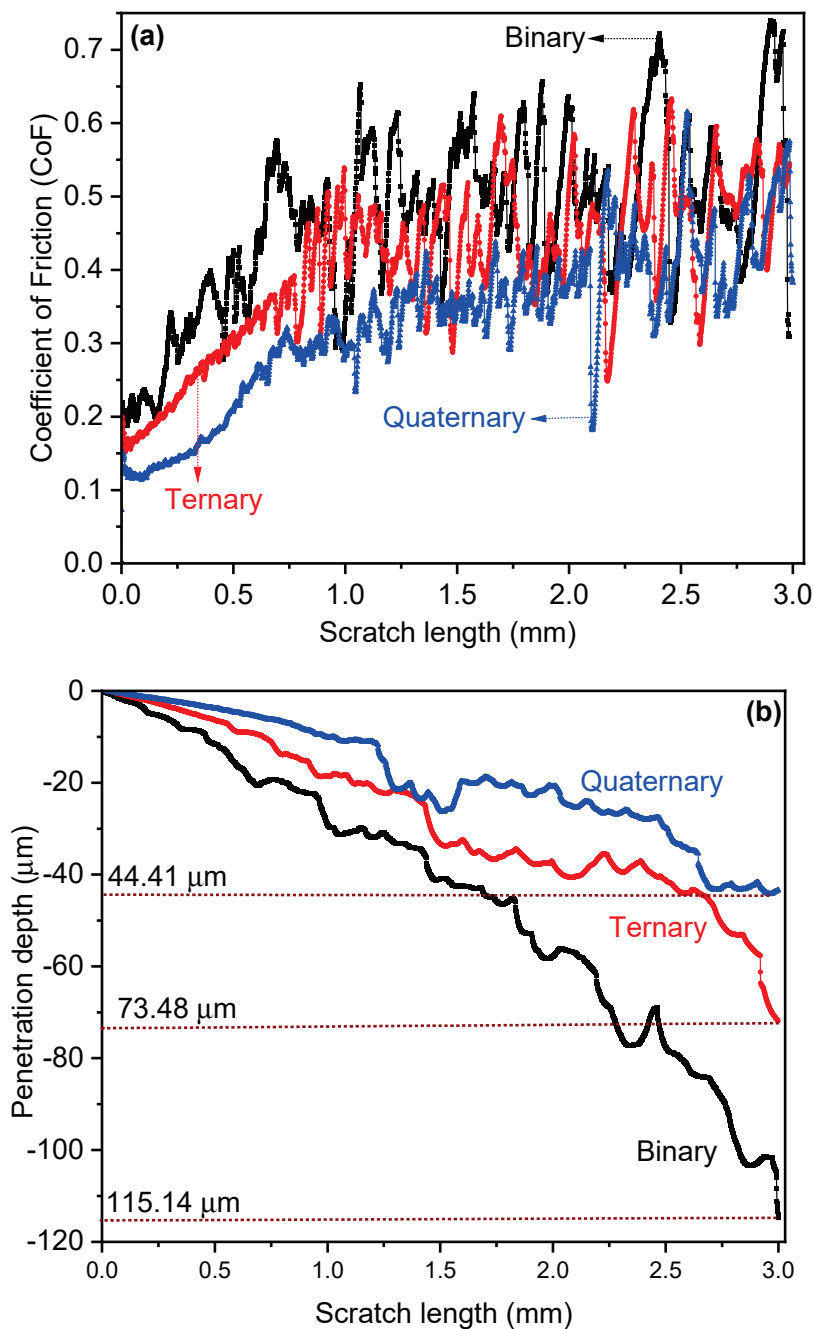


Figure 2. (a) Coefficient of friction (CoF) and (b) penetration depth of binary, ternary and quaternary UHTCs measured during progressive scratch testing (load variation: 1 N to 50 N; scratch length: 3 mm).

The typical aspect of the scratch-induced deformation is revealed from the superimposed SEM image, optical profilometry and acoustic emission (AE) data of 3 mm scratching in MC-UHTCs, shown in Figure 3. It is to be noted here that the overall scratch track shows deeper grooves in binary UHTCs followed by ternary and quaternary UHTCs, as seen from the SEM images in Figure 3. The perturbations in the AE plot, similar to the CoF and penetration depth plots, are attributed to the interaction of the tip with the porosity, pile-ups and with scratch-induced deformation in the material. Based on the depths seen in the optical profilometry (color-coded as light-green, turquoise, blue and darker blue regions), four critical loads at which events such as cracking, chipping, propagation and fracture occur in the samples are compared in Table 2. The load at which cracking initiates

(F_{c1}) increased from 6.9 N (in binary) to 10.4 N (in ternary) and 18.5 N (in quaternary). Similarly, the loads at which cracking propagates (F_{c2}) increased from 17.6 N (in binary) to 25.3 N (in ternary) and 37.9 N (in quaternary). Finally, the fracture (F_{c3}) begins at 28.6 N in binary UHTCs, 43.6 N in ternary UHTCs and 48.1 N in quaternary UHTCs. It is to be noted that binary and ternary samples showed more fracture (F_{c4}) along the progressive scratch length, respectively, at 46.5 N and 47.3 N based on the mapped optical profilometry and AE plot. The typical scratch width at the maximum loading (50 N) decreased from 354.07 μm in binary UHTCs to 245.78 μm in ternary and 207.12 μm in quaternary UHTCs. The result also suggests a high load-bearing ability of quaternary UHTCs compared to binary and ternary UHTCs. This has been attributed to near-full densification, processing-induced complete solid solutioning, and defects such as dislocations, inter-grain twisting and plasticity [36], revealed from high resolution microscopy in quaternary UHTCs. The wear volume arising from the overall scratch track (see Figure 3), presented in Table 2, backs up these findings. The quaternary UHTC, (Ta, Nb, Hf, Ti)C, has least wear volume loss of $3.16 \times 10^{-3} \text{ mm}^3$ calculated for a scratch length of 3 mm and progressive loading ranging from 1 to 50 N. It is to be mentioned here that the wear volume loss for the (HfMoTiWZr)C sample against an Al_2O_3 ball with a sliding speed of 6 mm/s, sliding distance of 200 m and wear track length of 2 mm is $\sim 2.1 \times 10^{-4} \text{ mm}^3$ [27]. Compared to the binary UHTC, an improvement in the wear resistance, respectively, by 29% and 49% is observed for ternary and quaternary UHTCs. The improved wear resistance resonates well with the CoF, penetration depth and hardness values. This shows that the addition of components in MC-UHTCs does increase the wear resistance of the material.

Table 2. Values of critical loads, scratch width and wear volume during the progressive load testing of binary, ternary and quaternary UHTCs.

Samples	Critical Loads (N)				Scratch Width at Max. Load (mm)	Wear Volume ($\times 10^{-3} \text{ mm}^3$)
	F_{c1}	F_{c2}	F_{c3}	F_{c4}		
Binary	6.9	17.6	28.6	46.5	354.07 ± 53.11	6.18 ± 0.91
Ternary	10.4	25.3	43.6	47.3	245.78 ± 62.54	4.38 ± 0.87
Quaternary	18.5	37.9	48.1	N.A.	207.12 ± 28.68	3.16 ± 0.03

Further, the SEM images shown in Figure 4 reveal the damage and failure mechanism in the binary UHTC. Based on the AE data, SEM images at the most critical regions corresponding to binary samples are compared in Figure 4. It is clear from Figure 4b that even under a lower loading condition in the binary sample, debris and grain deformation are seen. As the load progresses, the severe crack networking (Figure 4c,e), fracture grains and delamination are noted (Figure 4d,e). Moreover, critical damage is attributed to the edge and radial cracking observed in Figure 4c,e. This is due to the progressive increase in tangential stress. Heightened localized stress concentration induces a decrease in the systems' energy by instigating the formation and propagation of micro-cracks and radial cracks.

Similarly, the damage and failure mechanism in the ternary UHTC can be understood from the SEM micrographs shown in Figure 5. Under lower loading conditions in the ternary UHTC, grain pull-out/deformation and lateral micro-cracking along with unaffected regions are seen in Figure 5b (marked region in Figure 5a). As the load progresses, the cracking at the scratch edge progresses (marked in Figure 5a) along with grain deformation, as well as some fracture and delamination (Figure 5c,d). It is important to highlight that at higher loads, evidence of unaffected areas is seen (Figure 5c,d), in contrast to the binary UHTC. This remarks the improvement in wear resistance from binary to ternary UHTCs. The presence of slip lines near the fractured region in Figure 5e elicits the superior resistance against applied load during scratch testing when compared with the binary UHTC. Such microscopic slip lines indicate the occurrence of dislocation-induced plastic deformation and dislocation mobility at room temperature [37]. This has also been

evidenced by the high load indentation and flexural strength behavior of ternary UHTCs reported elsewhere [34,36].

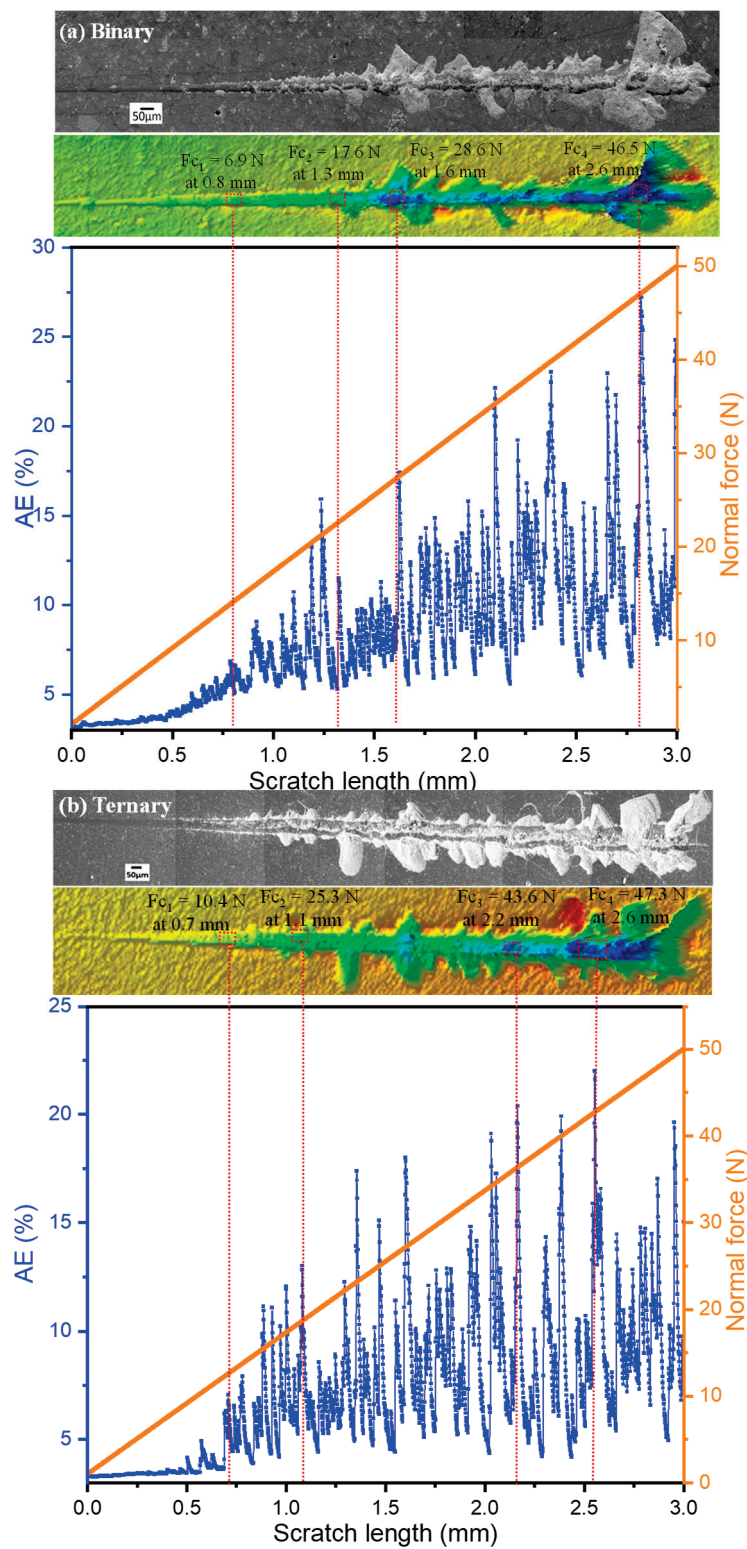


Figure 3. Cont.

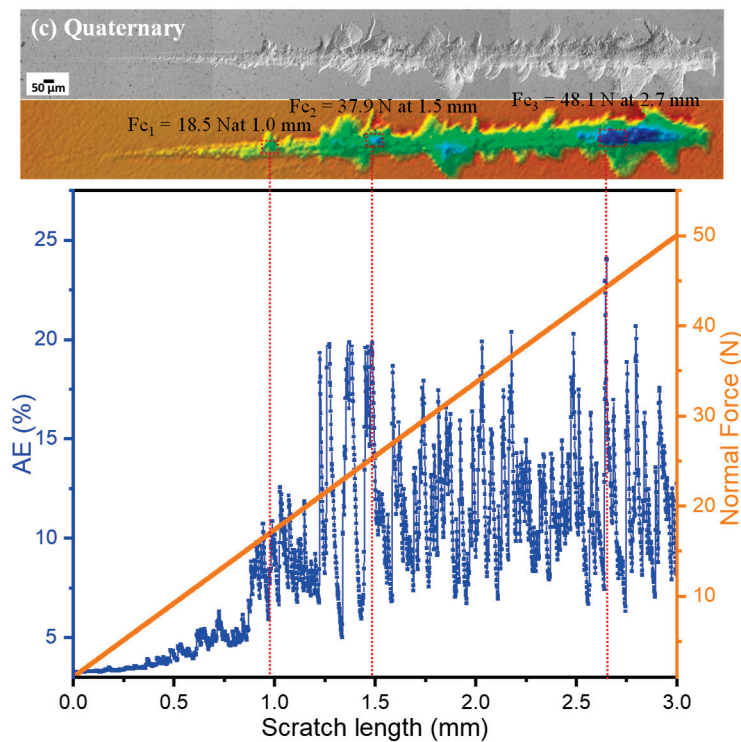


Figure 3. Superimposed SEM, profilometry images and AE data obtained during the scratch testing of (a) binary, (b) ternary, and (c) quaternary UHTCs.

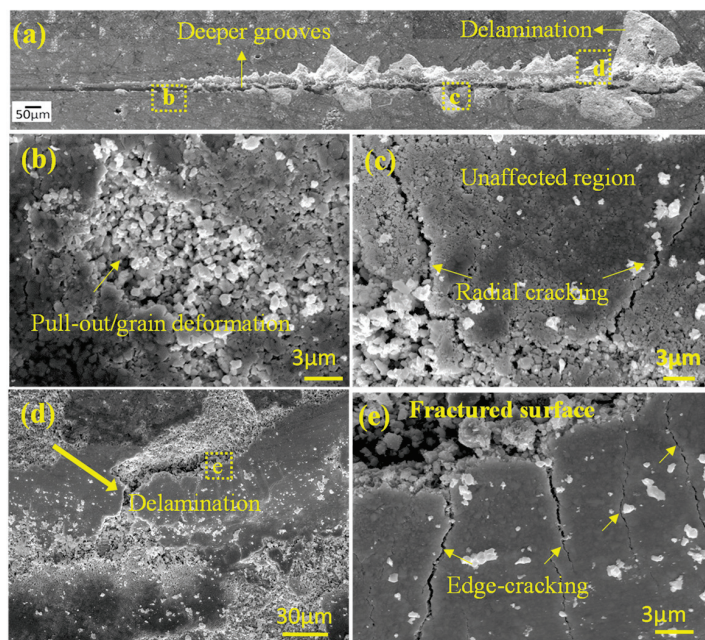


Figure 4. SEM micrographs of the (a) 3 mm progressive scratch track and (b–e) high magnification of the selected regions eliciting wear behavior in binary UHTCs.

Lastly, the SEM images eliciting the deformation in the quaternary UHTC during progressive scratch testing are presented in Figure 6. At lower load, most of the regions are unaffected (by the indenter during scratch loading) along with minor pull-out grain deformation; see Figure 6b. Comparing all the samples microstructurally, the presence of unaffected regions is most notable in the quaternary UHTC. As the load progressively increases in Figure 6c, grain deformation and pull-out increase. Even at the higher loading,

no micro-cracking was noticed, while most of the regions in the sample are unaffected (marked as dotted island area). This shows the improved wear resistance of the quaternary sample, attributed to its high hardness of 44.82 GPa (see Table 1). Under maximum loading conditions, some minor delamination, cracking, and pull-out are evident in Figure 6d. In quaternary UHTCs, the presence of multiple closely spaced slip lines (Figure 6e) is evident at several places throughout the progressive loading. This further confirms the ability of quaternary UHTCs to undergo plastic deformation, improving their wear resistance over binary and ternary UHTCs. In summary, pull-out, radial, and edge micro-cracking and delamination are the dominant wear mechanisms in binary and ternary UHTCs. However, in a quaternary system, grain deformation and minor delamination are the dominant wear mechanisms.

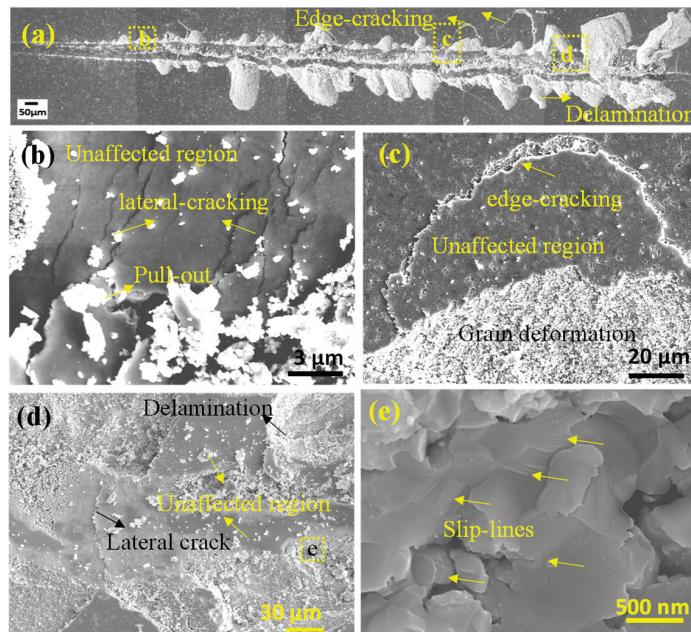


Figure 5. SEM micrographs of the (a) 3 mm progressive scratch track and (b–e) high magnification of the selected regions eliciting wear behavior in ternary UHTCs.

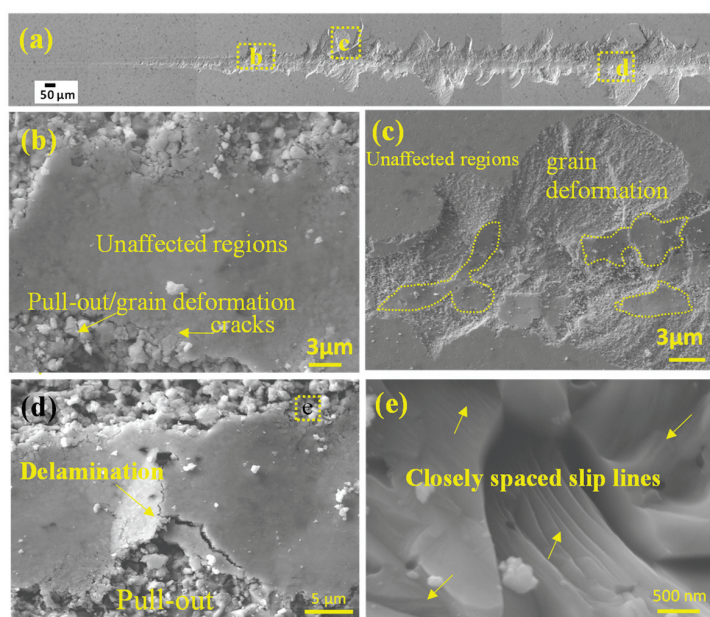


Figure 6. SEM micrographs of the (a) 3 mm progressive scratch track and (b–e) high magnification of the selected regions eliciting wear behavior in quaternary UHTCs.

4. Conclusions

The scratch-induced wear behavior of binary, ternary and quaternary UHTCs has been evaluated under progressive loading of 1 N to 50 N with a scratch length of 3 mm. The average CoFs for binary, ternary and quaternary UHTCs are 0.43, 0.41, and 0.34, respectively. Similarly, the penetration depth and wear volume decreased from ~115.14 mm and $\sim 6.18 \times 10^{-3} \text{ mm}^3$ in binary UHTCs to ~73.48 mm and $\sim 4.38 \times 10^{-3} \text{ mm}^3$ in ternary UHTCs and ~44.41 mm and $\sim 3.16 \times 10^{-3} \text{ mm}^3$ in quaternary UHTCs. This has been attributed to the reduction in deformation under the applied load elicited from the nearly full densification, higher hardness and complete solid-solution formation in the quaternary UHTC. The scratch width at the maximum loading (50 N) decreased from 354.07 μm in the binary UHTC to 245.78 μm in the ternary UHTC and 207.12 μm in quaternary UHTC; the microstructures support this assertion. Based on the AE plot, the critical loads at which cracking, propagation and fracture initiate increased from 6.9 N, 17.6 N and 28.6 N in binary UHTCs to 10.4 N, 25.3 N and 43.6 N in ternary UHTCs and 18.5 N, 37.9 N and 48.1 N in quaternary UHTCs, respectively. Microstructural analysis of the worn-out surface elicits the dominant wear mechanisms to be pull-out, radial and edge micro-cracking, and delamination in binary and ternary UHTCs. However, grain deformation and minor delamination are the dominant wear mechanisms in quaternary UHTCs. Thus, the addition of components in UHTCs, forming a multiple-component system, has been shown to significantly improve the wear resistance of quaternary UHTCs, making them viable candidates for applications where materials undergo inelastic deformation.

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Article

Evaluation of the Mechanical Properties and Fatigue Resistance of the $\text{ZrO}_2\text{CeYAl}_2\text{O}_3$ Composite

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Abstract: This work aimed to evaluate the fatigue limit of the zirconia ceramic composite stabilized with yttria and ceria reinforced with alumina platelets ($\text{ZrO}_2\text{CeYAl}_2\text{O}_3$) and characterize the mechanical properties of sintered specimens. Bar-shaped specimens were compacted by uniaxial pressing in a rigid die and sintered at 1500 °C-2 h. Subsequent characterizations included quantitative phase analysis by X-ray diffractometry, determination of density, modulus of elasticity, microhardness, fracture toughness, four-point flexural strength, and fatigue limit. Observations of fracture mechanisms were carried out using confocal and scanning electron microscopy (SEM). The sintered samples presented values above 98% of relative density. Complex microstructures with equiaxed, homogeneously distributed submicrometer grains and planar alumina platelets were observed by SEM. The composite samples showed high values of fracture toughness due to the transformation, during the test, from the tetragonal to monoclinic phase, causing an increase in volume and creating compression zones around the crack, making it difficult to propagate. The average flexural strength reached 445.55 MPa, with a Weibull modulus ($m = 16.8$), revealing low flexural rupture stress data dispersion. In the composite evaluated in this work, the occurrence of the tetragonal $\rightarrow$ monoclinic transformation that occurs in the Ce-TZP present at the triple points and grain boundaries during cyclic loading produces “crack tip shielding”, that is, a restricted elastic zone (zone shielding) that surrounds the crack tip. This phenomenon leads to a reduction in the stress intensity factor at the tip of the crack and slows down its growth, generating an increase in the fatigue resistance of the composite.

Keywords: ceramic composites; zirconia-ceria; alumina platelets; fatigue behavior; characterizations

1. Introduction

Biomaterials are used in dental and orthopedic implants, sutures, blood vessel prostheses, artificial organs, and pacemakers. They are generally defined as natural or synthetic substances designed for introduction into living tissue as part of a medical device in human or veterinary medicine [1]. Throughout the history of implantology, several materials have been tested for successful oral rehabilitation. The aim was to verify which of them presented biocompatibility and better osseointegration. Titanium is the most used material in the manufacture of dental implants due to its physical and biological properties [2,3]. Ceramic implants have become an object of study in recent years, mainly due to aesthetics [3]. Studies have shown that groups of patients presented reactions due to the use of metal, such as sensitivity, allergies, and gingival retraction, with exposure to part of the implant, which motivates the search for new bioinert materials, such as structural ceramics. Recently, yttria-stabilized zirconia ceramic ($\text{ZrO}_2\text{-Y}_2\text{O}_3$) has found application in prosthetic dentistry for manufacturing dental prostheses (crowns, bridges, and abutment-based implants). The material has good mechanical properties, biocompatibility, and a color similar to natural

teeth, making it a possible alternative to titanium implants. However, studies [4,5] have shown that tetragonal zirconia stabilized with 3 mol.% Y_2O_3 presents a worrying long-term hydrothermal degradation that may reduce its mechanical resistance, compromising its reliability when used in dental implants.

Ceramic composites are promising in applications that require hardness, biocompatibility, corrosion resistance, mechanical strength, fracture toughness, and fatigue resistance. Ceramics based on $ZrO_2CeYAl_2O_3$ are strong candidates for use as a dental material as they are more resistant to degradation at low temperatures [6], and therefore, studies focused on evaluating their mechanical properties are welcome.

Hasegawa [7] investigated the microstructural properties and flexural strength of yttrium oxide stabilized polycrystalline tetragonal zirconia (Y-TZP) samples. Zirconia powder was used. The results indicated flexural strength values for groups (T1, T2, and T3) of, respectively, 239.9 MPa, 308.1 MPa, and 285.7 MPa. The effect of adding tetragonal zirconia stabilized with ceria (Ce-TZP) on the fatigue behavior of alumina-based ceramic composites was studied by Coutinho et al. [8]. The results showed a reduction of fatigue resistance with (Ce, Y)-TZP/ Al_2O_3 powder addition. Garvie et al. [9] investigated the influence of Al_2O_3 addition and sintering parameters on the mechanical properties and cytotoxicity of tetragonal ZrO_2 containing 3 mol% Y_2O_3 (3Y-TZP). Hardness values were situated between 13.40 and 15.85 GPa according to the amount of Al_2O_3 in the ZrO_2 matrix, and fracture toughness results of approximately $7 \text{ MPa}\cdot\text{m}^{\frac{1}{2}}$ were observed for all compositions. The study in question demonstrated the non-cytotoxic behavior, reinforcing that ceramic composites are suitable biomaterials for applications in dental implants. Attaoui et al. [10] evaluated the influence of phase transformation on the growth of static and cyclic fatigue cracks in zirconia ceramics partially stabilized with ceria (Ce-TZP). Scanning electron microscopy observations of the path followed by the crack led to the conclusion that the phase transformation induced two mechanisms: (I) a crack-bridging mechanism by transformed monoclinic grains and (II) crack branching operating within a large zone in the presence of autocatalytic transformation. Tovar-Vargas et al. [11] developed ceria-stabilized zirconia-based composites to obtain ceramic materials with enhanced hardness, strength, fracture toughness, and resistance to low-temperature degradation. These composites were based on ceria-calcia stabilized zirconia (10 mol% CeO_2 -1 mol% CaO -TZP) and α -alumina (0–15 wt.%) as a second phase. Compared to the strength and hardness of 10Ce-TZP ceramics, an increase was observed for all compositions.

In recent years, a new commercial ceramic system composed of monoclinic zirconia (ZrO_2), yttria (Y_2O_3), and ceria (CeO_2) reinforced with alumina (Al_2O_3) was developed, aiming to obtain, after sintering, a zirconia tetragonal matrix composite containing alumina grains and platelets. This complex microstructural condition and the high sinterability of the material enable its use in structural applications, where there is a requirement for the association between high hydrothermal degradation resistance and mechanical resistance, guaranteeing high reliability in its use. Based on its potential for use in biomedical applications, studies were carried out to understand the mechanical behavior (hardness, fracture toughness, and flexural strength) as a function of surface roughness before and after aging tests by hydrothermal degradation [12]. Other works aimed at the preliminary biological assessment of cytotoxicity and cell growth [13], numerical finite element simulations of mechanical behavior in biaxial bending tests, and implant geometries [14,15]. All results have shown that using this material as a dental implant is promising. However, there is a gap regarding cyclic mechanical efforts that would simulate fatigue conditions and the understanding of how this complex microstructure can affect the mechanical behavior of the material in future applications in the medical and dental area. Despite the variety of studies contemplating the fatigue resistance of Y-TZP ceramics, most of which use three-point bending or biaxial bending tests, there are no studies that investigate the fatigue resistance of composites ($ZrO_2CeYAl_2O_3$), which present a complex microstructure composed of alumina platelets dispersed in a zirconia matrix, specifically using four-point bending tests, a technique that presents greater reliability than other conventional bending tests. It is

important to predict the fatigue behavior of the material by simulating the chewing process and producing results from cyclic tests of ceramic materials.

This work aims to evaluate the four-point bending fatigue limit and the mechanical properties of the zirconia composite doped with yttria and ceria, reinforced with alumina platelets. Dental and orthopedic implants must meet biological, aesthetic, and functional requirements. Adequate mechanical properties are important design criteria for biomaterials for use in implantology.

2. Materials and Methods

2.1. Ceramic Powder Processing

The present study used zirconia composite powder stabilized with yttria and ceria and reinforced with alumina platelets ($\text{ZrO}_2\text{CeYAl}_2\text{O}_3$) from Intense, Saint Gobain, France. The test specimens were produced using fine powders with high homogeneity, allowing a reduction in residual porosity and maximum densification during sintering. The powder was weighed on a SHIMADZU AUY220 digital scale from the Shimadzu Corporation, Kyoto, Japan, with an accuracy of 1.0×10^{-4} g.

Before the sintering stage, uniaxial cold pressing was carried out to manufacture the green body. The rigid matrix was cleaned with ethyl alcohol and lubricated to reduce the effects of powder friction on the matrix. The powders were weighed and deposited in the matrix. For compacting $\text{ZrO}_2\text{CeYAl}_2\text{O}_3$, no binder was used because it is an ultrafine, high-density powder and already contains additives. The material was compacted using a MARCON 10-ton mechanical press from Marcon Indústria Metalúrgica Ltd.a—Marilia, Brazil, with a pressure of 100 MPa for 60 s.

Sintering was carried out in a Nabertherm P310 furnace, from Nabertherm GmbH—Lilienthal, Germany, at 1500 °C, with an initial heating rate of 10 °C/h, a plateau of 2 h at 500 °C, heating at 1500 °C for 2 h, and cooling to room temperature. After sintering, the specimens were subjected to grinding using water sandpaper of dissimilar grit (400), (600), (800), (1000), and (1200). The sample surfaces were subjected to final polishing with a felt pad and application of 30, 15, 6, and 1 µm diamond paste.

2.2. Characterizations

The apparent density was measured using a SHIMADZU AUY220 (Shimadzu Corporation, Kyoto, Japan), precision electronic scale, applying the Archimedes method according to the recommendations of the ASTM C 373-18 standard [16]. The relative density was calculated by correlating the apparent density with the theoretical density of the sintered composition ($\rho_t \text{ZrO}_2\text{CeYAl}_2\text{O}_3 = 5.40 \text{ g/cm}^3$).

The crystalline phases present were determined in the starting powder, in the sintered specimens, and after the fatigue tests, using the diffractometer MRD—X'Pert Pro—Panalytical, Malvern Panalytical Ltd., Malvern, UK, operating with Co-K α radiation, with 2 θ range between 20° to 80°, an angular pitch of 0.03°, counting time per step of 150 s, power of 40 kV, and current of 40 mA. The crystalline peaks were identified using X'pert-Highscore software V5.2 (Philips, Almelo, The Netherlands) and the database in the ICDS files [17]. The quantification of the crystalline phases was performed using the Rietveld refinement [18] using Pseudo-Voigt curves for peak adjustment in Highscore-Plus software V5.2 [19].

To analyze the microstructure, the surfaces of the sintered specimens were grinded, polished, thermally etched at 1450 °C for 15 min, cooled, and covered with a thin layer of gold using the Leica EM SCD 500 metallizer, Leica Microsystems—Wetzlar, Germany. The microstructures were observed using a JEOL JSM 6610 scanning electron microscope, JEOL Ltd., Akishima, Tokyo, with an acceleration voltage of 30 KV, resolution of 3 nm, magnification of up to 300,000 $\times$, and an energy dispersive spectrometer (EDS). The surfaces of the samples fractured during the cyclic tests were evaluated to identify the failure origin and microstructure.

2.3. Mechanical Properties

Dynamic Modulus of Elasticity: Resonance methods enable the determination of elastic properties in dynamic mode and are based on the principle that a material has well defined resonance frequencies of mechanical vibrations. As a result, elastic properties can be calculated based on a given specimen's geometry, mass, and resonance. The dynamic Young's modulus is calculated using the resonance frequency in the bending or longitudinal vibration modes [20,21]. The values of the elastic moduli of the $\text{ZrO}_2\text{CeYAl}_2\text{O}_3$ specimens were calculated through non-destructive acoustic testing. Using the impulse excitation technique, 10 excitation measurements were carried out for each specimen. Using the Sonelastic software V6.0, ATPC Physical Engineering, Sonelastic Division, Ribeirão Preto-São Paulo-Brazil, data on the sample's length, width, thickness, and mass were selected and measured with a caliper and digital scale. The specimen was positioned on a support, and, through the excitation of an electromagnetic pulse, a slight "impact" was delivered to the specimen. The acoustic response was captured by a microphone, using the Sonelastic software V. 6.0, which uses a relationship between the natural frequencies of vibration, dimensions, and mass of the material to determine the elastic modulus of the samples. The ASTM C-1259-21 standard [21] shows that the Young's modulus (E) for test specimens in the shape of rectangular bars can be calculated according to Equation (1).

$$E = 0.9465 \left(\frac{mf_f^2}{b} \right) \left(\frac{L^3}{t^3} \right) T_1 \quad (1)$$

where: E is the Young's Modulus (Pa), b is the width of the bar (mm), m is the mass (g), L is the length (mm), f_f is the fundamental frequency for the bar in flexural mode (Hz), t is the thickness, and T_1 is the correction factor. Cables supported the specimen at a distance of $0.224L$ from their ends.

Vickers Microhardness: Microhardness was determined by Vickers microhardness tests using a diamond indenter. The surfaces of the specimens were grinded and polished to obtain a scratch-free finish. Twenty impressions were made on the surface of each sample and a load of 2 kgf (HV2) was applied for 10 s. The tests were carried out with an Emco Test DuraScan 20 microhardness meter from Zwick GmbH & Co. KG, Ulm, Germany. After measuring the indentation diagonals, Equation (2) was used to determine the Vickers microhardness.

$$HV = \frac{0.0018544 \times F}{d^2} \quad (2)$$

where HV is the microhardness (GPa), F is the load applied in (N), and d is the arithmetic mean of the length of the two diagonals (mm).

Fracture Toughness: The method for determining fracture toughness (K_{IC}) by Vickers indentation is a simple and widely used technique based on the fact that there is a correlation between the K_{IC} value of the material and the lengths of the cracks generated in the microhardness tests. The correlation depends on the load applied to the pyramidal indenter and the material's modulus of elasticity. After the Vickers microhardness test, the samples were analyzed using a confocal laser microscope. Measurements on the cracks at the vertices of the pyramidal indentations allowed the determination of fracture toughness in ceramics by ASTM C-1421-18 [22].

Half-penny cracks were identified in the composite samples with a c/a ratio greater than 2.5 [23]. Equation (3) was used to calculate the fracture toughness of the composite samples.

$$K_{IC} = 0.084 \left(\frac{E}{H} \right)^{\frac{2}{5}} \frac{P}{a l^{\frac{1}{2}}} \quad (3)$$

where E is the modulus of elasticity (GPa), H is the microhardness (GPa), a is the Vickers indentation semi-diagonal (m), l is the crack length (m), and P is the applied load (N).

Four-point Bending Test: The dimensions of the test specimens (polished rectangular section bars with 45 mm × 5 mm × 5 mm) complied with the standard ASTM C-1161-18 [24] that establishes a test method to obtain the flexural strength of advanced ceramics at room temperature. Four-point bending covers a larger volume of the tested specimen, which is placed under a more uniform tension when compared to three-point bending. A constant region of bending moment is obtained between the two internal load points. On the convex surface of the beam, where there is maximum stress, the material is in a state of pure stress, so failure is caused by the action of just one principal stress [25]. The test variables are size, sample length, environmental, and loading conditions [26]. The tests were carried out on an MTS LandMark 647 system Corporation universal testing machine, Eden Prairie, MN, USA, with a 5 kN load cell, following ASTM D-790-03 [27] and ASTM C-1161-18 [24] guidelines. Samples were selected by visual inspection using a magnifying glass at 10× to rule out superficial damage caused by manufacturing. After the samples ruptured in the flexural test, a fractographic analysis was carried out to characterize the fractures' types, locations, sizes, and origins. Twenty-one specimens were used in the tests, and the load was applied up to the resistance limit of the material. The calculations for determining the bending stress are described by Equation (4).

$$\sigma = \frac{3 F l}{4 b d^2} \quad (4)$$

where σ is the bending stress, F is the breaking load (N), l is the distance between the supports (mm), b is the width of the specimen (mm), and d is the thickness of the specimen (mm).

Weibull Distribution: The Weibull parameter is used because ceramic materials present high dispersion in mechanical resistance results. Fracture statistics are based on the weakest link criterion. Critical failures occur in regions of maximum mechanical stress due to unstable crack propagation from the largest defect, requiring an analysis that allows good agreement and reliability with experimental data. The statistical analysis of the distribution of flexural strength values was carried out using the Weibull distribution and following ASTM C-1239-13 [28]. For the parameters $\alpha > 0$ and $\beta > 0$, the distribution function is represented by an exponential distribution (expression (5)) for the 2-valued parameter.

$$F(x) = \begin{cases} 1 - e^{-\left(\frac{x-x_0}{x_0}\right)^m}, & x \geq 0 \\ 0, & x \leq 0 \end{cases} \quad (5)$$

where the parameters x and m represent the scale and location parameters (also called Weibull modulus). The value of m is dimensionless and informs the material's homogeneity, reliability, and quality. The higher the (m) , the smaller the dispersion of the material's mechanical resistance data. It is taken into account that minimum life is assumed with the value of $x_0 = 0$, that is, it is assumed that there is always a possibility of failure, no matter how low the stress. Rearranging and applying the logarithm to both sides of expression (5), we have:

$$\ln \left[\ln \left(\frac{1}{1 - F(x)} \right) \right] = m \ln(x) - m \ln(x_0) \quad (6)$$

The m and x parameters can be determined by applying linear regression to expression (6).

Kolmogorov–Smirnov Test: To analyze whether the Weibull distribution applied to the breaking strength values of the ceramic samples will have a normal data distribution, a non-parametric or free distribution test called the Kolmogorov–Smirnov test (K–S test) was applied. An empirical distribution function can be defined as follows:

$$F_n(x) = \frac{i}{n}; x_{(i)} < x < x_{(i+1)} \quad (7)$$

The null hypothesis in the test is represented by H_0 and the alternative by H_1 , described in Equation (8):

$$\begin{cases} H_0 : F(x) = F_0(x) \\ H_1 : F(x) \neq F_0(x) \end{cases} \quad (8)$$

The Kolmogorov–Smirnov test is based on the absolute value of the largest difference D between $F_n(x)$ and a cumulative distribution function [29]. The D value is computed in 3 stages. The first is D^+ :

$$D^+ = \max \left[\frac{i}{n} - F_0(x_{(i)}) \right] \quad (9)$$

D^- is defined as:

$$D^- = \max \left[F_0(x_{(i)}) - \frac{(i-1)}{n} \right] \quad (10)$$

The final value of D is:

$$D = \max(D^+, D^-) \quad (11)$$

The test (K–S test) provides the p -value (significance). Based on it, the hypothesis that the errors have a normal distribution is rejected or not. If $p\text{-value} \leq \alpha$, the null hypothesis in the test is rejected. If $p\text{-value} > \alpha$, the evaluated data are accepted for a normal distribution:

Statistical Analysis: To ensure the differences observed in the values of repeated tests, the Student's t hypothesis test was used, guaranteeing confidence in the results above the value for the chosen fatigue limit. A confidence level of 90% is used for the sample mean and the standard deviation of n samples. Equation (12) can be used to calculate the lower confidence limit.

$$S_{aX\%} = S_{\text{med}} - t_{a,n-1} \cdot \frac{s}{\sqrt{n}} \quad (12)$$

where S_{med} is the average stress, $t_{a,n-1}$ is the value of the t distribution for $(1 - a)$, s is the standard deviation, and n is the number of data. The average fatigue limit found can be used to reduce the fatigue limit, in which the failure probability limits are taken into account. The chi-square test guarantees the confidence interval for the standard deviation. It is used to ensure that the standard deviations for repeated testing are below an upper limit obtained from the fatigue test standard deviation results with a confidence level. A confidence interval for the standard deviation can be calculated by using Equation (13):

$$S_{X\%} = \sqrt{\frac{n-1}{x^2_{\alpha,n-1}}} \times s \quad (13)$$

where $s_{X\%}$ is the confidence interval for the standard deviation, x^2_{α} and $n-1$ are the tabulated chi-square values, s is the standard deviation, and n is the number of data.

3. Results and Discussion

3.1. Characterization of the Starting Powder and Sintered Samples

Figure 1 presents XRD patterns of raw material. Analyzing the diffractograms of the starting powder, it can be identified by using the Rietveld refinement ($\chi^2 = 1.14$) that the raw material used in this work is composed of 64.5% ZrO_2 -monoclinic, a small portion of ZrO_2 -tetragonal (1.9%), 23.8% Al_2O_3 , and 9.8% CeO_2 . The addition of CeO_2 aims at complete stabilization of the ZrO_2 -tetragonal phase from the ZrO_2 -monoclinic portion after sintering.

The peaks in Figure 2a for the sintered samples show effective sintering at a temperature of 1550 °C-2 h, observing the presence of retained tetragonal zirconia. Most of the peaks occupy positions related to the tetragonal phase, indicating that the monoclinic ZrO₂ phase has been transformed. The only phases present in the material are Al₂O₃ (24.4%) and ZrO₂-tetragonal (75.6%). This indicates that during sintering, there is stability of Al₂O₃ and the formation of ZrO₂-tetragonal by the reaction between ZrO₂-monoclinic and CeO₂. This diffractogram did not detect superficial transformations, which could have been caused by the grinding/polishing process. The compressive surface tensions arising from surface mechanical treatments apparently did not induce the transformation of tetragonal particles into monoclinic ones. Figure 2b displays the X-ray diffraction results on the fracture surface of the samples after fatigue tests. The peaks indicate that the application of stresses during the tests generated transformations from the tetragonal to the monoclinic phase. The standard analysis of the diffractogram reveals the presence of the monoclinic ZrO₂-phase in the proportion of 7.6% and the predominance of the tetragonal phase in 92.4%. Considering the Al₂O₃ phase resulting from sintering (ZrO₂-tetragonal and Al₂O₃), we have the proportion of ZrO₂-tetragonal (69.85%), Al₂O₃ (24.4%), and a small amount of unstabilized monoclinic ZrO₂—(5.75%). The results show a high tetragonality ($c/a\sqrt{2} = 1.017$), indicating that the toughening mechanisms due to $t \rightarrow m$ phase transformation were active during crack propagation. This behavior was observed in other samples subjected to fatigue and in the same order of magnitude.

Figure 3 shows SEM micrographs of the sintered samples. The aforementioned figures show the matrix with equiaxed submicron grains of zirconia (lighter phase), alumina grains (dark phase) distributed homogeneously in the ZrO₂ matrix, and alumina platelets in an elongated and planar format dispersed in smaller amounts in the matrix.

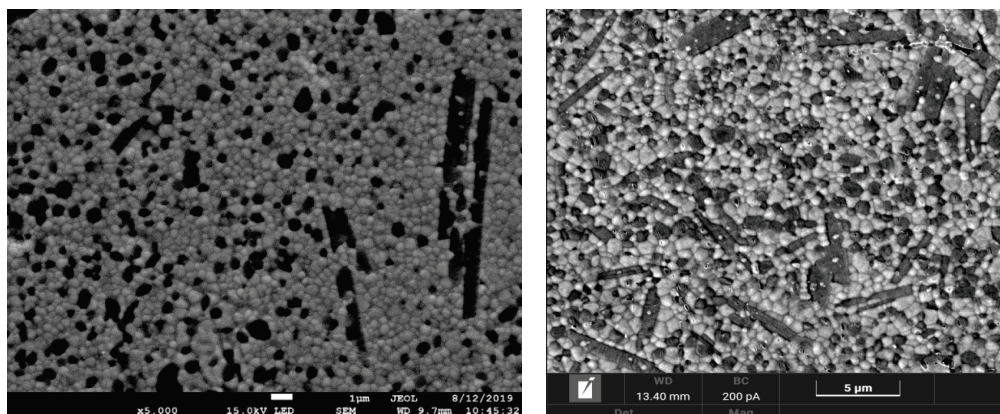


Figure 3. Micrographs of sintered ZrO₂CeYAl₂O₃ samples.

The fractographic analysis of the specimens demonstrates that the failures started from the surface subjected to maximum traction during the fatigue tests, most frequently in the space between the internal loading rollers of the four-point bending device. In the image in Figure 4a, the appearance of the fracture surface is depicted. The origin of the crack is represented by the arrow (Figure 4a) on the side subjected to tension, and it propagates to the compression curve (CC), located close to the surface subjected to compression. Figure 4b shows a fracture surface with a predominantly intergranular appearance. This image demonstrates the complex microstructure of this type of composite [30,31]. White rectangles represent the presence of intergranular pores with irregular shapes.

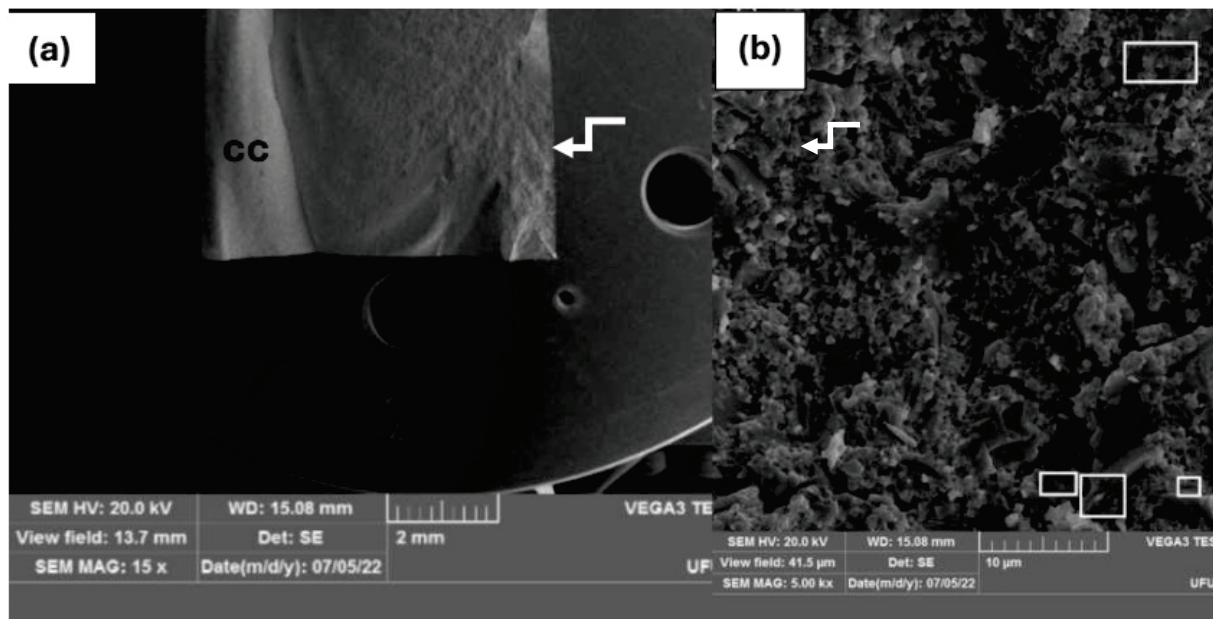


Figure 4. Fractography of $\text{ZrO}_2\text{CeYAl}_2\text{O}_3$ samples showing (a) origin and propagation of the crack and (b) intergranular appearance and pores.

Figure 5 illustrates SEM images of the fracture surfaces of a sample subjected to fatigue testing. This microstructure acts as an obstacle during the propagation of a crack due to the action of different toughening mechanisms. In Figure 5a, lighter submicron ZrO_2 grains, darker alumina grains, and alumina platelets can be seen in the intergranular spaces. Figure 5b shows a fracture with an intergranular appearance, with a predominance of submicrometric grains.

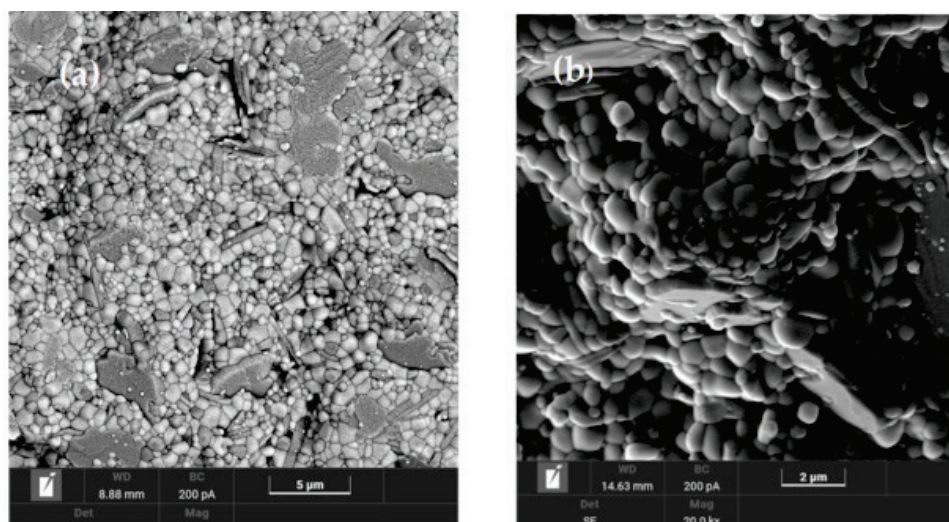


Figure 5. Lighter submicron grains of ZrO_2 , darker grains of Al_2O_3 , and alumina platelets in the intergranular spaces (a) Fracture with an intergranular appearance is observed, with a predominance of submicrometric grains (b).

The EDS analysis of the fracture surface of a composite sample is shown in Figure 6a. In this figure, grains of ZrO_2 tetragonal can be observed in spot 6. The elongated platelets (white arrow) are a reinforcing phase of the composite and allow the deflection of cracks. The platelets require higher energy for crack propagation and correspond to cerium hex-aluminate $\text{CeAl}_{11}\text{O}_{10}$ (H6A), which are developed in situ during solid-state sintering of $\text{ZrO}_2\text{CeYAl}_2\text{O}_3$ by the reduction of tetravalent Ce, which reacts with Al_2O_3 at temperatures

above 1450 °C. The EDS spectra presented in Figure 6b,c correspond to the spectroscopic analyses carried out respectively on the H6A platelet and on the ZrO₂ grain observed in spot 6.

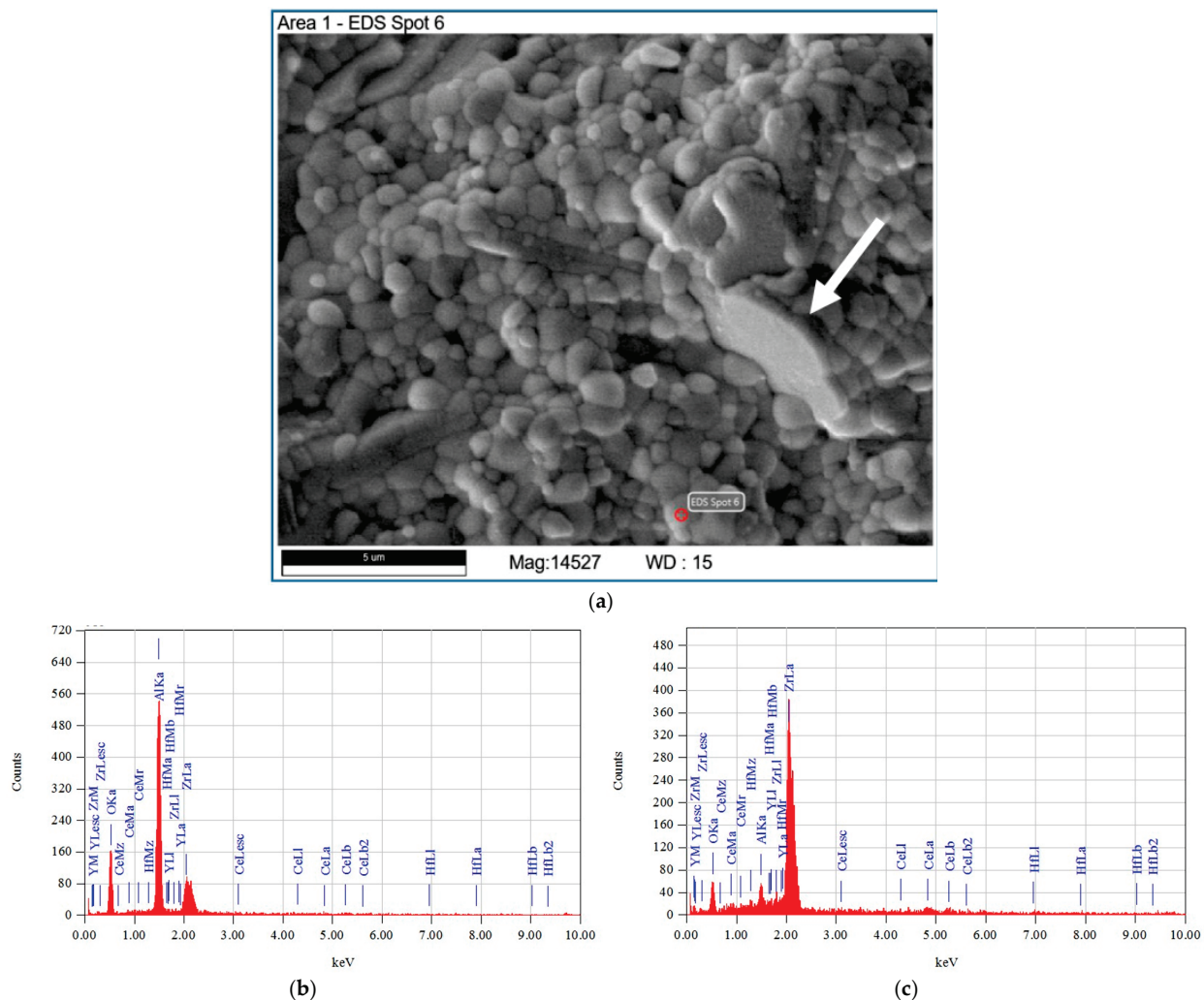


Figure 6. EDS analysis of the fracture surface of the sample tested under fatigue, observing the fracture surface (a) and EDS spectrum of the H6A platelet (b) and the ZrO₂ grain identified in spot 6 (c).

3.2. Mechanical Properties

Table 2 presents the measurement of the samples' elastic modulus, carried out using the Sonelastic software V6.0. Additionally, Vickers hardness and fracture toughness are presented.

Table 2. Modulus of elasticity and standard deviation of the composite sintered at 1550 °C-2 h.

Sample	Modulus of Elasticity (GPa)	Microhardness (GPa)	$K_{IC}(\text{MPa} \cdot \text{m}^{\frac{1}{2}})$ $c/a = 1.91$ (Palmqvist)
ZrO ₂ CeYAl ₂ O ₃	247.54 ± 0.22	13.68 ± 0.2	7.07 ± 0.37

Previous works [32,33] determined elastic modulus values between 190 and 220 GPa for monolithic zirconia. The value found for the composite evaluated in the present work reached approximately 247.54 GPa, showing coherence for the composition developed. This value is higher than that of monolithic zirconia due to the modulus of elasticity of the

alumina present in this material. The modulus of elasticity values were used to calculate fracture toughness. The hardness value found is compatible with similar compositions based on zirconia [34].

After the Vickers indentation microhardness test, an analysis was carried out using confocal laser microscopy. The measurements of the dimensions of the cracks generated in microhardness were obtained with the aid of the IMAGE J software v1.53. The types of cracks generated in the samples were considered to calculate the fracture toughness values. This result is due to the tension-induced toughening mechanism generated by $t \rightarrow m$ phase transformation [35,36]. When the crack tip comes across a tetragonal zirconia grain and promotes its transformation to monoclinic, 3 to 5% volumetric expansion generates a local compressive stress that slows down its growth. Figure 7 illustrates superficial radial cracks that appeared during the Vickers microhardness test. The toughening mechanisms ($t \rightarrow m$ transformation and stress-induced microcracking) have been important in recent research for explaining the toughness of Y-TZP ceramics. Ce-TZP materials, due to microstructure optimization, have a larger shielding zone compared to Y-TZP. Complex mechanisms that take into account the refined microstructure of the material and a platelet-shaped reinforcement phase end up interacting with the toughening mechanisms [31,36].

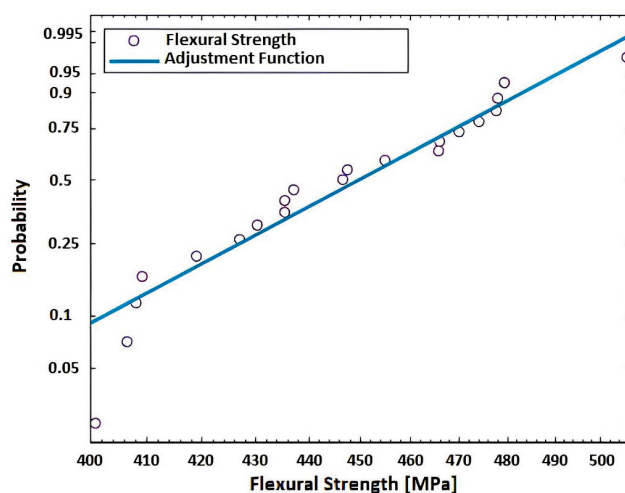


Figure 7. Weibull graph for the $\text{ZrO}_2\text{CeYAl}_2\text{O}_3$ samples generated by Matlab software v9.13.

3.3. Four-Point Bending Test

Twenty-one samples of the composite were subjected to the four-point bending test. A displacement rate of 0.05 mm/min was applied. Table 3 presents the results of the flexural tests after treatment by Weibull statistics for the $\text{ZrO}_2\text{CeYAl}_2\text{O}_3$ specimens. This statistical treatment is essential due to the dispersion in bending results in ceramic materials. The probability of micro-defects that act as stress concentrators can affect the flexural strength of these materials [37].

Table 3. Flexural strength results of four points for ceramic samples.

Sample	$\sigma_{\max}$ (MPa)	σ_{med} (MPa)	$\sigma_{\min}$ (MPa)	σ_0 (MPa)	m
$\text{ZrO}_2\text{CeYAl}_2\text{O}_3$	505.7	445.55	400.8	459.8 ± 6.32	16.82

where ($\sigma_{\max}$) is maximum rupture stress, (σ_{average}) is average rupture stress, ($\sigma_{\min}$) is minimum rupture stress, (σ_0) is characteristic resistance, and (m) is the modulus of Weibull.

In Figure 7, experimental data of rupture stress are presented after Weibull statistical treatment. Two outlier values and a Weibull modulus ($m = 16.82$) were observed for the composite samples, resulting in less dispersion of the rupture stress data. The values are within the expected range for ceramic materials [38], with higher quality and high reliability. The dispersion of mechanical resistance values is due to the distribution of defects or random flaws present throughout the volume of the sintered specimens.

To analyze whether the Weibull distribution applied to the breaking strength values of the ceramic samples will have a normal distribution of data, the Kolmogorov–Smirnov (K-S) free distribution test was used. It allows obtaining the p -value (significance) making it possible to evaluate the hypothesis of whether or not the errors have a normal distribution. From the results shown in Tables 3 and 4, it can be inferred that the set of rupture stress data from the Weibull distribution for the $\text{ZrO}_2\text{CeYAl}_2\text{O}_3$ samples has a *normal* distribution since the significance obtained (p -value) indicates that the distribution has the value ($p > 0.05$), that is, under an error of 5%. Observing the regressions of the Weibull distribution data in Figure 8, it is noted that the observed cumulative distribution function (CDF) presents a good estimator of the function (ECDF), showing the proximity of the two curves.

Table 4. Kolmogorov–Smirnov test for rupture stress values.

Sample	Value- p	k	D	Conclusion
$\text{ZrO}_2\text{CeYAl}_2\text{O}_3$	0.8409	0.1277	0.2873	H_0 not rejected

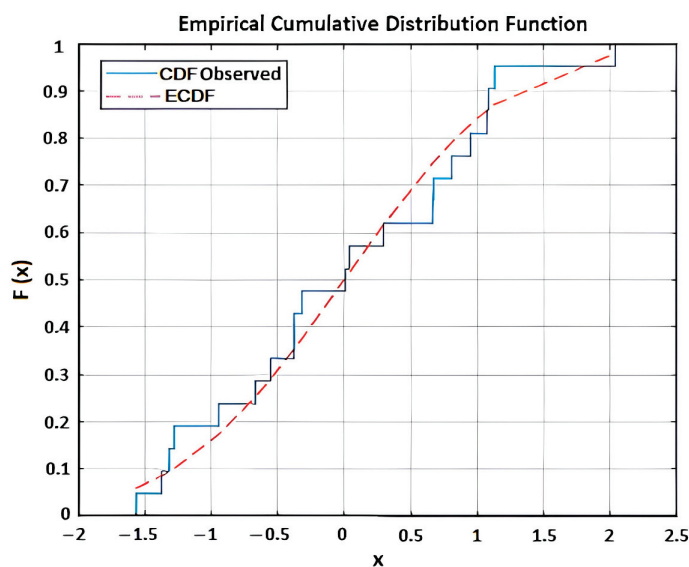


Figure 8. Graph of empirical cumulative distribution function (ECDF) for $\text{ZrO}_2\text{CeYAl}_2\text{O}_3$ samples using the Kolmogorov–Smirnov test.

3.4. Four-Point Bending Fatigue Test

Fatigue limits were obtained using the modified staircase method. Table 5 presents the maximum stress and standard deviations in 2×10^6 cycles. After the fatigue test results, a descriptive statistical analysis of the analytical results was carried out. A confidence interval was used for each value of the mean stress amplitude. Using the Student's t test, differences between means were evaluated with a 90% confidence interval.

Table 5. Four-point bending fatigue limit of $\text{ZrO}_2\text{CeYAl}_2\text{O}_3$ specimens.

Sample (MPa)	Fatigue Limit (MPa)	Standard Deviation
$\text{ZrO}_2\text{CeYAl}_2\text{O}_3$	286.64	24.18

Figure 9 illustrates the points obtained by the modified staircase method on the composite samples.

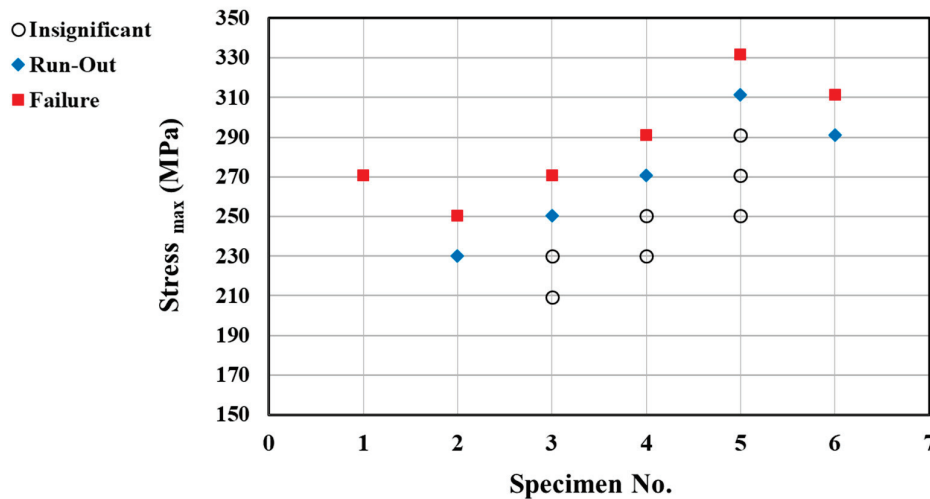


Figure 9. Result of the modified staircase method for $\text{ZrO}_2\text{CeYAl}_2\text{O}_3$ samples.

The modified staircase method to evaluate fatigue resistance used a reduced number of specimens and a high fatigue cycle (~ 2 million cycles). The fatigue resistance values of the composite were strongly influenced by the complex microstructure of the material. During cyclic loading, the occurrence of the tetragonal–monoclinic transformation that occurs in the Ce-TZP grains present in the triple points and grain boundaries produces “crack tip shielding”, that is, a restricted elastic zone (shielding zone) that surrounds the crack tip. This phenomenon reduces the stress intensity factor at the crack tip and slows down its growth. Under cyclic loading conditions, the relationship between stress intensity factors can be expressed on the microscale by Equations (14) and (15) [39].

$$K_{tip} = K_I - K_s \quad (14)$$

$$\Delta K_{tip} = \Delta K - K_s \quad (15)$$

where K_{tip} and ΔK_{tip} are the stress intensity factors near the crack tip and the stress intensity range in the same region, respectively. K_I is the nominal or applied stress intensity factor, and ΔK is the nominal or applied stress intensity range, given by $K_{max} - K_{min}$. K_s is the stress intensity factor due to the crack shielding zone. The high fatigue cycle used in the tests and a good reliability of 90% indicate that the results obtained by the modified staircase method are satisfactory. The bending and fatigue results for the composite serve as a basis for further studies on the joint influence of hydrothermal fatigue and strength degradation due to aging [40,41].

4. Conclusions

The flexural strength results showed a high Weibull modulus for the composite ($m = 16.82$), revealing a lower dispersion of flexural rupture stress values and high reliability for structural applicability. The Weibull distribution rupture stress data set for the $\text{ZrO}_2\text{CeYAl}_2\text{O}_3$ samples has a normal distribution since the significance obtained (p -value) indicates that the distribution has the value ($p > 0.05$), i.e., under a 5% error. The observed cumulative distribution function (CDF) presents a good estimator of the function (ECDF), showing the proximity of the two curves.

- The elongated platelets are a reinforcement phase of the composite and allow the deflection of cracks, dissipating more energy for their propagation. These platelets correspond to cerium hexaluminate $\text{CeAl}_{11}\text{O}_{18}$ (H6A), which are developed in situ during solid-state sintering of $\text{ZrO}_2\text{CeYAl}_2\text{O}_3$ by the reduction of tetravalent Ce, which react with Al_2O_3 at temperatures above 1450°C ;
- The Kolmogorov–Smirnov test indicated that the flexural strength results for the composite samples were within normal limits with a significance level of 5%;

- The peaks in the X-ray diffractometry of the samples after fatigue testing indicate tension-induced transformations from the tetragonal to the monoclinic phase, contributing to the toughening of the material. The results show a high tetragonality, indicating that the toughening mechanisms due to t→m phase transformation were active during crack propagation. This behavior was observed in other samples subjected to fatigue and in the same order of magnitude;
- The fractographic analysis of the specimens demonstrates that the failures started from the surface subject to maximum traction during the fatigue tests, most frequently in the corners of the samples and in the internal gap of the loading rollers of the four-point bending device;
- In the composite evaluated in this work, the occurrence of the tetragonal → monoclinic transformation that occurs in the Ce-TZP grains present in the triple points and grain boundaries during cyclic loading produces “crack tip shielding”, that is, a restricted elastic zone (shielding zone) surrounding the crack tip. This phenomenon leads to a reduction in the stress intensity factor at the tip of the crack and slows down its growth, generating an increase in the fatigue resistance of the composite.

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Article

Microstructure and Mechanical Properties of Diamond–Ceramic Composites Fabricated via Reactive Spark Plasma Sintering

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Abstract: In order to prepare diamond composites with excellent mechanical properties under non-extreme conditions, in this study, a diamond–ceramic composite was successfully prepared via reactive spark plasma sintering using a diamond–Ti–Si powder mixture as the raw material. The microstructures and mechanical properties of the diamond–ceramic composite sintered at different temperatures were studied. When the sintering temperature was 1500 °C, the diamond–ceramic composite exhibited a volume density of 3.65 g/cm³, whereas the bending strength and fracture toughness were high at 366 MPa and 6.17 MPa·m^{1/2}, respectively. In addition, variable-temperature sintering activated the chemical reaction at a higher temperature, whereas lowering the temperature prevented excessive graphitisation, which is conducive to optimising the microstructure and mechanical properties of the composite.

Keywords: diamond–ceramic composite; sintering temperature; microstructure; mechanical properties

1. Introduction

Diamond is an allotrope of graphite, and natural diamond is an elemental crystal formed from carbon under high pressure and temperature deep in the earth. Because the C–C bonds in diamond are extremely strong, all the valence electrons form covalent bonds, leaving no free electrons. Therefore, diamond has an extremely high hardness, making it the hardest substance in nature, with a Mohs hardness of grade 10 and microhardness of 10,000 kg/mm² [1,2]. These excellent mechanical properties provide a diamond with outstanding tribological properties and better wear resistance than those of cemented carbides and ceramics. Moreover, using diamond as a processing tool not only improves processing efficiency but also increases precision surface [3]. The application of diamond tools solves the processing problems of various difficult-to-process materials, thereby guaranteeing the application and promotion of new tools and materials [4].

The carbon atoms in the diamond lattice structure are bonded via strong covalent bonds, with no impurities or defects present. Owing to the high sound speed and elastic modulus, heat transfers quickly through the diamond, resulting in high thermal conductivity of approximately 2000 W/m·K at room temperature, which is five times that of Cu (400 W/m·K). Therefore, in addition to its use in processing tools, diamond is often combined with metals for thermal management in electronic components [5,6].

In these applications, diamonds are often prepared as diamond–metal composites [7–9]. However, these composites deteriorate rapidly at high temperatures. To address this issue, diamond–ceramic composites are being developed [10–13]. Typically, the preparation of diamond–ceramic composite requires extreme conditions [14]. For example, Jaworska et al. fabricated diamond–ceramic layers in diamond-stable conditions at a high pressure and temperature of 8 GPa and 1800 °C [15], respectively. Lai et al. prepared B₄C–diamond

ceramics with high toughness via high-pressure sintering at 5 GPa and 1600 °C [16]. Previous studies have shown that under oxygen-free conditions, diamonds tend to graphitise at 750 °C [17]. However, the extremely high pressures involved in these studies inhibited the graphitisation of diamond, which would have caused the rapid deterioration of its properties. Additionally, because of the rapid heating rate of spark plasma sintering, diamond graphitisation was suppressed to a certain extent [18]. To further weaken the influence of diamond graphitisation on the properties of the composites, carbide-forming elements such as Si, Ti, and B are added to the diamond. These elements react with C to form SiC, TiC, and B₄C, which possess high hardness and are chemically bonded to diamond, thus effectively holding the diamond particles [19,20].

As shown in Figure 1, the Gibbs free energy of the reaction of Ti with C is significantly more negative than that of B or Si with C, indicating that Ti reacts more readily with C than B or Si. Therefore, Ti can play the role of consuming graphite. Although the reaction between B and C is as difficult as that between Si and C, Si has a high melting point of 1410 °C, and its liquid phase sintering significantly promotes densification [21]. Taking the above factors into consideration, in order to achieve the preparation of diamond composites with excellent mechanical properties under non-extreme conditions, Ti and Si were selected as absorbents to adsorb the products of diamond graphitisation and combined with spark plasma sintering to fabricate diamond–ceramic composites.

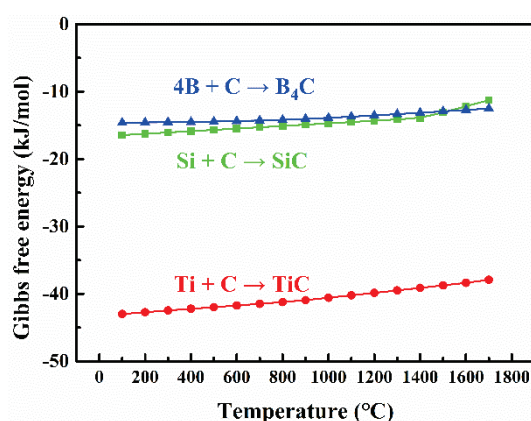


Figure 1. Gibbs free energy of the reaction of B/Si/Ti with C.

2. Experimental Procedure

Commercially available diamond (purity = 99%, 800 mesh, Fandeng Industry and Trade Co., Ltd., Yongkang, China), Ti (purity = 99.99%, ≥300 mesh, Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China), and Si powders (purity = 99.9%, 1–3 μm, Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China) were used as raw materials.

Figure 2 shows the SEM images and corresponding XRD patterns of the diamond, Ti, and Si powders. As shown in Figure 2A,C, the powder particle sizes of diamond and Ti are larger than those of Si. The average size of the diamond particles was approximately 20 μm, and the size distribution was uniform. Ti powder exhibited a larger average particle size; however, its size distribution was not uniform. The large Ti particles were 50 μm, whereas the smaller Ti particles were <10 μm. Furthermore, as shown in Figure 2E, the size of the Si particles was small. In addition, no impurity peaks were observed in the XRD patterns of the diamond, Ti, and Si powders (Figure 2B,D,F), confirming their high purity.

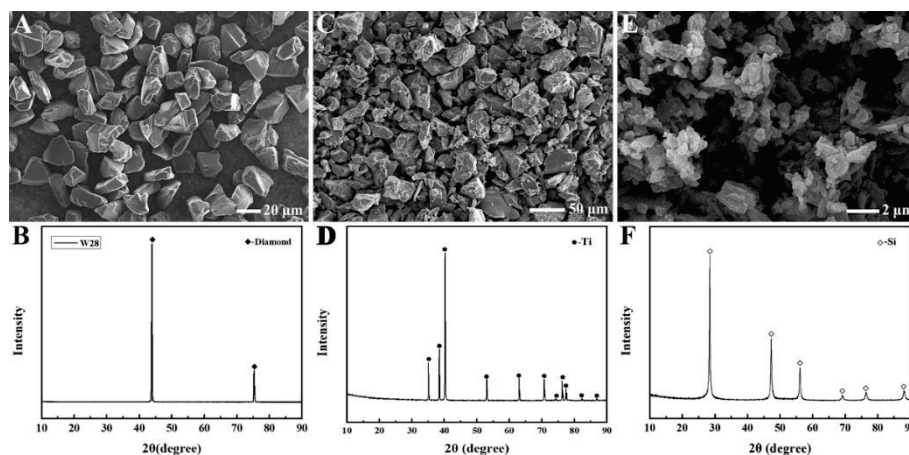


Figure 2. SEM images and corresponding XRD patterns of the raw materials: (A,B) diamond; (C,D) Ti; and (E,F) Si.

The diamond, Ti, and Si powders were weighed in a 4:3:3 mass ratio and placed in a 250 mL polyethylene jar. After injecting anhydrous ethanol into the jar, the mixture was milled using a planet mill (QXQM-2, Changsha Tianchuang Powder Technology Co., Ltd., Changsha, China) at 200 rpm for 2 h. The collected slurry was separated using a rotary evaporator (R206B, Shanghai SENCO Technology Co., Ltd., Shanghai, China) and then dried in a vacuum drying chamber (DZF-6020, Shanghai Jinghong Laboratory Instrument Co., Ltd., Shanghai, China) for 24 h to remove residual ethanol. The as-received powder mixture was sieved through a 100-mesh sieve to minimise agglomeration. Subsequently, the powder was placed in a graphite die with an internal diameter of 50 mm and sintered in a spark plasma sintering furnace (D60, FCT Systeme GmbH, Rauenstein, Germany). As shown in Figure 3, four different sintering processes were designed: first, the temperature was increased from room temperature to 400 °C in 5 min and further to 1500 °C, 1550 °C, and 1600 °C at a speed of 100 °C/min, each held for 10 min. In another experiment, after the sintering temperature rose to 1600 °C, it dropped to 1550 °C within 10 min. Sintering was performed in an Ar atmosphere, and the axial pressure was maintained at 50 MPa. The samples prepared at the sintering temperatures of 1500 °C, 1550 °C, 1600 °C, and 1600→1550 °C are denoted as S1, S2, S3, and S4, respectively.

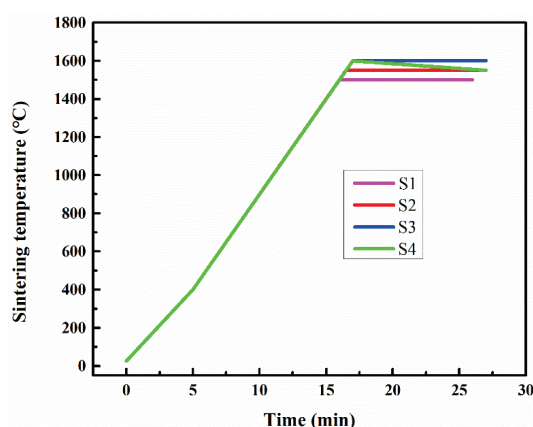


Figure 3. Variation in sintering temperature with time.

After sintering, the surfaces of the samples were levelled using a precision grinder (ACC-63DX, Okamoto Machinery Co., Ltd., Tokyo, Japan) and then cut into bars. Density was measured using the Archimedes method, and mechanical properties were tested using a ceramic testing system (CMT6503, Jinan Meitesi Testing Technology Co., Ltd., Jinan, China). The bending strength was measured via the three-point bending test on bars

sized $3\text{ mm} \times 4\text{ mm} \times 36\text{ mm}$ with a span of 30 mm and a loading rate of 0.5 mm/min. The fracture toughness was evaluated via the single-edge notched beam test on the $2.5\text{ mm} \times 5\text{ mm} \times 25\text{ mm}$ bars with a span of 20 mm and a loading rate of 0.05 mm/min. The final average values were determined using five bars. The phase components and microstructures were investigated using X-ray diffraction (XRD; PANalytical Empyrean, Einhorn, the Netherlands), scanning electron microscopy (SEM; Hitachi 3400, Tokyo, Japan), and field-emission scanning electron microscopy (FESEM; Hitachi/Regulus 8230, Tokyo, Japan) combined with energy-dispersive spectroscopy (EDS; Oxford/UltimMax 170, Oxford, UK). The Gibbs free energy of the reaction was evaluated using the chemical thermodynamics simulation software HSC Chemistry 6 (H: enthalpy, S: entropy, and C: heat capacity).

3. Results and Discussion

As shown in Figure 4, the size of large particles in the powder mixture after ball milling was around 20 μm , while Ti particles with a size close to 50 μm had disappeared. After ball milling, the diamond particles were preserved well because of their great hardness, and the Ti particles were effectively refined, which was considered to be beneficial to the process of reaction sintering.

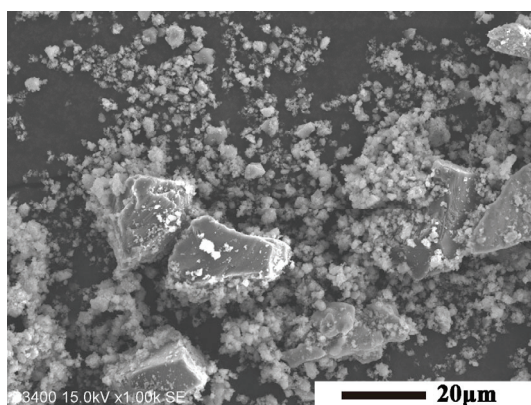


Figure 4. SEM image of diamond-Ti-Si powder mixture milled at 200 rpm for 2 h.

Figure 5 shows the XRD patterns of S1, S2, S3, and S4. Ti and Si disappeared from the spectra. The diamond peak intensity decreased gradually with increasing sintering temperatures, indicating increased diamond graphitisation. Simultaneously, the amounts of the main reaction products, SiC and TiC, increased. This is because, as the sintering temperature increased, both the carbon source (graphite) and the reaction-driving force increased simultaneously. As shown in Figure 5A, the intermediate product, TiB_2 , existed only at sintering temperatures below 1500 $^{\circ}\text{C}$. At 1550 $^{\circ}\text{C}$, the XRD peak of TiSi_2 enhanced, and a new product, Ti_3SiC_2 , appeared. Increasing the sintering temperature further enhanced the crystallinity and the diffraction peak intensity of TiSi_2 . Because diamond graphitisation was increased at higher temperatures, C reacted with TiSi_2 to form Ti_3SiC_2 . When the temperature rose to 1600 $^{\circ}\text{C}$, the content and crystallinity of Ti_3SiC_2 were further increased. At this point, the diffraction peak of TiSi_2 disappeared, and in the presence of sufficient graphite, all the TiSi_2 was transformed into Ti_3SiC_2 according to Equation (1).



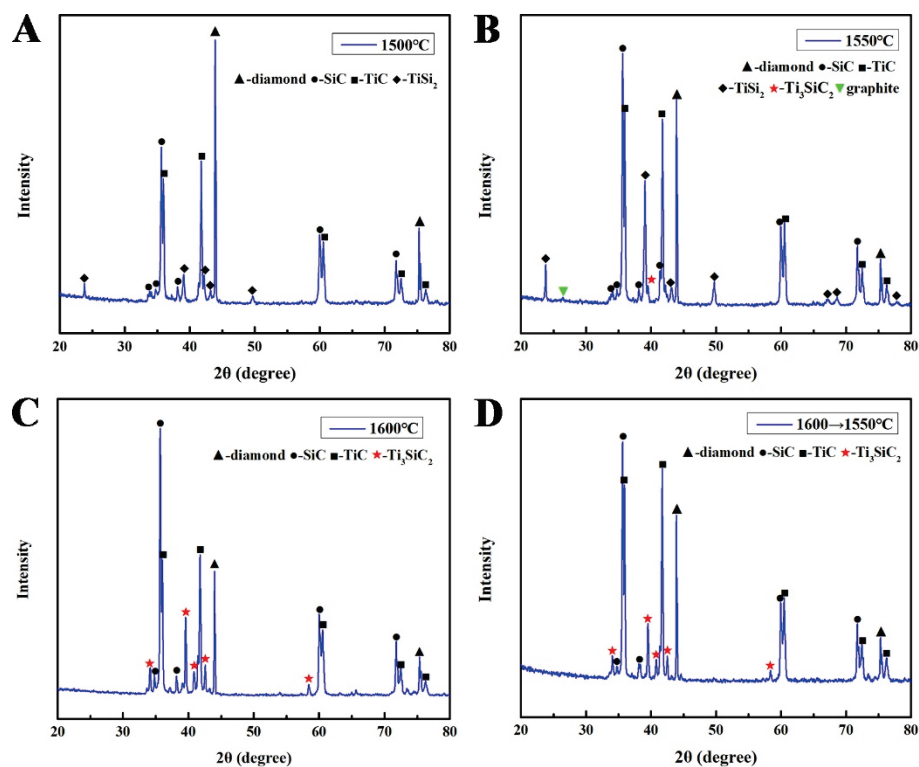


Figure 5. XRD patterns of diamond–ceramic composites sintered at different temperatures, (A) 1500 °C, (B) 1550 °C, (C) 1600 °C and (D) 1600→1550 °C.

Equation (1) also explains the synchronous increase in the XRD peak intensity of SiC in Figure 5C. As shown in Figure 5D, the temperature during the sintering of S4 dropped from 1600 °C to 1550 °C at a constant rate, and the average temperature of the whole process was <1600 °C. Consequently, more TiC was retained, resulting in a higher diffraction peak intensity for TiC than that for SiC in Figure 5C. Notably, only a weak graphite characteristic peak was observed in Figure 5B. Although diamond graphitises more easily at higher sintering temperatures, reaction (1) is easier to carry out, thus consuming more graphite. When the sintering temperature was 1600 °C, the composite was composed of diamond, SiC, TiC and Ti_3SiC_2 , and the semi-quantitative ratio analysis showed the phase composition was 21.4 wt%Diamond-39.8 wt%SiC-24.1 wt%TiC-14.7 wt% Ti_3SiC_2 .

Figure 6A shows a backscattered electron scanning image of the fracture surface. The black regions with the highest carbon concentration correspond to diamond grains. The grey-black regions with the highest Si concentration and a moderate C concentration correspond to SiC grains. The grey-white regions representing the highest Ti concentration with some Si or C elements correspond to TiC or TiSi_2 grains.

As shown in Table 1, the volume densities of the diamond–ceramic composites gradually decreased with increasing sintering temperatures. The phase differences between S1, S2, S3, and S4 prepared at four different sintering temperatures were mainly caused by reaction (1). The parameters of the reactants and products of this reaction are listed in Table 2. Evidently, the volume density of the reactants was 4.60 g/cm^3 , which is higher than that of the products (4.21 g/cm^3).

Table 1. Volume density of diamond–ceramic composites sintered at different temperatures.

Samples	S1 (1500 °C)	S2 (1550 °C)	S3 (1600 °C)	S4 (1600→1550 °C)
Volume density (g/cm ³)	3.647	3.604	3.555	3.596

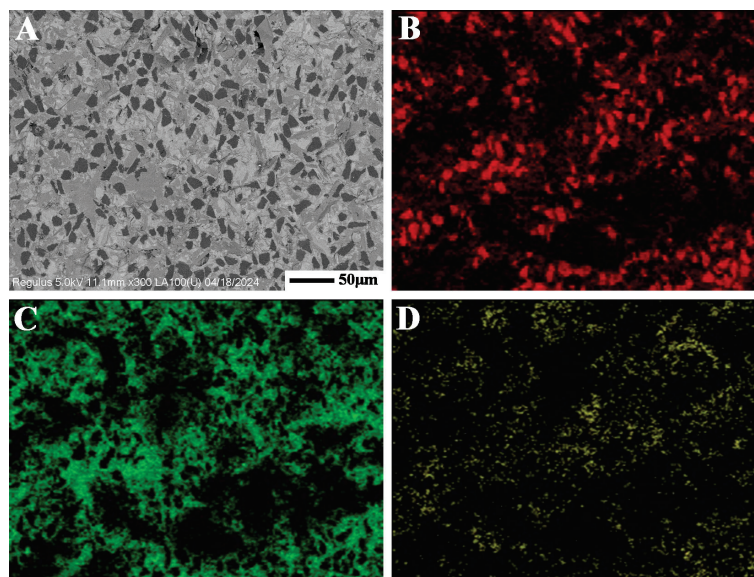


Figure 6. Element distribution of the diamond–ceramic composite sintered at 1500 °C: (A) backscattered electron image, (B) C, (C) Si, (D) Ti.

Table 2. Properties of the reactants and products in reaction (1).

Matter	Reactants			Products	
	2TiC	TiSi ₂	C	Ti ₃ SiC ₂	SiC
Relative atomic mass	119.76	104.05	12.01	195.72	41
Density/(g/cm ³)	4.93	4.39	3.52	4.53	3.2
		4.60		4.21	

Figure 7 shows the fracture surfaces of the diamond–ceramic composites. The samples prepared at different sintering temperatures exhibited a high degree of densification. However, some holes with larger dimensions were observed, as indicated by the yellow arrows. Compared to the results in Figure 2A, these holes were only slightly smaller than the raw diamond particles. This implies that these holes were caused by the elimination of the diamond particles. Moreover, Figure 7 shows that the number of holes on the fracture surface increased with increasing sintering temperature. At high temperatures, diamond transformed into graphite, which possessed a weak interlayer binding force. Therefore, after the outer layer of the diamond graphitised, the diamond particles were easily removed when the material fractured. The graphitisation rate of diamond increased with increasing sintering temperature, and because the graphite could not react with Ti or Si over time, the pull-out phenomenon of diamond particles increased. Although no graphite phase was detected in the XRD patterns, it can be inferred that a small amount of graphite was present in these samples. This is also why the volume density of the sample decreased with increasing sintering temperature.

As shown in Figure 8A, the fracture toughness of the diamond–ceramic composites decreased with increasing sintering temperature. The fracture surfaces in Figure 7 reveal that the fracture mode of the diamond–ceramic composite was a combination of transgranular and intergranular fractures. Intergranular fractures contributed to the toughening of crack deflection [22]. Crack deflection mainly occurred around the diamond phase because the thermal expansion coefficients of the diamond and ceramic phases differed significantly, and an interface with a weak bonding force was formed after diamond graphitisation. The prolonged cracks caused by crack deflection consumed more fracture energy, resulting in increased fracture toughness [23]. The degree of crack deflection depends on the size

of the diamond particles, and the energy consumed per unit length of the crack depends on the interface bonding strength. With increasing sintering temperature, the degree of graphitisation of the diamond increased, thus decreasing the diamond size and weakening the interface bonding. Consequently, the fracture toughness of the diamond–ceramic composite was reduced.

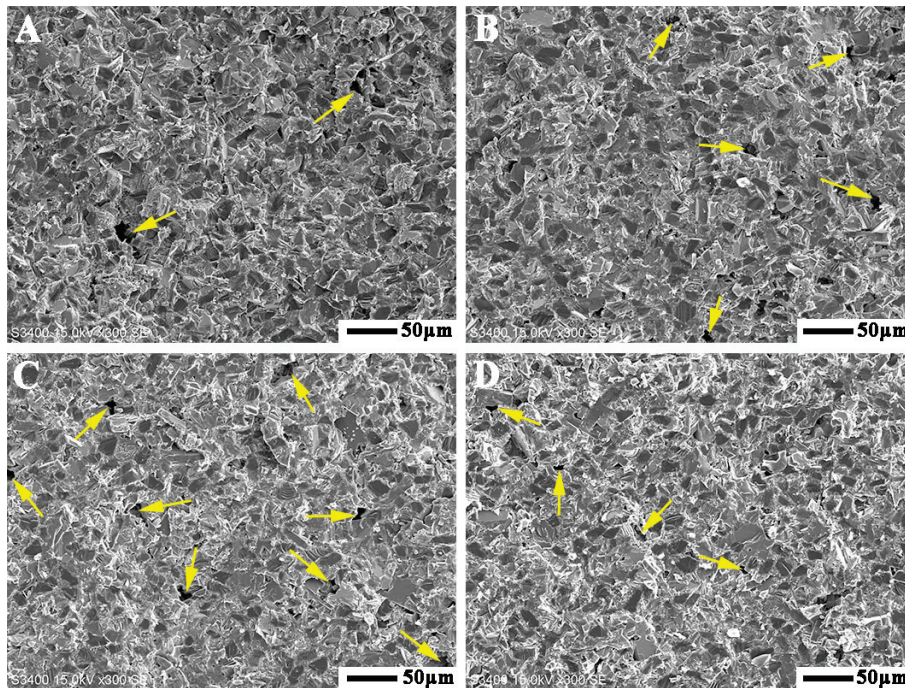


Figure 7. SEM images of diamond–ceramic composites sintered at different temperatures, (A) 1500 °C, (B) 1550 °C, (C) 1600 °C and (D) 1600→1550 °C.

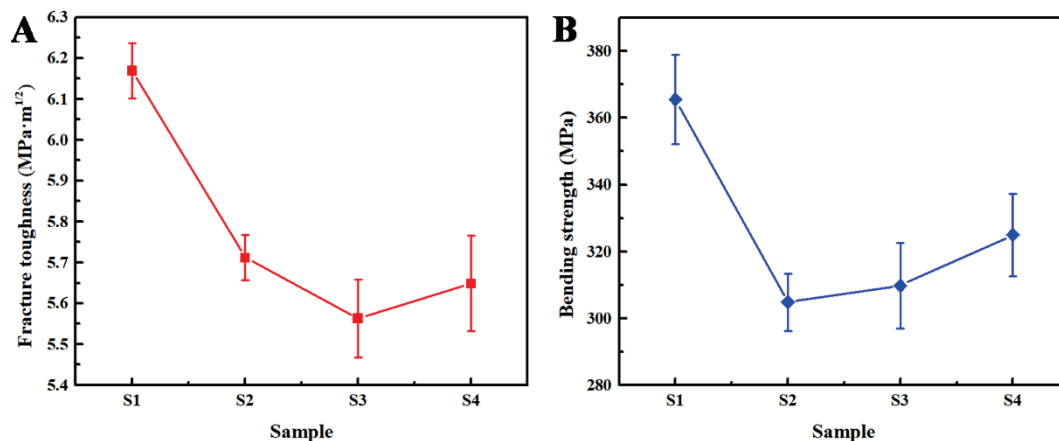


Figure 8. Fracture toughness (A) and bending strength (B) of diamond–ceramic composites sintered at different temperatures.

As shown in Figure 8B, the bending strength was the lowest when the sintering temperature was 1550 °C. At this temperature, although the graphitisation of the diamond was low, its size was only slightly reduced; however, graphite was not consumed in time, resulting in an extremely weakened diamond interface. This resulted in larger defects that cause crack initiation in S2, resulting in easy failure under load [24]. When the sintering temperature rose to 1600 °C, the size of the diamond was further reduced, and graphite was consumed by reaction (1), resulting in a slightly higher bending strength of S3 than

that of S2. In summary, when the sintering temperature was 1500 °C, the bending strength and fracture toughness reached 366 MPa and 6.17 MPa·m^{1/2}, respectively. Therefore, the optimal sintering temperature is 1500 °C. As shown in Table 3, the mechanical properties of this work are superior to those of the same types of materials.

Table 3. Bending strength and fracture toughness of diamond–ceramic composites.

Sample	Bending Strength (MPa)	Fracture Toughness (MPa·m ^{1/2})	Ref.
Diamond–SiC–TiC	366	6.17	This work
Diamond–SiC	248	4.65	[25]
SiC–Diamond	400	4.5	[26]
Diamond–SiC	287	5.0	[27]
Diamond–SiC	237	—	[28]
Diamond–SiC	378	4.0	[29]

Compared with XRD, Raman spectroscopy is more sensitive in detecting graphite. Therefore, Raman spectroscopy was performed to characterise the reaction product accumulation area around the diamond. As shown in Figure 9, the characteristic peaks at 796 cm^{−1} and 970 cm^{−1} correspond to SiC, and the characteristic peak of graphite was observed at 1524 cm^{−1} [30]. Although the average temperature of S4 was higher than that of S2, the higher initial temperature activated reaction (1), resulting in higher graphite consumption and a weaker characteristic peak strength of graphite in S4 than that in S2. Consequently, the diamonds in S4 had smaller sizes and stronger interfacial bonds. This unique variable-temperature sintering results in a higher bending strength of S4 than that of S2 and S3.

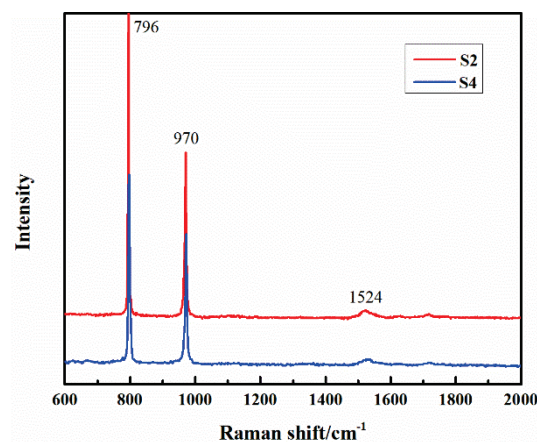


Figure 9. Raman spectra of diamond–ceramic composites sintered at different temperatures.

Figure 10A,B show the line-scan images of the diamond–ceramic composite. The grey-white, grey-black, and black regions correspond to Ti₃SiC₂, SiC, and diamond, respectively. Figure 10C shows an enlarged image of Line 1 (yellow line), and the structure of the above regions can be determined after analysis in combination with Figure 10D. As shown in Section I of Figure 10C, Ti, Si, and C were present simultaneously with their stable contents, confirming that this region was Ti₃SiC₂. In Section II, Ti disappeared, the Si content increased, and the Si and C contents were relatively stable, indicating the region as SiC. Section III contained only Si and C elements; however, their contents were unstable, indicating that a part of this region was graphite and the other part was a solid solution formed after Si elements were diffused into the diamond. The remaining area contained only C with a stable content, indicating a stable structure of diamond. Complex structures around diamonds were formed by a combination of diffusion, phase transitions, and chemical reactions.

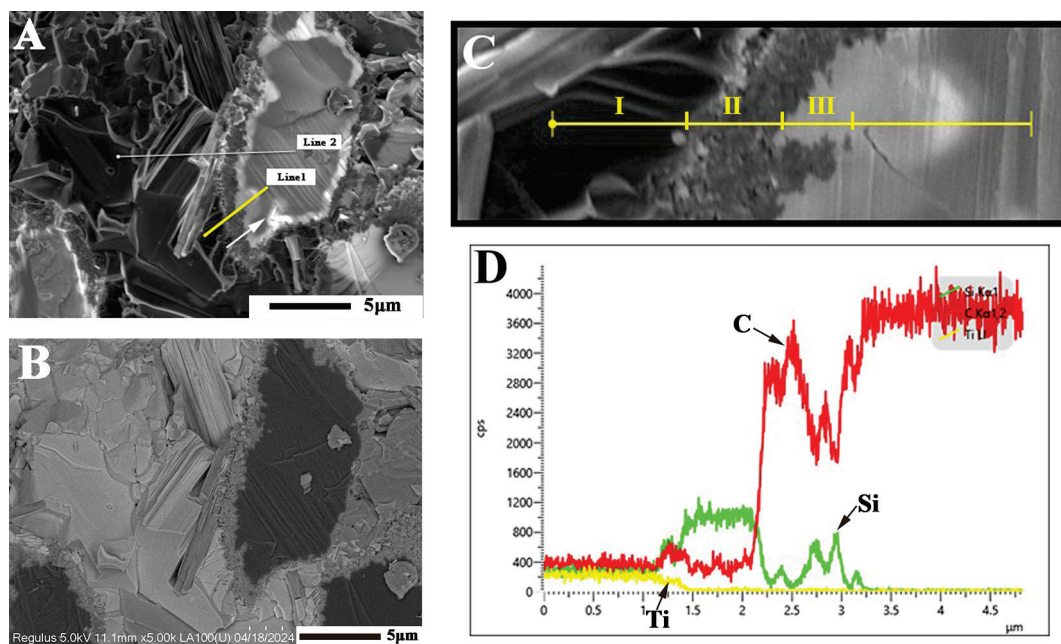


Figure 10. Line-scan element distribution images of the diamond–ceramic composite sintered at 1500 °C, (A) SEM image, (B) BSE image, (C) enlarged view of the line sweep area and (D) element content.

4. Conclusions

Diamond–SiC composites are generally prepared by Si infiltration or HTHP (high temperature high pressure). The above methods easily cause Si residue and have strict requirements for the equipment. In this study, the silicon residue in the composite was eliminated by introducing Ti, which reacted more easily with graphite. In addition, the conductivity of the composite was improved, which was conducive to improving the machinability. The following conclusions were drawn:

- (1) Through the absorption of graphite by Ti and Si, the liquid phase provided by Si, and spark plasma sintering, diamond–ceramic composites were successfully prepared under conventional conditions.
- (2) Characteristic of variable-temperature sintering, the chemical reaction was activated at a higher temperature, and then the sintering temperature was reduced to prevent excessive graphitisation. This method is particularly suitable for preparing diamond–ceramic composites and has certain research value.

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Article

Properties of a Pressureless Sintered 2Y-TZP Material Combining High Strength and Toughness

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Abstract: Yttria stabilized zirconia materials are frequently used in mechanical engineering and biomedical applications. Demanding loading conditions require materials combining a high level of strength and fracture toughness. A ready-to-press alumina doped 2 mol% yttria-stabilized zirconia powder was shaped by axial pressing and sintering in air at 1250–1500 °C for 2 h. At 1350 °C the best combination of strength (1450 MPa) and toughness (7.8 MPa√m) was achieved. Materials sintered in the middle of the chosen temperature range combine full density, high transformability and small grain size. Toughness measurements by direct crack length measurements delivered unrealistically high fracture toughness values.

Keywords: zirconia; high toughness; microstructure; phase composition

1. Introduction

Partially stabilized zirconia materials are structural ceramics which combine high strength and fracture toughness by exploiting the effect of transformation toughening (TT) [1]. TT describes a reinforcement mechanism based on the martensitic transformation of metastable tetragonal phase to stable monoclinic phase associated with volume expansion and shear. If a crack in partially stabilized zirconia is exposed to tensile stress, a transformation zone forms at the crack tip. As the crack expands, the transformation zone in the wake of the crack exerts compressive stress which leads to reduction of the stress intensity at the crack tip. The shear component can be accommodated by twin-like orientation of the transformed monoclinic domains [2,3]. In order to obtain a metastable tetragonal phase after sintering, zirconia has to be stabilized by the addition of oxides containing aliovalent or isovalent cations which stabilize the tetragonal phase by expanding the lattice, by introduction of oxygen vacancies or both [4,5]. Today, yttria is probably the technologically most important stabilizer oxide. As yttria is trivalent, yttria addition introduces oxygen vacancies to retain charge neutrality. Moreover, as Y^{3+} is an oversized dopant (larger than Zr^{4+}), additional stabilization by lattice expansion is obtained. Yttria forms tetragonal and cubic solid solutions with zirconia [6]. The yttria content in yttria stabilized tetragonal zirconia polycrystals (Y-TZP) is typically adjusted at 3 mol% Y_2O_3 (3Y-TZP) [7]. At a typical sintering temperature of ~1400 °C, 3Y-TZP is a composition within the t + c field, a miscibility gap. At this temperature, this gap ranges from 2.5 to 6.5 mol% Y_2O_3 [6]. Hence, 3Y-TZP sintered at this temperature should, by rule of the lever, decompose to ~20% cubic and ~80% tetragonal phase. However, as the powders are typically produced by co-precipitation, the initial distribution of yttria in zirconia is homogeneous at atomic level. Phase segregation is therefore inhibited and requires high sintering temperatures [8]. The tetragonal phase in 3Y-TZP sintered at moderate temperatures is, therefore, super-saturated and not very transformable. This leads to materials with high strength (>1000 MPa) but very moderate toughness (4–6 MPa√m) [9]. In order to improve the toughness of Y-TZP produced from co-precipitated powder two pathways are possible. The first is to sinter

TZP at temperatures $\gg 1500$ °C for long dwell time to trigger the phase segregation and increase the grain size of the tetragonal grains to make the material more transformable [10]. The second is to reduce the stabilizer content to a level of 2.5 mol% to obtain an entirely tetragonal material. Further reduction of the stabilizer content below 2.5 mol% leads to a more transformable tetragonal phase [11]. Both procedures face some difficulties. The first route leads to very coarse-grained materials with reduced strength. At the same time these materials become very prone to degrade by low temperature degradation (LTD) in the presence of humidity [12]. In case of the second route, it has to be considered that the critical grain size beyond which the material will transform spontaneously during cooling from sintering temperature is reduced with declining stabilizer content [13]. This requires very fine and sinterable starting powders to obtain fully dense and fine rain ceramics at moderate sintering temperatures. Moreover, we may expect that entirely tetragonal compositions with a stabilizer content < 2.5 mol% will show less stabilizer segregation to the grain boundary which prevents grain growth by solute drag [8]. The concept has been known for decades and is well described in the literature [14]. The difficulties described above have for a long time prevented implementation of understabilized Y-TZP, as it was considered too dangerous to use for fear of spontaneous transformation and LTD. Recently different powder producers offer fine understabilized Y-TZPs (with 1.5–2 mol% Y_2O_3) and there are a few new studies. Innovnano's 2Y-TZP, which was produced by detonation synthesis, delivered an impressive combination of strength and toughness but has disappeared from the market [15]. Tosoh's ZGAIA 1.5Y-TZP promised extreme toughness in combination with attractive strength [16]. Recent studies by Imariouane showed that indentation toughness values were exaggerated; still, a fracture toughness of $9 \text{ MPa}\sqrt{\text{m}}$ combined with a strength of 1000 MPa is respectable [17].

The material is, however, tricky to sinter and requires high cooling rates to retain the metastable tetragonal phase [18]. In the present study, a new alumina doped 2Y-TZP issued by Treibacher Industries in Austria was tested and compared to literature values shown in Table 1. Literature values appear controversial. On the one hand, this is due to different strength and toughness measurement protocols. Ref. [15] allows a comparison of three different strength measurement protocols, with 4PB being the strictest. Concerning the toughness measurement, the DCM method seems to deliver systematically higher values than conservative methods. Kern shows that in the compositional range between 1.5Y and 2Y-TZP, strength and toughness show adverse trends [19]. Further deviations are presumably caused by powder properties, shaping technology and sintering protocols.

Table 1. Strength and toughness data for Y-TZP with 1.5–2 mol% Y_2O_3 stabilizer.

Composition Mol% Y_2O_3	Strength ¹ [MPa]	Toughness ² [MPa $\sqrt{\text{m}}$]	References
1.5	1088, 3PB	14.5, DCM 4.7, SCF	[11]
1.5	2600, P3B	13.8, DCM	[20]
1.5	1438, P3B	4.8, SEVNB	[21]
1.5	1270, 3PB	22, DCM	[16]
1.5	995, 4PB 1320, 3B3B	8.5, SEVNB	[17]
2	994 3PB	6.4, SEVNB	[22]
2	1560, 4PB 2088, P3B 1670, 3B3B	9.6, ISB	[15]
2	n.d.	5.9, DCM	[23]

Table 1. Cont.

Composition Mol% Y ₂ O ₃	Strength ¹ [MPa]	Toughness ² [MPa√m]	References
2 (3Y + 0Y)	1270, 3PB	10.3, DCM	[19]
1.5 (3Y + 0Y)	630, 3PB	14.5, DCM	
1.75 (3Y + 0Y)	680, 3PB	10.3, DCM	
2 (3Y + 0Y)	1050, 3PB	8, DCM	
2	1250, BA	7.7, DCM	[24]

¹ Abbreviations for strength measurement: 3PB = 3pt bending, 4PB = 4pt bending, P3B = piston on three balls, 3B3B = three balls on three balls, BA = biaxial; ² Abbreviations for toughness measurement: DCM = direct crack length measurement (indentation toughness), SCF = surface crack in flexure, SEVNB = single edge V-notched beam, ISB = indentation strength in flexure.

2. Materials and Methods

The starting material used in this study is a zirconia powder stabilized with 2 mol% of yttria and alloyed with 0.4 wt-% of alumina. The powder was delivered as a ready to press (RTP) granulate by the manufacturer (Auertec® 2Y-40A-B, Treibacher, Althofen, Austria, $S_{BET} = 11.15 \text{ m}^2/\text{g}$). The loss on ignition (correlates to binder content) was specified as 4.3 wt-%. The granules had an average diameter of 45 µm. The powder was cold-pressed in a rectangular steel die of 35 × 35 mm² diameter (Graveurbetrieb Leonhardt, Hochdorf, Germany) at 125 MPa pressure in a manually operated press (Paul Weber, Remshalden, Germany). An amount of 9 g of powder were weighed per plate resulting in a sintered plate of approx. 2 mm thickness. The plates were subsequently debindered in air (1 °C/min to 600 °C, 3 h dwell, Linn, Eschenfelden, Germany) and sintered in air in a dental furnace (MIHM-Vogt HT speed, Stutensee, Germany) at 2 °C/min to 1200 °C and 1 °C/min to final temperature (1250–1500 °C in 50 °C increments). Cooling was carried out at 12 °C/min to room temperature.

The plates (4 plates per sintering temperature) were then lapped on both sides with 15 µm diamond suspension and polished on one side with 15 µm, 6 µm, 3 µm and 1 µm diamond suspension to obtain a mirror-like finish using an automatic machine (Struers Rotopol, Copenhagen, Denmark). The plates were cut into bars with 4 mm width (Struers Accutom, Copenhagen, Denmark) with a diamond wheel. The as-cut sides were lapped with 15 µm suspension to remove cutting-induced defects. Finally, the edges were beveled manually using a 40 µm diamond disk.

The density of the samples was measured by the buoyancy method using polished plates prior to cutting (Kern&Sohn, Lörrach, Germany). Vickers hardness measurements HV10 (n = 5) (Bareiss, Oberdischingen, Germany) were carried out to determine the hardness and the indentation fracture toughness K_{DCM} by direct crack length measurements. The indentation toughness was calculated according to the Niihara Palmqvist crack model [25]. For the fully dense Y-TZP samples, a Young's modulus of 210 GPa was assumed [15]. Four-point bending tests were carried out in a setup with 20 mm outer and 10 mm inner span at a crosshead speed of 0.5 mm/min (n = 12) (ZwickRoell, Ulm, Germany). Indentation strength in bending (ISB) tests were carried out in the same setup at 2.5 mm/min crosshead speed. For the ISB tests, the samples were indented with 4 indents at a distance of 2 mm with cracks parallel and perpendicular to the sides. The indented region was placed on the tensile side within the inner span and the residual strength was measured. Placing dummy indentations was necessary due to the inhomogeneity of the crack patterns in order to obtain at least one valid indentation per bar. The ISB toughness K_{ISB} was then calculated using the model of Chantikul [26]. It is known from literature that in understabilized Y-TZP materials transformation zones around the indents may cause crack trapping effects, which lead to overestimated toughness values [27]. Hence, a modified SIGB (stable indentation crack growth in bending) test according to Dransmann was applied [28]. In order to suppress transformation and obtain starter cracks exceeding

the transformation zone around the crack, HV10 Vickers indents were introduced at elevated temperature (250–300 °C). The samples were then progressively loaded at 5 mm/min and the crack growth was measured after each loading step ($n = 2$ with 4 indents each). A detailed description of the SIGB test is given by Benzaid [29].

The phase composition of as-fired samples without preparation and polished samples in the 27–33° 2 θ range (containing the -111 , 111 monoclinic and the 101 tetragonal peaks) was measured by XRD (X'Pert MPD, Panalytical, Eindhoven, The Netherlands, CuK α 1, Ge-monochromator, Bragg-Brentano setup, accelerator detector) according to the protocol of Toraya [30]. The phase composition was also determined in fracture surfaces in order to determine the transformability and the transformation zone size according to Kosmac [31]. The fourth order peaks in the 72–75° 2 θ range were studied to obtain tetragonality values and confirm absence of cubic phase. The crystallite size in the starting powder was estimated using the Scherrer analysis tool of Highscore (Panalytical, Eindhoven, The Netherlands) software package.

The transformation toughness values were calculated according to McMeeking and Evans assuming a transformation efficiency of 0.27 (predominantly dilational transformation) [32].

SEM images were taken from polished and thermally etched samples (10 °C/min to 1150 °C, 10 dwell in air) in order to determine the grain size [33] and identify possible thermal transformation effects. SEM was also used to characterize the powder and granulate.

The tensile sides of fractured bars were checked by optical microscopy for formation of transformation bands which would indicate transformation related failure [34].

3. Results

3.1. Powder Characterization

Figure 1a shows an SEM image of spray dried granules of the RTP granulate. Granules are perfectly round; they have a smooth surface and are free of defects and satellites. The size of the individual granules varies between 15 and 50 μm ; the average size correlates to manufacturer's specification. Figure 1b shows an image of the granulate surface with size markers for different grains. The grains are compact and densely packed, with a size range of 40–140 nm. Only a few agglomerates are visible. XRD analysis shows that the phase composition of the starting powder is 94 vol% monoclinic and 6% tetragonal. The average crystallite size estimated from the line broadening of the monoclinic -111 and 111 peaks is 40 ± 2.5 nm. The block-shaped structure of the grains and the predominantly monoclinic phase composition implies that the powder has been milled to size.

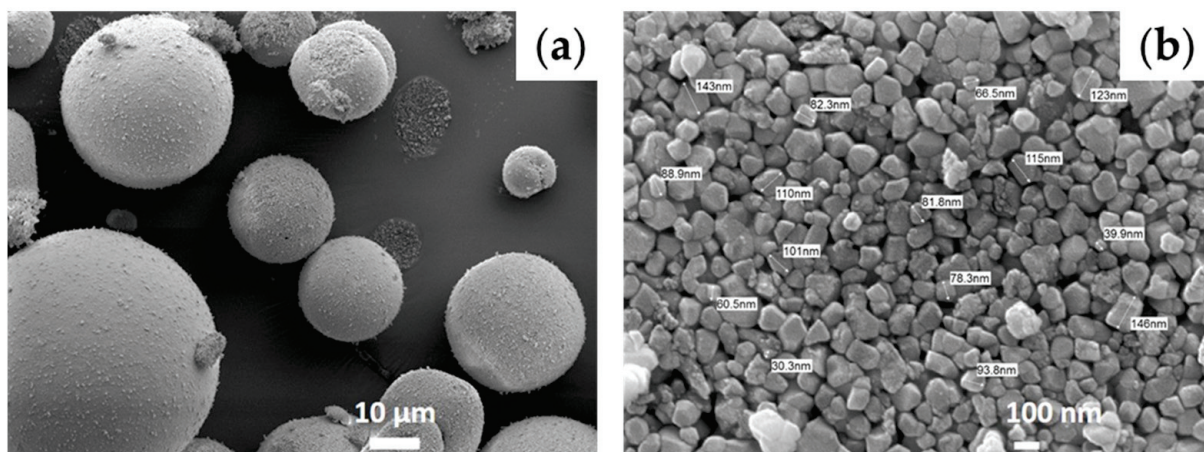


Figure 1. SEM images of ready-to-press (RTP) granulate: (a) granules, (b) grains embedded in granulate.

3.2. Density and Mechanical Properties

The density ρ/ρ_{th} of the TZP samples sintered at different temperatures is shown in Figure 2. Evidently, sintering at 1250 °C is not sufficient to obtain fully dense material (relative density 97.9%). At sintering temperatures ≥ 1300 °C, the obtained materials are practically fully dense (99.3–99.7% assuming a theoretical density of $\rho_{th} = 6.1$ g/cm³).

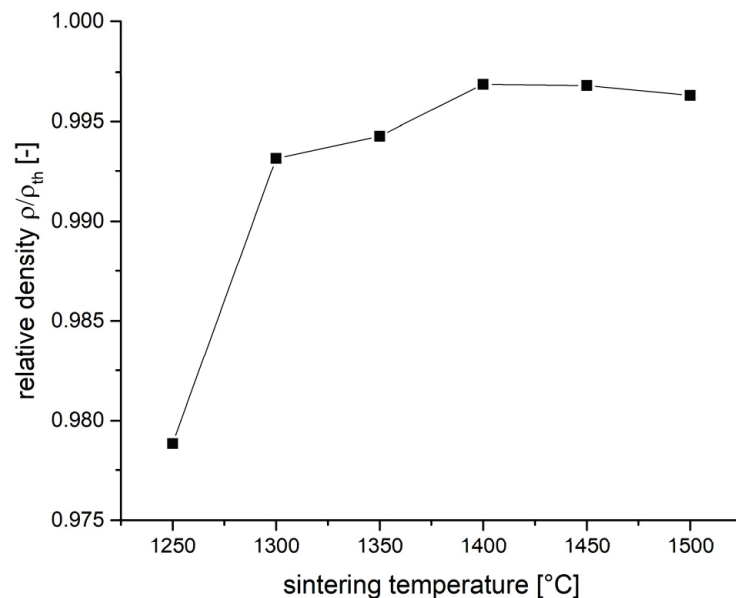


Figure 2. Relative density ρ/ρ_{th} of TZP samples sintered at different temperatures.

Figure 3 shows the Vickers hardness HV10 and the bending strength σ_{4pt} of the TZPs sintered at different temperatures. The Vickers hardness shows a strong correlation to the density values. The hardness increases from 1175 HV10 to 1250 HV10 between 1250 and 1300 °C. Then, the hardness further increases until 1400 °C. The slight reduction in hardness at even higher temperatures is probably related to increasing grain size. All samples reach average bending strength values >1200 MPa. The strength maximum is obtained at 1350 °C with 1440 ± 110 MPa. Direct evidence for transformation-induced failure, such as transformation bands on the tensile side of fractured bars or non-linearity of stress–strain curves, were not observed.

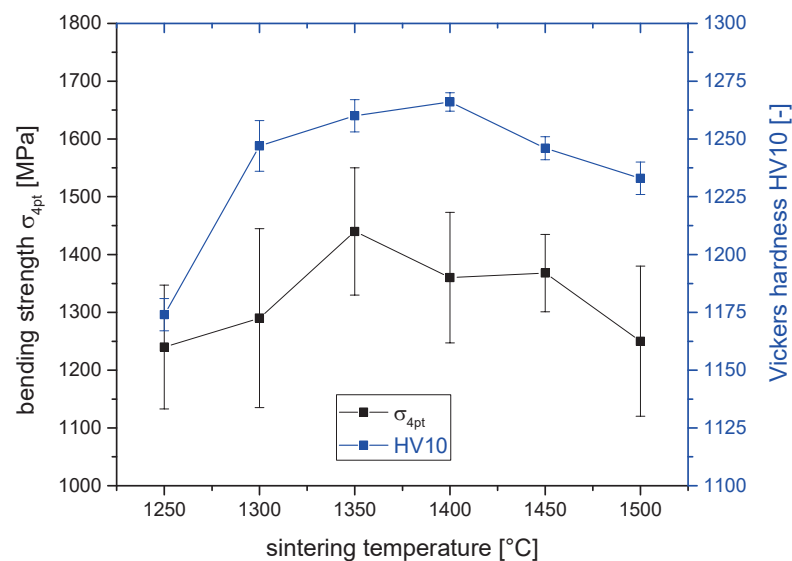


Figure 3. Vickers hardness HV10 and bending strength σ_{4pt} of TZPs sintered at different temperatures.

Figure 4 compares the toughness values determined by direct crack length measurement K_{DCM} and by indentation strength in bending K_{ISB} . In both cases, samples were indented at ambient temperature. Note: Both calculation methods require a value for the Young's modulus E ; E was assumed as 210 GPa for all samples except the sample sintered at 1250 °C which was not dense (assumed value 200 GPa).

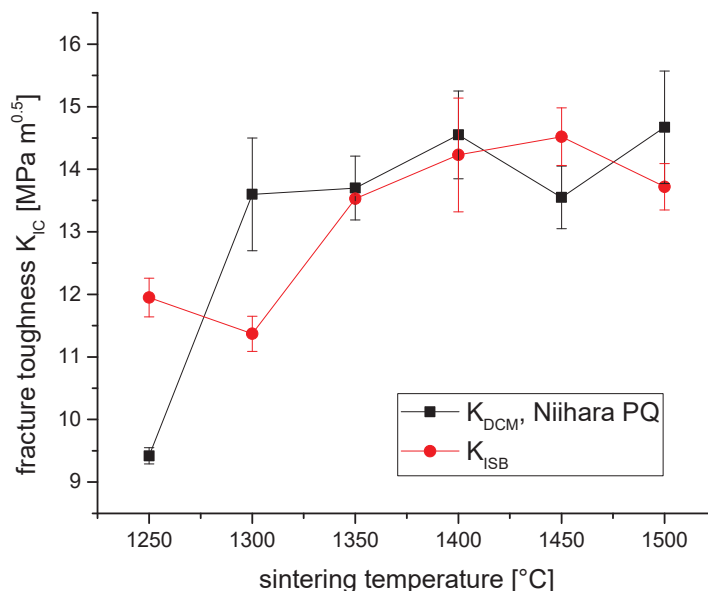


Figure 4. Fracture toughness values K_{DCM} and K_{ISB} of TZPs sintered at different temperatures.

The toughness levels determined by both testing protocols are comparable and extremely high. Maximum values of 13–15 $\text{MPa}\sqrt{\text{m}}$ were measured at sintering temperatures between 1300 °C and 1500 °C. These results correlate very well with indentation toughness data obtained by Billovits for the same material [35] and Matsui for ZGAIA 1.5Y-TZP [16]. Realistically, the strength–toughness correlations published by Swain [36] raise some doubts about the correctness of these indentation-based toughness values. With the given strength of 1200–1440 MPa (strength can be measured reliably), the corresponding toughness can be achieved either on the defect size-related branch of the curve at 6 $\text{MPa}\sqrt{\text{m}}$ or on the transformation-dominated side at 8 $\text{MPa}\sqrt{\text{m}}$ (note that Swain's data are indentation toughness data; strength data are from 3pt measurements). Moreover, the observed crack patterns which are frequently incomplete are a clear indication of trapping effects. As the ISB test is based on the assumption of semicircular crack geometries (geometry factor $Y = 1.27$), a correction factor needs to be introduced. Dransmann experimentally determined a value of $Y = 1.08$ for 3Y-TZP [28]. In the present case of even tougher 2Y-TZP, we assumed $Y = 0.95$. This would reduce the uncorrected maximum ISB-toughness values by 25% to corrected values of $\sim 10.5 \text{ MPa}\sqrt{\text{m}}$.

The following graph (Figure 5) shows the fracture toughness values determined from the strongest survivors in the SIGB test using samples which were indented at elevated temperature. Note that no extrapolation to infinite crack lengths was carried out which may lead to a slight underestimation of toughness [28,29]. The sample sintered at 1500 °C was not measurable. It was thermally unstable and transformed during the heating procedure. For the peak toughness materials, indentation at 250 °C increases the crack length $2c$ (from crack tip to crack tip in a HV10 indent) from approximately 0.14 μm to 0.18 μm . In fact, as expected due to larger starting cracks and suppression of transformation-induced crack trapping, the warm-indented samples fail at stress levels of 500–540 MPa. ISB samples indented at ambient temperature reach residual strength levels of 1000 MPa. The toughness levels by SIGB range from 5.5 $\text{MPa}\sqrt{\text{m}}$ to 7.8 $\text{MPa}\sqrt{\text{m}}$. Such values seem reasonable with respect to Swain's reference data [36]. The maximum toughness is achieved at 1350 °C sintering temperature. The toughness dip at 1300 °C is probably related to the incomplete

densification at 1250 °C. The presence of porosity in the 1250 °C sample reduces the elastic constraint and facilitates transformation. Moreover, pores may stop cracks. The same toughness minimum at 1300 °C is seen in ISB-toughness values (Figure 4).

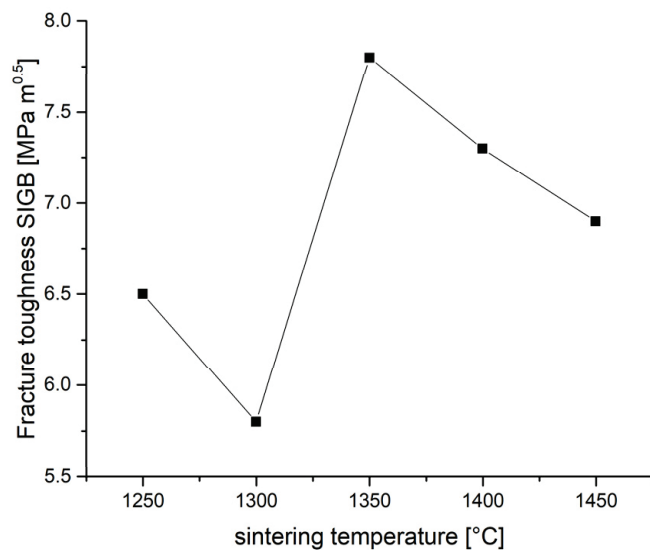


Figure 5. Fracture toughness values K_{SIGB} of TZPs sintered at different temperatures; samples notched at elevated temperature.

3.3. Microstructure

Figure 6 shows the microstructure of polished and thermally etched samples sintered at different sintering temperatures. Considerable porosity is visible in the sample sintered at 1250 °C/2 h. At higher sintering temperatures porosity is significantly reduced. Some isolated pores are visible even at the highest sintering temperature. Microstructure images are in accord with measured densities (Figure 2).

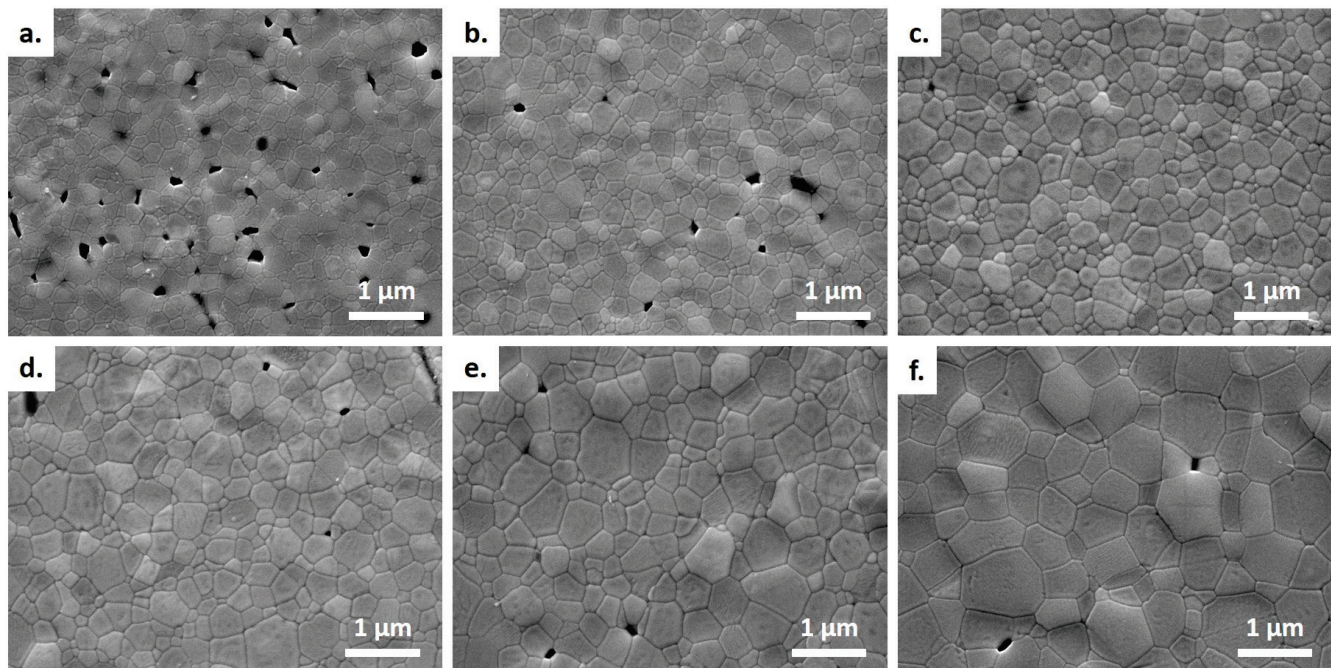


Figure 6. Microstructure of 2Y-TZP (polished and thermally etched surfaces). (a) 1250 °C/2 h; (b) 1300 °C/2 h; (c) 1350 °C/2 h; (d) 1400 °C/2 h; (e) 1450 °C/2 h; (f) 1500 °C/2 h.

The uneven surface structure especially at sintering temperatures $> 1400\text{ }^{\circ}\text{C}$ may indicate a certain degree of t-m phase transformation after thermal etching associated with volume expansion. Figure 7 shows the evolution of average grain size with sintering temperature. As expected, the grain size increases with sintering temperature. Considering a maximum grain size of 400 nm as required for high-strength dental applications (three or more element bridges) according to EN 6872, the sintering temperature should be limited to 1350–1400 $^{\circ}\text{C}$.

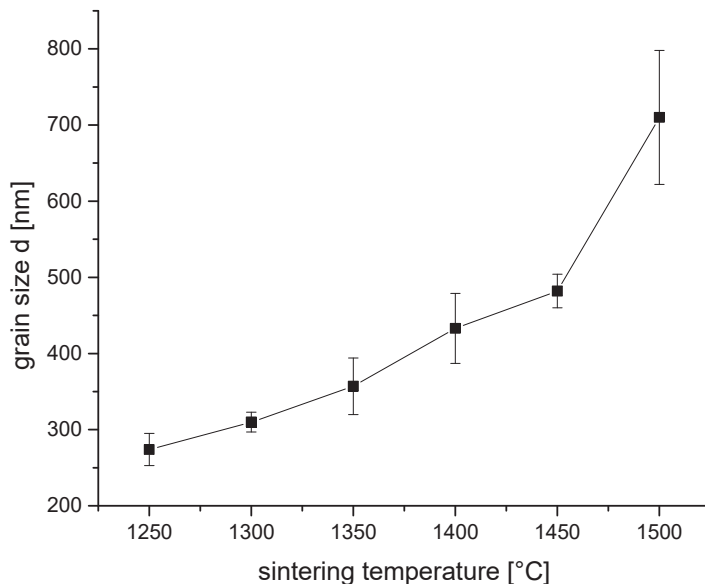


Figure 7. Grain size of 2Y-TZP determined by line intercept method (correction factor 1.56).

3.4. Phase Composition and Transformation Toughening Effect

Figure 8 shows the XRD traces of as-fired surfaces (a) and fracture surfaces (b) of 2Y-TZP sintered at different temperatures in the monoclinic/tetragonal fingerprint range between 27 and $33^{\circ} 2\theta$. In case of polished TZP surfaces, the intensity of the monoclinic peaks is almost negligible, see Figure 8a. Besides the dominant 101_t peak at $30.2^{\circ} 2\theta$, only the -111_m peak at $28.1^{\circ} 2\theta$ is clearly distinguishable. In Figure 8b, all three peaks can be clearly seen. A decline of the intensity of the 101_t peak of tetragonal phase and a concurrent increase of the intensity of the -111 and 111 peaks of monoclinic phase with increasing sintering temperature are clearly visible. Hence, the transformability of tetragonal phase increases with sintering temperature.

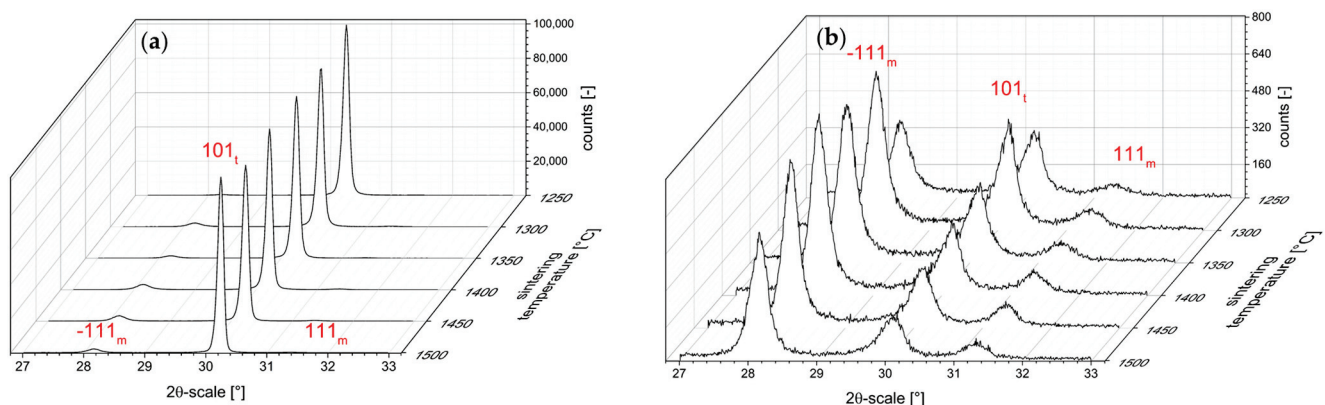


Figure 8. XRD traces in the t-m fingerprint range of 2Y-TZP sintered at different temperatures: (a) as-fired surfaces; (b) fracture surfaces.

Figure 9 summarizes the quantitative evaluation of the XRD studies and shows the monoclinic contents in as-fired surfaces, polished surfaces and fracture surfaces of bars after 4pt bending test. The as-fired surfaces exhibit a considerable monoclinic content which increases from 3 vol.% at 1250 °C to 13 vol.% at 1450 °C sintering temperature. The polished surfaces show significantly lower monoclinic contents in the range of 1–2 vol.%. Seemingly, the as-fired surface suffers from transformation during cooling, while the bulk is almost entirely tetragonal. The monoclinic content in the fracture surfaces increases with sintering temperature from 61 vol.% at 1250 °C to 75 vol.% at 1400 °C, then no further increase is observed. At high sintering temperature, the measured monoclinic contents are close to the theoretically possible values of ~85 vol.% quoted by Mamivand [37]. The transformability V_f , which is required to calculate the transformation toughness, is calculated as $V_f = V_{m,FF} - V_{m,pol}$.

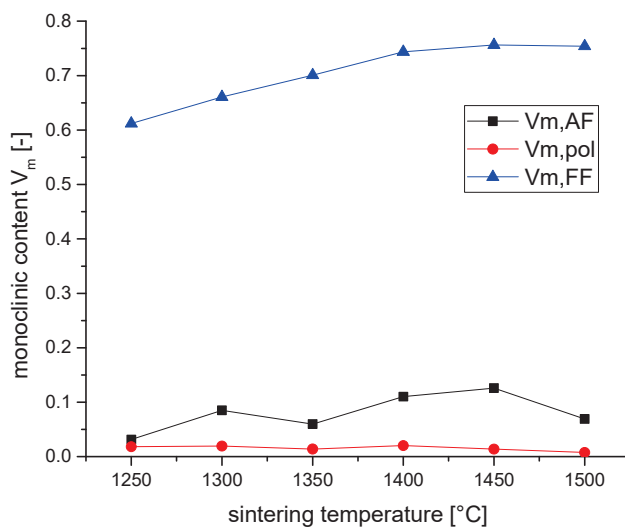


Figure 9. Monoclinic contents of TZP materials sintered at different temperatures measured by XRD $V_{m,AF}$ in as-fired surface, $V_{m,pol}$ in polished surface and $V_{m,FF}$ in fracture surface.

Figure 10 shows the transformation zone sizes h according to Kosmac [31] and the corresponding transformation toughness values ΔK_{IC}^T according to McMeeking [32], which were obtained by evaluation of XRD data of polished and fractured surfaces.

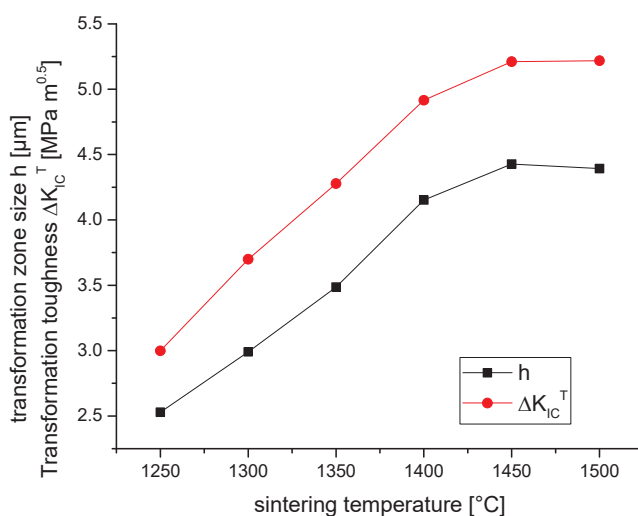


Figure 10. Transformation zone size h and transformation toughness ΔK_{IC}^T of TZP materials sintered at different temperatures.

Transformation zone sizes reach a maximum of 4.5 μm at sintering temperatures between 1400 and 1500 $^{\circ}\text{C}$. The calculated transformation toughness increases from 3 $\text{MPa}\sqrt{\text{m}}$ at 1250 $^{\circ}\text{C}$ to 5 $\text{MPa}\sqrt{\text{m}}$ at 1400 $^{\circ}\text{C}$. At 1450–1500 $^{\circ}\text{C}$ TT levels off.

Assuming that toughening effects are additive, the total fracture toughness can be calculated as $K_{\text{IC}} = K_0 + K_{\text{IC}}^{\text{T}}$ in absence of other toughening mechanisms than TT. Literature data for the crack tip toughness or intrinsic toughness K_0 (in absence of reinforcement effects) are between $K_0 = 3 \text{ MPa}\sqrt{\text{m}}$ [29] and $K_0 = 4 \text{ MPa}\sqrt{\text{m}}$ [36,38]. Therefore, on the basis of XRD data and theoretical considerations, the maximum toughness of the material may not exceed 8–9 $\text{MPa}\sqrt{\text{m}}$. This implies that both DCM and ISB values (Figure 4) are exaggerated and that the measured SIGB toughness data (Figure 5) are within the calculated range or slightly below.

4. Discussion

The 2Y-TZP material investigated shows an attractive combination of strength and fracture toughness. An in-depth study of transformation behavior and calculation of the maximum transformation toughness increment confirms that direct crack length measurement and ISB tests both lead to drastic overestimations of the fracture toughness values. The reason for this can be found in crack-trapping effects as described by Cook [27]. The cracks induced by HV10 indents are trapped in the transformation zone resulting not only in extremely short crack lengths but also very frequently in irregular crack patterns which are difficult to interpret. Similar conclusions are obtained comparing the results of Matsui and Imariouane who studied a quite similar understabilized 1.5Y-TZP material [16,17]. In ISB tests, cracks are extended due to tensile stress during loading the sample to failure. However, if the cracks are trapped within the transformation zone, the sample will fail at short crack extension immediately when the crack exits the shielded zone around the indent rather than grow evenly. This sudden bursting of ISB bars resulted in residual strength levels of up to 1000 MPa. The chosen procedure to place indentations at elevated temperature (250–300 $^{\circ}\text{C}$) at least reduces the transformability and allows the cracks to grow during the SIGB test. However, this solution cannot be applied in all samples, the sample sintered at 1500 $^{\circ}\text{C}$ turned out to be vulnerable to heating and transformed; hence, no measurement of the sample sintered at this temperature was possible (Figure 5). XRD measurements and the calculation of fracture toughness using the model of McMeeking and Evans [32] allows to estimate the possible maximum toughness in this 2Y-TZP (8–9 $\text{MPa}\sqrt{\text{m}}$). The SIGB tests carried out with samples indented at elevated temperature lead to toughness values within or below this range. It has to be considered that samples are small, and toughness values were not extrapolated to larger crack lengths; this may account for slight underestimations. Moreover, a constant transformation efficiency of $X = 0.27$ (predominantly but not exclusively dilational) was applied for calculation. It could be that at high sintering temperatures and large grain sizes the transformation efficiency may decline as in the case of Ce-TZP materials [2].

Another point worth discussing in the context of Ref. [18] is the elevated monoclinic content of the as-fired surface compared to polished surfaces. Thermal etching also leads to uneven surfaces especially for samples sintered at higher temperatures. In the sintering cycles for the study, the samples were cooled down with 12 $^{\circ}\text{C}/\text{min}$ (or in the case of lower temperature, as fast as the thermal inertia of the furnace allowed it). These observations of thermal vulnerability are in line with results of Imariouane on ageing of 1.5Y-TZP [18]. Maybe even faster cooling would be beneficial to prevent phase transformation. This increases the requirements of the furnace and kiln furniture and indicates possible difficulties in net-shape manufacturing of larger components.

The starting powder is relatively coarse and homogeneous in grain size but, nevertheless, very sinterable. This is a favorable combination in terms of processability, not only by pressing but also by other shaping technologies such as ceramic injection molding or stereolithography.

A comparison with literature values (Table 1) shows that the tested pressureless sintered 2Y-TZP shows a similar toughness as other 1.5-2Y TZP materials that were tested using conservative methods. The strength is slightly higher than recently determined for 1.5Y-TZP [17], which is probably due to the absence of transformation-induced failure.

5. Conclusions

The alumina-doped 2Y-TZP tested in this study provides a combination of high toughness and high strength, which makes the material attractive for structural applications requiring high damage tolerance for catastrophic events. Transformation toughness increments of up to $5 \text{ MPa}\sqrt{\text{m}}$ represent the maximum of the theoretically possible value for Y-TZP materials. Transformation-induced failure was not observed. However, as the R-curve dependent toughness is so high the materials are probably prone to suffer from sub-critical crack growth, i.e., they are not well suited to bear high constant or alternating loads. Indentation-based measurements may lead to overestimation of fracture toughness due to crack trapping and result in mistakes in the design of components. The best sintering condition is probably $1350^\circ\text{C}/2\text{h}$. Here, both strength and toughness reach their optimum, grain growth is still moderate and the material is fully dense. Overfiring shifts the material into the transformation-dominated range. Strength and toughness decrease and low temperature degradation may become an issue.

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Article

Effects of Composition Variations on Mechanochemically Synthesized Lithium Metazirconate-Based Ceramics and Their Resistance to External Influences

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Abstract: The study examines the influence of variations in the compositions of components for the production of lithium-containing ceramics based on lithium metazirconate obtained by the method of mechanochemical grinding and subsequent thermal sintering. For component variation, two compositions were used, consisting of zirconium dioxide (ZrO_2) and two distinct types of lithium-containing materials: lithium perchlorate ($\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$) and lithium carbonate (Li_2CO_3). Adjusting the concentration of these components allowed for the production of two-phase ceramics with varying levels of impurity phases. Using X-ray phase analysis methods, it was determined that the use of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ results in the formation of a monoclinic phase, Li_2ZrO_3 , with impurity inclusions in the orthorhombic phase, LiO_2 . On the other hand, when Li_2CO_3 is used, the resulting ceramics comprise a mixture of two phases, Li_2ZrO_3 and $\text{Li}_6\text{Zr}_2\text{O}_7$. During the studies, it was established that the formation of impurity inclusions in the composition of ceramics leads to an increase in the stability of strength properties with varying mechanical test conditions, as well as stabilization of thermophysical parameters and a decrease in thermal expansion during long-term high-temperature tests. It has been established that in the case of two-phase ceramics $\text{Li}_2\text{ZrO}_3/\text{Li}_6\text{Zr}_2\text{O}_7$ in which the dominance of the $\text{Li}_6\text{Zr}_2\text{O}_7$ phase is observed during high-temperature mechanical tests, a more pronounced decrease in resistance to cracking is observed, due to thermal expansion of the crystal lattice.

Keywords: lithium-containing ceramics; blankets; strength; thermal stability; phase transformations

1. Introduction

The future progress of a country's energy sector will be closely tied to the adoption of alternative energy sources, with nuclear, hydrogen, and thermonuclear energy emerging as the most promising for substantial energy generation [1–3]. The expansion of their role in the energy sector is contingent not only on worldwide efforts to diminish reliance on fossil fuels and reduce harmful emissions but also on the imperative to bolster energy production capacity in response to growing energy demands from the populace [4,5]. One of the ways to solve the problems in the energy sector is to create new types of nuclear reactors, including high-temperature reactors, in which ceramic materials are to be used as core and nuclear fuel, as well as thermonuclear reactors based on technological solutions related to the production of energy from tritium. At the same time, to produce tritium, which, along with hydrogen, is one of the key types of nuclear fuel for thermonuclear installations, it is proposed to use lithium ceramics. Interest in lithium ceramics for the production of tritium is primarily due to the possibility of nuclear reactions involving the interaction of neutrons with lithium, which results in the formation of tritium, which can be used to support thermonuclear reactions and fuel production. At the same time, interest in the

development of ceramic materials containing lithium in this direction is primarily due to the possibility of creating sustainable materials for tritium multiplication (in order to maintain thermonuclear reactions), as well as those that are highly resistant to mechanical, thermal and radiation influences, which are integral factors accompanying the operation of ceramic materials.

A crucial aspect of ceramic production, or, in simpler terms, selecting a ceramic manufacturing method, involves examining the impact of manufacturing process variables and the specific procedures used in crafting ceramics [6–8]. The selection of these conditions plays a pivotal role in shaping the uniformity of the resultant ceramic compositions, along with a combination of physicochemical, structural, and thermophysical properties [9,10]. The methods currently available for obtaining lithium-containing ceramics can be categorized into several groups that share common technological processes. The most common method is the so-called melt method, combined with the sol-gel method, the use of which makes it possible to obtain spherical lithium-containing ceramics from compounds of lithium carbonate with zirconium, titanium or silicon oxides, depending on the type of ceramics that is planned to be obtained [11–15].

The aim of this work is to study the effect of component variations in the manufacture of lithium-containing ceramics based on lithium metazirconate on their phase composition, structural and strength characteristics, as well as stress resistance to temperature tests. The relevance of this work consists in the possibility of creating lithium-containing ceramics by mechanochemical synthesis with a controlled phase composition, which plays a very important role in determining the strength and thermophysical characteristics. Furthermore, the focus on ceramics based on lithium metazirconate primarily arises from its exceptional strength properties and its resistance to prolonged mechanical or radiation stress, along with its resistance to thermal expansion and degradation [16–20]. It is essential to emphasize that the objective of this study was not to produce single-phase ceramics but rather to precisely gauge the impact of impurity phases formed during mechanochemical mixing and subsequent thermal sintering on factors such as strength, thermophysical characteristics, thermal stability, and resistance to external influences [21–23]. This work is based on the hypothesis that the formation of impurity inclusions makes it possible to create additional barriers in ceramics for the propagation of microcracks under external influences, thereby increasing the strength of ceramics [24,25]. Moreover, since these inclusions also consist of the original components, this makes it possible to increase the concentration of lithium in the ceramic composition.

2. Materials and Research Methods

The synthesis of lithium-containing ceramics was carried out by using two types of compositions of the initial mixtures: (1) ZrO_2 and $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ and (2) ZrO_2 and Li_2CO_3 with varying the molar ratio of the components from 0.25 to 0.75 M. In the future, these compositions will be designated as 1 and 2. The selection of these two compositions, featuring different components, stems from the potential to create lithium-containing ceramics with diverse phase compositions, strength, and thermophysical properties. Additionally, the choice of using $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ and Li_2CO_3 as the lithium component was made to evaluate the feasibility of the mechanochemical synthesis method in producing stable ceramics with high lithium concentrations, which constitutes a crucial criterion when selecting ceramics for tritium production.

The primary approach employed to manufacture lithium-containing ceramics was the mechanochemical solid-phase synthesis method. This method entails mechanically blending the initial components within a PULVERISETTE 6 planetary mill (Fritsch, Berlin, Germany) for 5 h at a grinding speed of 300 rpm, with the aim of achieving a uniform particle size distribution. Subsequently, the resulting powders were compacted into 10 mm diameter and 1 mm thickness tablets, considering the requirements of the measuring instruments used to determine properties such as hardness, fracture resistance, and thermal conductivity. The tablets were pressed using a mold specially made for this purpose

under a pressure of 250 MPa. After pressing, the resulting tablets were subjected to thermal annealing at a temperature of 900 °C in a muffle furnace SNOL 39/1100 (AB UMEGA-GROUP, Ukmergė, Lithuania). Annealing was carried out for 8 h in an air atmosphere, followed by cooling for 24 h with the furnace. The selection of these annealing conditions, encompassing temperature, duration, and cooling process, was informed by prior experimental investigations [26,27], alongside a priori knowledge concerning phase and structural transformations in lithium-containing ceramics derived through mechanochemical or solid-phase synthesis.

The analysis of structural parameters and phase composition in the examined ceramics, contingent on the type of initial component composition and its variations, was conducted through an assessment of the X-ray diffraction patterns. These patterns were captured in the Bragg-Brentano configuration ($2\theta = 25\text{--}100^\circ$) with an increment of 0.03° . A Cu— α X-ray tube with a wavelength of $1.54 \text{ \AA}$ was used as an X-ray source. The diffraction data was collected using a D8 Advance ECO X-ray diffractometer (Bruker, Berlin, Germany). The interpretation of the acquired diffraction patterns was facilitated by the Diffrac EVA v.4.2 software (Bruker, Berlin, Germany), enabling the determination of structural parameters such as crystal lattice dimensions, volume, and the structural order degree, along with the calculation of phase contributions within the samples. The weight contributions of each identified phase within the samples were ascertained by calculating the areas of all diffraction reflections characteristic of a given phase and then determining their ratio relative to other established phases. The degree of structural ordering (degree of crystallinity) was determined as the ratio of the contributions of the intensities of all diffraction reflections to the area of background radiation recorded during the angular dependence of the change in the intensity of X-ray diffraction patterns.

The mechanical properties, including alterations in hardness and resistance to cracking during a single compression, were evaluated for the investigated ceramics with regard to variations in their phase composition using established methods. Hardness assessments were conducted by applying a load of 100 N on a Vickers diamond pyramid indenter for 15 s, followed by the evaluation of the resultant indenter imprint on the sample. These experiments were carried out using a Duroline M1 microhardness tester (Metkon, Bursa, Turkey). The assessments of the hardening factors were based on the data concerning changes in hardness, attributable to adjustments in component ratios, as well as the introduction of impurity phases within the structure.

A single compression, based on the data of which the dynamics of changes in cracking with increasing pressure on the sample was established, was carried out using a mechanical testing machine LFM-L 10 kN (Walter + Bai AG, Leuningen, Switzerland). At the same time, to establish the effect of crack resistance when varying the compression rate, a series of experiments were carried out on samples in which the samples were subjected to compression at different compression rates. The influence of thermal expansion on crack resistance was determined by conducting experiments on single compression of samples heated in a chamber at a temperature of 500 °C.

Thermal conductivity coefficient measurements were conducted in the temperature range of 25 to 700 °C using the longitudinal heat flow method. The KIT-800 instrument from Teplofon, Moscow, Russia, was employed for these measurements.

The coefficient of thermal expansion for the ceramic samples, influenced by prolonged thermal exposure during 500 h of heating at 700 °C, was determined by assessing changes in the crystal lattice volume before and after thermal exposure. Using Formula (1), alterations in material properties due to high-temperature degradation were calculated based on the acquired data.

$$\beta_V(T) = \frac{1}{V_{\text{initial}}} \frac{\Delta V}{\Delta T}, \quad (1)$$

where ΔV is the change in the volume of the crystal lattice before and after high-temperature heating, ΔT is the difference in measurement temperatures, and V_{initial} is the volume of the crystal lattice of the initial sample. The crystal lattice volume was determined by

calculating the crystal lattice parameters for each test sample by analyzing the obtained X-ray diffraction patterns of the ceramic samples under study. Moreover, in the case of thermal tests, before they were carried out, the parameters and volume of the crystal lattice of each test sample were measured, after which, after thermal exposure, X-ray diffraction patterns were obtained, on the basis of which the parameters of the crystal lattice of the samples after thermal exposure were determined. Through comparative analysis, the values of changes in the volume of the crystal lattice were calculated, indicating changes in the properties of ceramics as a result of external influences.

3. Results and Discussion

In previous studies [28,29], it was demonstrated that modifications in the synthesis conditions, such as adjusting the proportions of the initial solution components, result in alterations in the ceramics' phase composition. This, in turn, directly influences the material's hardening effects and thermophysical properties. It is important to note that these studies explored the use of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ as a lithium-containing component. Changes in its concentration or variations in the thermal sintering conditions lead to the formation of impurity inclusions in the form of oxide phases. As indicated in [28], these inclusions enhance resistance to radiation-induced swelling during the accumulation of helium in the surface layer.

Figure 1 presents the X-ray diffraction results for the ceramic samples obtained from composition 1, with varying proportions of the components. These diffraction patterns reveal the impact of altering the initial component concentrations on the phase composition, specifically the changes in the relative amounts of the identified components within the samples. The X-ray diffraction data indicate that the primary phase in all three samples is the Li_2ZrO_3 (PDF-00-033-0843) monoclinic phase, and characteristic reflections of the LiO_2 (PDF-01-080-3472) orthorhombic phase are also detected. An analysis of the weight percentages of these phases, based on the determination of the weight ratio of the areas of diffraction reflections for each established phase, is detailed in Table 1. As per the provided data, an increase in the $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ mixture composition results in a rise in the contribution of the LiO_2 impurity phase, increasing from 1.4 wt% to 5.7 and 7.3 wt%. Concurrently, the assessment of structural parameters, also depicted in Figure 2, signifies an improvement in the crystal lattice of the primary Li_2ZrO_3 phase, as evidenced by a reduction in the parameters and volume of the crystal lattice. Comparable alterations in structural parameters with variations in the component ratios are also observed for the LiO_2 impurity orthorhombic phase.

Analyzing the data obtained, we can conclude that when lithium perchlorate ($\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$) is used as a lithium-containing component, the main phase in the ceramics is the monoclinic phase Li_2ZrO_3 . At the same time, at high concentrations of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ in the composition, the formation of the orthorhombic phase of LiO_2 in the form of inclusions is observed, the maximum content of which is no more than 7.3 wt%. Moreover, according to the data of works [28,29], the content of impurity inclusions, even in the case of varying thermal sintering conditions, does not exceed 10 wt%.

Therefore, upon examining the observed alterations in structural parameters, it can be deduced that as the concentration of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ increases, the ceramics become denser owing to the structural organization of the recognized phases. Furthermore, upon assessing the phase composition, an augmentation in the LiO_2 impurity phase within the ceramic composition was ascertained. This, in turn, can potentially impact modifications in the thermophysical and strength properties of the ceramics.

Figure 2 shows the data on changes in X-ray phase analysis of the studied ceramic samples obtained from composition 2 (in which Li_2CO_3 was used as a lithium-containing component). According to the assessment of structural parameters, as well as the shape and position of diffraction reflections, a change in the concentration of the Li_2CO_3 component (due to its increase in content) leads to more pronounced changes in the phase composition during mechanochemical stirring and subsequent thermal annealing. At a low

concentration of Li_2CO_3 in the ceramic composition, the presence of two monoclinic phases, Li_2ZrO_3 (PDF-00-033-0843) and $\text{Li}_6\text{Zr}_2\text{O}_7$ (PDF-01-081-2375), is observed. Simultaneously, the dominant phase, Li_2ZrO_3 , comprises over 90% of the composition. It is noteworthy that the close-to-symmetrical configuration of the diffraction reflections suggests a minimal presence of structural distortions within the structure. As the Li_2CO_3 concentration within the ceramic composition changes, there is a more than twofold surge in the $\text{Li}_6\text{Zr}_2\text{O}_7$ phase contribution in the composition when the component ratios in composition 2 are equal. It exhibits dominance, exceeding 80%, when the component ratio is 0.75 to 0.25. This shift in the phase composition signifies that the inclusion of Li_2CO_3 in the initial mixtures, followed by mechanochemical milling and subsequent thermal annealing, triggers phase transformation processes. These processes are linked to the transformation of the Li_2ZrO_3 phase into $\text{Li}_6\text{Zr}_2\text{O}_7$, all while preserving the structural motif and crystal lattice type. Simultaneously, an examination of the crystal lattice parameters and volume, as detailed in Table 2, highlights that the prevalence of $\text{Li}_6\text{Zr}_2\text{O}_7$ results in more pronounced structural ordering. The changes in lattice parameters and volume are more significant at concentrations of 0.75 to 0.25 than at other concentrations.

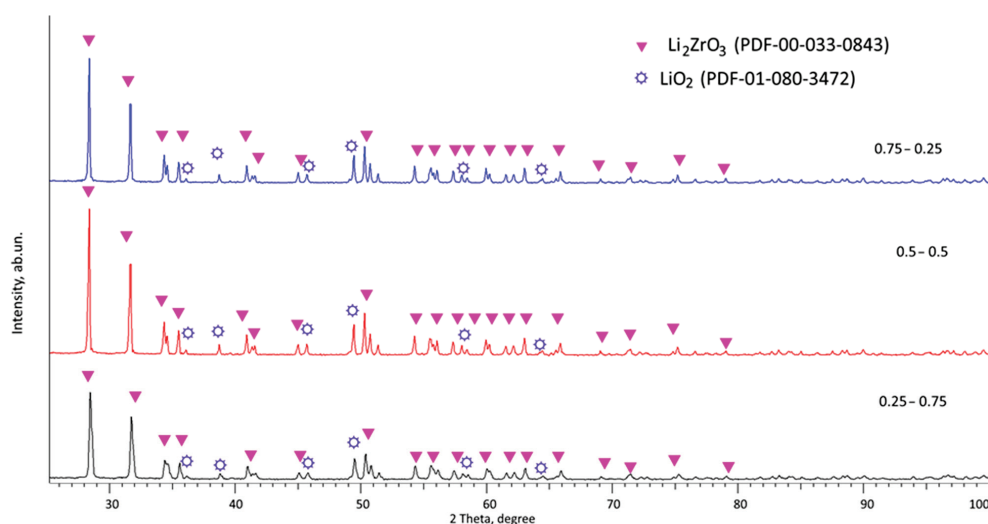


Figure 1. Results of X-ray phase analysis of the studied samples of lithium-containing ceramics depending on the variation in the concentration of the initial components.

Table 1. Data from phase analysis and structural parameters of the studied ceramics obtained from composition 1.

0.25–0.75	0.5–0.5	0.75–0.25
Li_2ZrO_3 Monoclinic, C2/c(15) (PDF-00-033-0843)		
$a = 5.3936 \text{ \AA}$, $b = 8.9584 \text{ \AA}$, $c = 5.3201 \text{ \AA}$, $\beta = 112.477^\circ$, $V = 237.53 \text{ \AA}^3$	$a = 5.3883 \text{ \AA}$, $b = 8.9548 \text{ \AA}$, $c = 5.3191 \text{ \AA}$, $\beta = 112.387^\circ$, $V = 237.30 \text{ \AA}^3$	$a = 5.3839 \text{ \AA}$, $b = 8.9477 \text{ \AA}$, $c = 5.3148 \text{ \AA}$, $\beta = 112.297^\circ$, $V = 236.89 \text{ \AA}^3$
LiO_2 Orthorhombic, Pnnm(58) (PDF-01-080-3472)		
$a = 3.9875 \text{ \AA}$, $b = 4.8722 \text{ \AA}$, $c = 2.9581 \text{ \AA}$, $V = 57.37 \text{ \AA}^3$	$a = 3.9803 \text{ \AA}$, $b = 4.8742 \text{ \AA}$, $c = 2.9558 \text{ \AA}$, $V = 57.34 \text{ \AA}^3$	$a = 3.9771 \text{ \AA}$, $b = 4.8683 \text{ \AA}$, $c = 2.9534 \text{ \AA}$, $V = 57.18 \text{ \AA}^3$

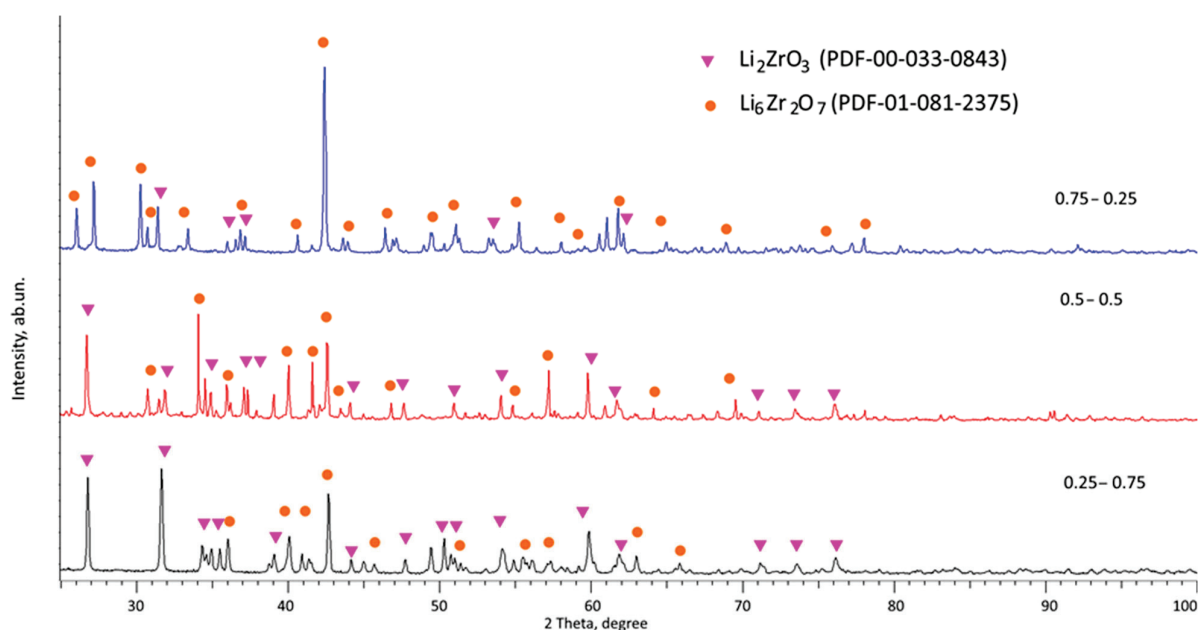


Figure 2. Results of X-ray phase analysis of the studied samples of lithium-containing ceramics depending on the variation in the concentration of the initial components.

Table 2. Data from phase analysis and structural parameters of the studied ceramics obtained from composition 2.

0.25–0.75	0.5–0.5	0.75–0.25
Li ₂ ZrO ₃ Monoclinic, C2/c(15) (PDF-00-033-0843)		
a = 5.3953 Å, b = 9.0068 Å, c = 5.3889 Å, β = 112.414°, V = 242.09 Å ³	a = 5.4006 Å, b = 8.9803 Å, c = 5.3773 Å, β = 112.171°, V = 241.51 Å ³	a = 5.3826 Å, b = 8.9645 Å, c = 5.3657 Å, β = 111.973°, V = 240.10 Å ³
Li ₆ Zr ₂ O ₇ Monoclinic, C2/c(15) (PDF-01-081-2375)		
a = 10.4216 Å, b = 5.9710 Å, c = 10.1699 Å, β = 99.994°, V = 623.25 Å ³	a = 10.3909 Å, b = 5.9559 Å, c = 10.2358 Å, β = 99.975°, V = 623.88 Å ³	a = 10.3644 Å, b = 5.9336 Å, c = 10.1937 Å, β = 100.034°, V = 617.31 Å ³

The main difference in the use of lithium-containing components in the form of Li₂CO₃ and LiClO₄·3H₂O is that when lithium carbonate is used, the phase composition of the ceramics is presented in the form of two monoclinic phases Li₂ZrO₃ and Li₆Zr₂O₇, the contributions of which vary with changes in the concentration of lithium carbonate. Moreover, in the case of using lithium perchlorate, the dominant phase in the composition of the resulting ceramics is the monoclinic phase Li₂ZrO₃, and also in the composition of the ceramics, the presence of impurity inclusions in the form of the orthorhombic phase LiO₂ is observed, the content of which varies from 1.4 to 7.3 wt%.

Figure 3 depicts the results concerning the variations in the strength characteristics of the lithium-containing ceramics studied. These ceramics were obtained from different compositions where the components were altered to achieve two-phase ceramics. The general trend observed in the strength parameter data indicates a favorable impact from

the introduction of impurity phases, such as LiO_2 (for composition 1) and $\text{Li}_6\text{Zr}_2\text{O}_7$ (for composition 2). Furthermore, in the case of composition 2, where $\text{Li}_6\text{Zr}_2\text{O}_7$ predominates in the composition of the ceramic, a more noticeable shift in strength parameters is observed. This can be attributed to the effects of structural ordering, which ranges from 89% to 93% in ceramic samples. Additionally, the formation of interphase boundaries hinders the propagation of microcracks and fractures within the ceramics. Moreover, in the case of using composition 1, the formation of the LiO_2 impurity phase at high concentrations of the lithium-containing component $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ leads to maximum strengthening of no more than 7–8%, while when using composition 2, strengthening and resistance to cracking under external load exceeds 9–11%.

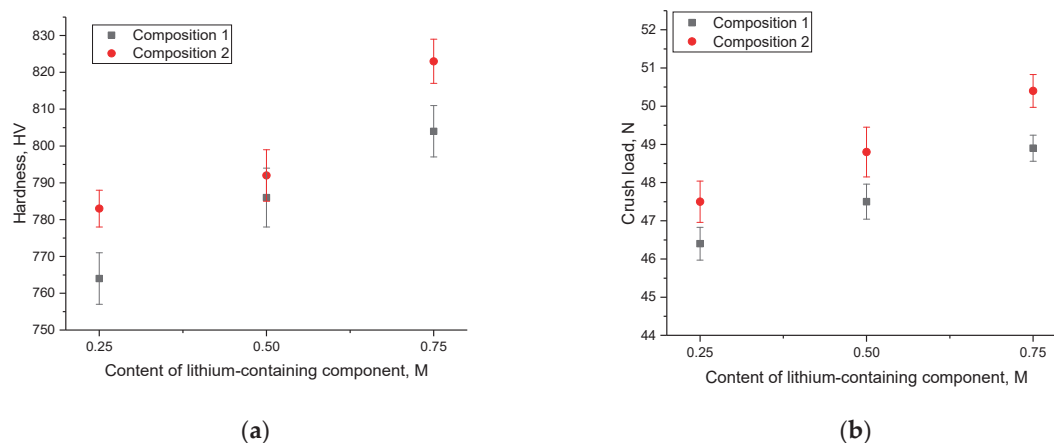


Figure 3. Results of changes in the strength parameters of lithium-containing ceramics depending on the concentration of the lithium-containing component: (a) results of changes in hardness and (b) results of changes in resistance to single compression at a compression speed of 0.1 mm/min.

Figure 4 demonstrates the results of a comparative analysis of alterations in the strengthening efficiency of ceramics obtained from different compositions, depending on the concentration of the impurity phase (in the case of composition 1— LiO_2 phase, in the case of composition 2— $\text{Li}_6\text{Zr}_2\text{O}_7$ phase). As a comparison, the values of hardness and resistance of ceramics to cracking under single compression were taken from works [28,29]. The hardening values were calculated taking into account changes in hardness values and the maximum pressure that the ceramics could withstand during a single compression at a speed of 0.1 mm/min. The overall trend observed in the data suggests that the most significant alterations in the strength characteristics of ceramics due to variations in impurity inclusions occur at low concentrations. This is true for ceramics obtained from both composition 1 and composition 2. Furthermore, in the case of composition 2, when the $\text{Li}_6\text{Zr}_2\text{O}_7$ phase dominates at high concentrations, the strengthening effect is minimal, not exceeding 10%. This can be attributed to the dominance of the $\text{Li}_6\text{Zr}_2\text{O}_7$ phase in the ceramic composition, which results in a reduction of its strengthening properties. The strengthening effect in ceramics resulting from an increase in impurity inclusions is attributed to the presence of interphase boundaries. A higher concentration of these boundaries hinders the propagation of microcracks and cleavages under external loads and compression of the samples. However, when the $\text{Li}_6\text{Zr}_2\text{O}_7$ phase prevails in the ceramic composition, a slight decrease in the rate of strength characteristics' growth is observed. This can be explained by the dominance of this phase, which has lower strength and a decrease in interphase boundaries. Thus, by analyzing the general alterations in strength characteristics depending on the production conditions (i.e., with variations in the ratio of the initial components), the following conclusion can be drawn. The formation of impurity inclusions in the form of LiO_2 or $\text{Li}_6\text{Zr}_2\text{O}_7$ results in a growth in strength characteristics (hardening of ceramics), which can be explained by the effects of interphase boundaries, the formation of which leads to a rise in resistance to cracking under external mechanical

influences. In this case, the most pronounced changes are observed for two-phase ceramics, in which the $\text{Li}_6\text{Zr}_2\text{O}_7$ phase dominates.

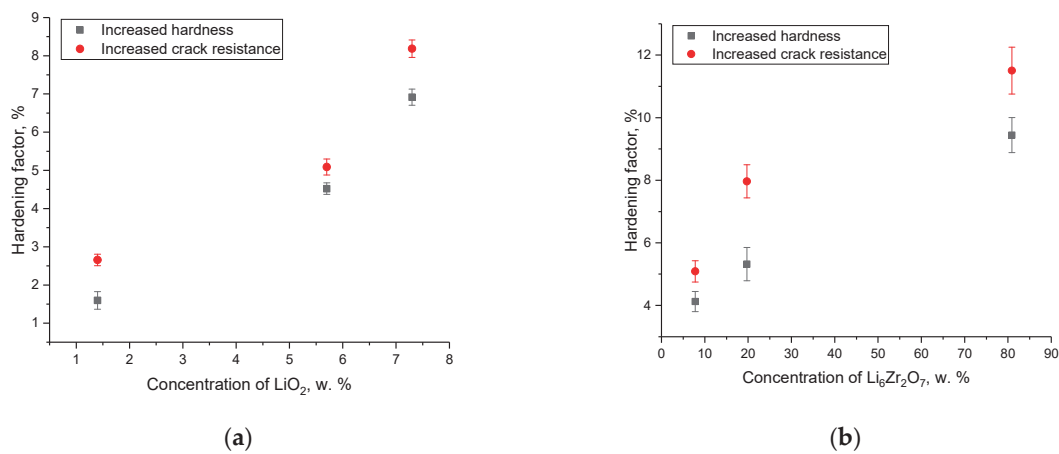


Figure 4. Results of strengthening depending on the concentration of impurity phases: (a) when changing the concentration of LiO_2 and (b) when changing the concentration of $\text{Li}_6\text{Zr}_2\text{O}_7$.

A change in the speed of mechanical influence on samples leads to an acceleration of the propagation of microcracks in the samples, which in turn leads to accelerated cracking at lower values of external load. In this case, the accelerated mechanical impact on the samples leads to the rapid spread of deformations and an increase in stress in the samples, which is accompanied by an acceleration of the destructive propagation of cracks. The results of experiments on changing the loading rate on samples under single compression are presented in Figure 5. The compression rate varied within the range of 0.1 mm/min, 0.3 mm/min, 0.5 mm/min, 1 mm/min, and 2 mm/min.

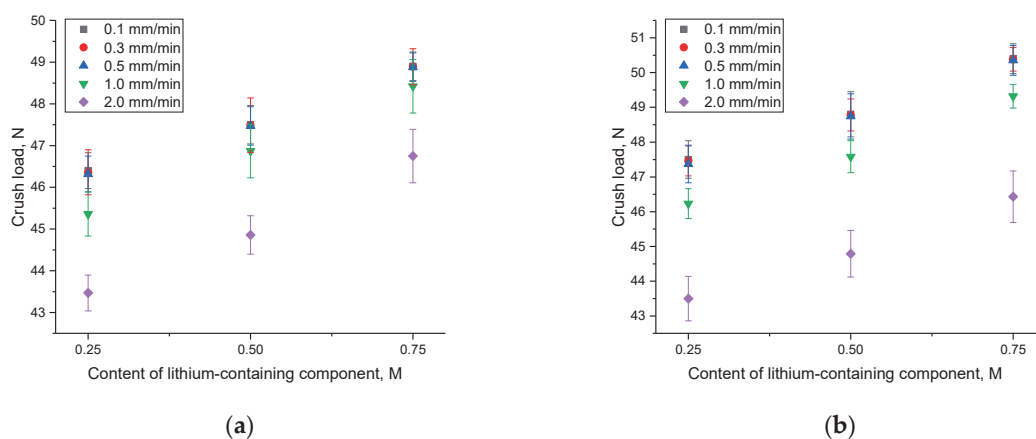


Figure 5. Results of tests on the crack resistance of ceramics when changing the rate of single compression in the case of varying ceramic compositions: (a) composition 1 and (b) composition 2.

An examination of the data displayed in Figure 5 revealed that at low compression rates, there are minimal alterations in the crack resistance value (the maximum pressure ceramics can endure during a single compression). This suggests that ceramics exhibit remarkable resistance to minor fluctuations in the speed of external influences. However, as the compression rate escalates, a reduction in crack resistance becomes evident (refer to Figure 6), signifying that at elevated rates of external influences, there is a rapid surge in the propagation of microcracks and structural deformations, resulting in cracking at lower external load values. It is worth mentioning that when the concentration of impurity inclusions increases, a reduction in the extent of changes in crack resistance at high speeds is evident. This signifies a favorable trend in the impact of interphase boundaries on resistance to structural deformations under external loads and underscores the enhanced

stability of ceramics' strength properties. Additionally, an analysis of these variations, as depicted in Figures 5 and 6, highlights that the ceramics obtained from composition 1 exhibit the highest resistance to external influences. This is evident as the decline in resistance to external influences under heavy loads is less pronounced for them.

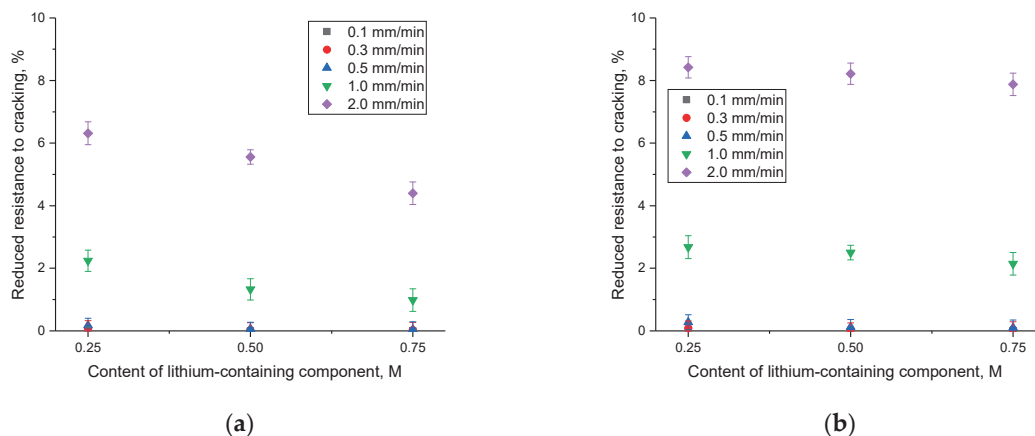


Figure 6. Results of changes in cracking resistance with changes in compression rate: (a) composition 1 and (b) composition 2.

An evaluation of the thermal conductivity variation in ceramics concerning different compositions and component concentrations is depicted in Figure 7. These measurements encompassed a temperature range from 25 to 700 °C and employed the longitudinal thermal conductivity flow measurement method. It is noteworthy that the increase in temperature from 25 to 700 °C did not yield substantial alterations in the thermal conductivity coefficient. This underscores the remarkable stability of thermophysical parameters across the entire temperature range under consideration.

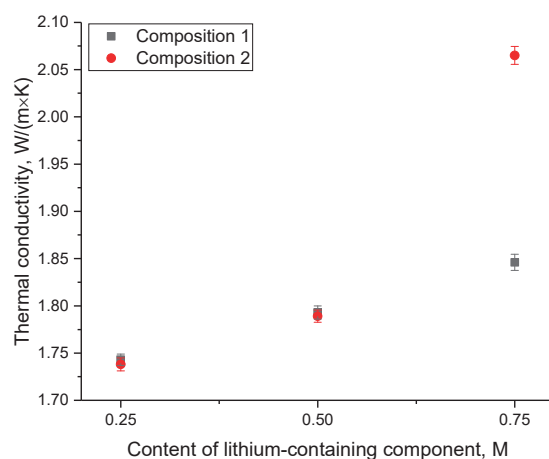


Figure 7. Results of changes in the thermal conductivity coefficient of the studied ceramics depending on changes in the concentration of lithium-containing components.

As evident from the data presented, the variations in the thermal conductivity coefficient are indicative of the beneficial impact of minor impurity inclusions, which contribute to an increase in thermal conductivity. When using Li_2CO_3 as the lithium-containing component at elevated concentrations, leading to the dominance of the $\text{Li}_6\text{Zr}_2\text{O}_7$ phase, a marked escalation in thermal conductivity is observed in comparison to composition 1. This decrease can be elucidated by the predominance of the $\text{Li}_6\text{Zr}_2\text{O}_7$ phase, characterized by superior thermal conductivity properties when contrasted with the Li_2ZrO_3 phase [30]. It is noteworthy that the thermal conductivity values for the acquired ceramic samples surpass the thermal conductivity values of analogous samples obtained through the Hot

Wire Method [31]. These disparities can be ascribed to not only the presence of interphase boundaries but also an upsurge in the degree of structural ordering. A modification in the degree of structural ordering results in fewer structural deformations in the crystal lattice, subsequently leading to a reduction in the defective inclusions that impede phonon heat transfer.

One of the important parameters for assessing the resistance of ceramics to external influences is the determination of their resistance to external influences under conditions of elevated temperatures corresponding to conditions as close as possible to operating conditions. Under such circumstances, the impact on the samples may be more severe, given that the ceramic specimens are subject to thermal expansion. This, in turn, can have adverse effects on the ceramics' strength properties and stability dynamics. The experiments were conducted using a testing apparatus equipped with a heating chamber, which facilitates the heating of samples up to 500 °C, enabling temperature stabilization, followed by a single compression test. Figure 8 illustrates a comparative assessment of variations in the resistance to single compression, both at room temperature and at 500 °C, offering insights into the data related to resistance to external forces.

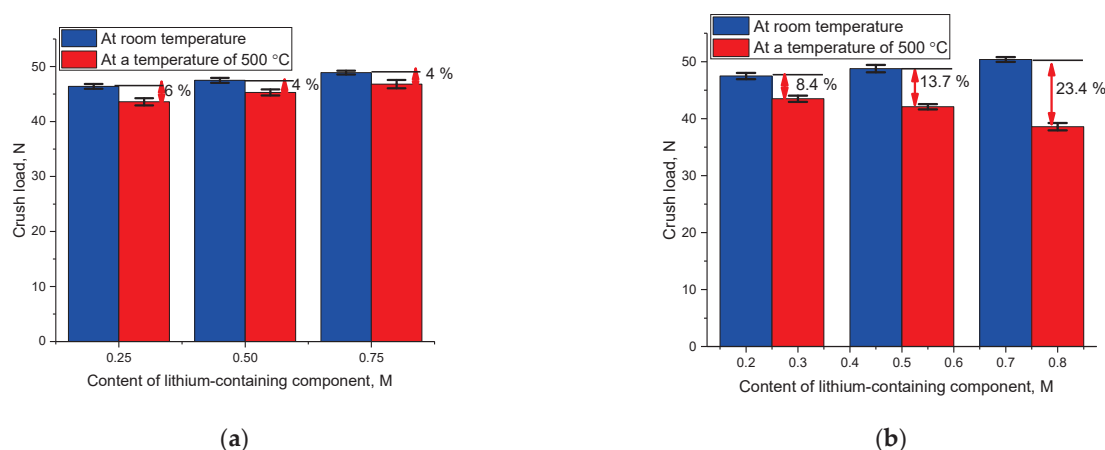


Figure 8. Results of a study of resistance to single compression at different temperatures of lithium-containing ceramics: (a) composition 1 and (b) composition 2.

The data presented indicate that when dealing with ceramics containing the LiO_2 impurity phase, raising the testing temperature from room temperature to 500 °C results in a minor reduction in the resistance to single compression (within a range of 4–6%). Furthermore, an increase in the concentration of the LiO_2 impurity phase diminishes the disparities in the data concerning variations in resistance to single compression, which can be attributed to heightened resistance to thermal expansion of ceramics when subjected to heat. For two-phase ceramics of the $\text{Li}_2\text{ZrO}_3/\text{Li}_6\text{Zr}_2\text{O}_7$ composition, an elevated concentration of the $\text{Li}_6\text{Zr}_2\text{O}_7$ phase with rising test temperatures during single compression results in a significant decrease in stability. This phenomenon can be attributed to variations in the thermal expansion of the crystal lattice, alongside a reduced resistance of ceramics to external forces stemming from thermal expansion.

Figure 9 shows the results of changes in the value of volumetric expansion of samples after thermal tests for resistance to long-term temperature heating of 500 h.

The data analysis reveals that an increase in the concentration of impurity inclusions in the form of the LiO_2 phase in the ceramic composition leads to enhanced stabilization of the crystal lattice's thermal expansion. This is substantiated by the findings on the stability of strength characteristics, as shown in Figure 9b. Conversely, the prevalence of the $\text{Li}_6\text{Zr}_2\text{O}_7$ phase in the ceramic composition (derived from composition 2) disrupts both thermal stability (significantly elevating the coefficient of volumetric thermal expansion by over 1.5 times) and the hardness of the ceramics. These findings indicate a decline in strength characteristics' stability during high-temperature aging.

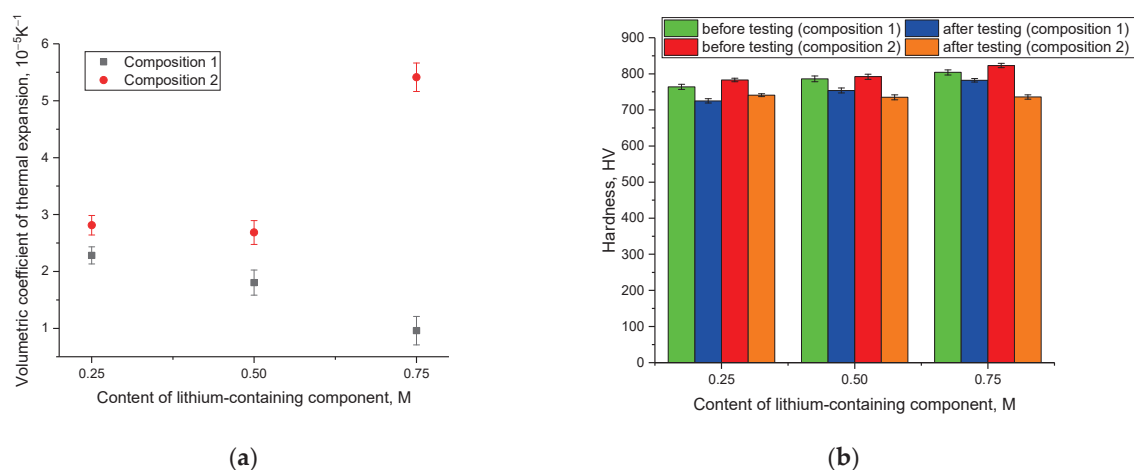


Figure 9. (a) Results of changes in the coefficient of volumetric thermal expansion and (b) results of changes in hardness values of ceramic samples after thermal stability tests.

In the case of two-phase ceramics, it was found that an increase in the contribution of the $\text{Li}_6\text{Zr}_2\text{O}_7$ phase leads to increased stability to high-temperature aging and degradation, due to increased stability to softening, as well as a decrease in the effect of thermal volumetric expansion of the crystal structure. In turn, the increase in resistance to cracking during long-term high-temperature degradation (high-temperature aging) for two-phase ceramics in the case of the dominance of the $\text{Li}_6\text{Zr}_2\text{O}_7$ phase can be explained by interphase boundaries, the presence of which is an obstacle to the propagation of microcracks under external influences (mechanical pressure), and the presence of interphase boundaries leads to an increase in resistance to volumetric thermal expansion of the crystal structure as a result of prolonged thermal effects.

4. Conclusions

During the X-ray phase analysis studies, it was determined that incorporating $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ as a lithium-containing component in the ceramic manufacturing process results in the formation of a predominant monoclinic phase, Li_2ZrO_3 , with impurity inclusions in the shape of the LiO_2 orthorhombic phase. The maximum proportion of LiO_2 impurity does not surpass 7–8%. Conversely, when employing Li_2CO_3 as the lithium-containing component in ceramics production using the proposed methodology, it was possible to create two-phase ceramics composed of monoclinic phases, Li_2ZrO_3 and $\text{Li}_6\text{Zr}_2\text{O}_7$. Analysis of mechanical tests revealed a positive effect of impurity inclusions on resistance to mechanical tests and an increase in hardness, both at room temperatures and during long-term high-temperature aging. The change in resistance to mechanical damage (under single compression) is due to the presence of impurity inclusions, an increase in the concentration of which leads to an increase in the contribution of interphase boundaries that prevent the propagation of microcracks in the samples.

The potential for practical application of the research results obtained consists of the proposed technology for creating lithium-containing ceramics by simple and inexpensive mechanochemical solid-phase synthesis combined with thermal annealing of the resulting powders. Moreover, the use of the proposed technology for creating ceramics by varying different concentrations of the initial components makes it possible to obtain ceramics with a given phase composition, the alteration of which affects the strengthening and increasing the resistance of ceramics to external influences.

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Review

Latest Developments in 3D-Printed Engineered Cementitious Composites: Technologies, Prospects, and Challenges

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Abstract

Engineered cementitious composites (ECCs) are fiber-reinforced materials with enhanced tensile strength, ultra-high ductility, crack resistance, and long-term durability. This review aims to explore the latest developments when combining ECC and 3D printing in depth. It will analyze the main technologies used, the specific properties of the materials employed, the results achieved so far, and the challenges still to be addressed for the wider deployment of these innovative solutions. The goal is to provide a comprehensive and up-to-date overview, highlighting the potential of this technology.

Keywords: engineered cementitious composites; ECC; 3D printing; 3D-printable strain-hardening cementitious composites; 3D-SHCCs; mechanical properties

1. Introduction

Concrete is by far the most used construction material on Earth, and it is characterized by a high compressive strength as well as a low tensile strength (corresponding to about 10–12% of the compressive strength) [1]. Thus, fibers have been added to concrete mixes for more than 60 years to increase the fracture toughness of hardened materials. In this case, the resistance against cracking is improved by controlling crack opening and propagation [2,3]. When opening cracks are bridged by fibers, then debonding, fiber fracture, and fiber pull-out may happen between fibers and the matrix at rupture, leading to pseudo post-cracking ductility on stress–strain curves and decreasing brittleness. The tensile strength of composite materials can also be increased due to the presence of fiber reinforcement. Engineered cementitious composites (ECCs) or Strain-Hardening Cementitious Composites (SHCCs) [4] or bendable concretes are fiber-reinforced high-performance materials designed by Prof. Victor Li and co-workers [5] at the University of Michigan in the 1990s. These materials have ultra-high tensile ductility and crack widths limited to less than 100 μm , combined with an ultimate tensile strain capacity of more than 3%, while keeping a fiber volume fraction below 2% [6], as shown in Figure 1. These features are obtained by the addition of high-strength fibers into the cementitious matrix, which dissipate the fracture energy, distribute and limit crack apertures when the material is under stress, and prevent sudden brittle failure under tensile loads [7]. The mechanical concept behind SHCCs/ECCs is the following: when the first initial microcrack appears, the fibers supply the tensile force. Then, when the fibers bridge the crack, the force equilibrium of the damaged element is restored. If the applied force rises again, a new crack will appear at a different place, and the same mechanism repeats. This process happens repeatedly, until the tensile force within the concrete specimen surpasses the fiber bridging capacity of the formed cracks. At that point, the crack will be localized, leading to material failure. This mechanism can

be activated if two micro-mechanical conditions are fulfilled: the matrix cracking strength is lower than the maximum fiber bridging capacity of the already formed cracks, and the fiber can bridge the matrix crack [8]. When the fiber/matrix interface is too weak, the fibers are simply pulled out, while when the interface is too strong, the fibers break. In these cases, the complementary energy will not be enough to create a steady-state crack, and the composite will rather display a strain softening behavior. On the contrary, for strain-hardening behavior, it is of paramount importance that the fiber has just enough freedom to deform. Then, only in this condition, complementary energy is needed to reach a steady-state crack propagation and the correlated strain-hardening behavior [8].

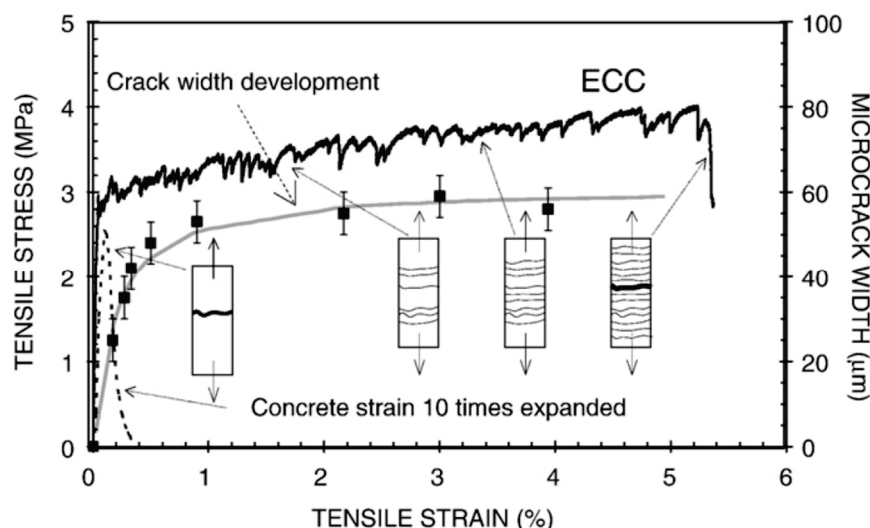


Figure 1. Tensile stress–strain curve of an ECC compared to a traditional concrete. In ECC, when the first microcrack appears, fibers supply the tensile force and bridge it. When further increasing the applied force, a new crack will appear at a different place, and the same mechanism repeats. This process goes on until the tensile force within the concrete specimen is higher than the fiber bridging capacity of the formed cracks. Then, the crack will be localized, leading to material failure. Thus, the strain value is 300–500 times higher than that of concrete. Reprinted from ref. [9] with permission from Elsevier.

ECC is in fact a family of materials that display different tensile strengths and ductility values adapted for a particular structure due to a design based on micromechanical theory (Table 1).

Table 1. Main properties of ECC [6].

Compressive Strength (MPa)	First Crack Strength (MPa)	Ultimate Tensile Strength (MPa)	Ultimate Tensile Strain (%)	Young's Modulus (GPa)	Flexural Strength (MPa)	Density (g/cm ³)
20–150	3–10	4–20	3–12	18–40	10–50	0.95–2.3

ECC can be used in new constructions and structures in place of conventional concrete for structural elements such as beams, walls, and columns. The high ductility of ECC notably increases the element's capacity to absorb impact energy, limiting structural damage. Thus, ECC coupling beams have been proposed in place of reinforced-concrete coupling beams for tall building designs in Europe, Japan, and the United States (like the Glorio-Tower, a 27-story structure located in central Tokyo, the Nabule Yokohama Tower, a 41-story skyscraper situated in Yokohama, and the Kitahama Tower, a 60-story tower located in Osaka) [10]. In addition, infrastructural elements, such as water irrigation

channels, dams, and road pavements, also use ECC to increase their operational efficiency and increase their lifespan [7]. The water permeability of ECC can be effectively controlled during the strain-hardening phase thanks to its limited crack width [11].

ECC's composition can be adapted to many structural requirements: blast resistance ability is guaranteed by high-tensile-strength ECC, while building damper properties are reached by high-compressive-strength ECC, and structural durability is ensured by tight-crack ECC [12]. Thus, using ECC guarantees increased service life, improved functionalities such as leak-proofing and energy absorption, and limiting installed costs [13]. In the case of earthquakes or to decrease the brittleness of building materials, ECC can be useful for several structural applications too. ECCs present high ductility and toughness, which make them ideal candidates for scenarios where elevated deformations and cracking resistance are requested. The use of ECC within the plastic connection zone in place of concrete and as a partial replacement for transverse reinforcement can significantly increase energy absorption capacity, joint shear resistance, and cracking response. Moreover, joint seismic resistance will be increased while simultaneously reducing reinforcement congestion, simplifying the construction [14]. Experimental results demonstrated that polypropylene fiber-reinforced ECC was able to replace transverse reinforcements in the beam–column links of railway rigid-framed bridges [15].

Several review papers on ECCs are available in the literature and deal with material properties and applications [11,16,17], durability in various environments [18], structural design and performance [19], and self-healing properties [20].

The strain-hardening ability of ECCs makes them appeal also for 3D concrete printing techniques. While conventional printable mortars show brittle failure when submitted to tensile loads, ECCs can withstand them, making them much safer for structural applications [21]. Pioneering works on 3D-printed ECCs showed promising results. Actually, printed concrete structures often need post-tensioning systems for reinforcement [22,23]. While these systems introduce positive compressive stresses in the printed materials, they also generate tensile stresses perpendicular to the direction of reinforcement [24].

Thus, this review aims to explore the latest developments when combining ECCs and 3D printing in depth. It will analyze the main technologies used, the specific properties of the materials employed, the results achieved so far, and the challenges still to be addressed for the wider deployment of these innovative solutions. The goal is to provide a comprehensive and up-to-date overview, highlighting the potential of this technology able to revolutionize how we design and build our environment.

2. Composition of ECC

The composition of ECC includes fibers, fine aggregates, cement, water, supplementary cementitious materials (SCMs), and admixtures [7]. The first ECC materials relied on high-modulus polyethylene (PE) fibers and reached a compressive strength of 65.6 MPa, with a tensile strain capacity of 5.6% [25]. Then, in the early 2000s, Li et al. [26] replaced PE fibers with polyvinyl alcohol (PVA) ones for manufacturing ECCs for structural applications. These new materials showed a tensile strength and strain capacity of up to 5.0 MPa and 4.6%, respectively. To prevent PVA fiber breakage in the cementitious matrix as a result of strong chemical bonding, their surface was coated with oil [27].

Fibers can have different features, shapes, and sizes. However, their selection should be carried out with attention, as glass, basalt, and recycled polyethylene terephthalate fibers can be degraded over time due to the high pH value of cementitious materials [28–30]. Fibers can lower the total cost of the construction of concrete structures, as they can replace traditional rebars [29,31]. In addition, the labor and maintenance costs will be reduced, as well as time during the phase of the structure's construction and the final building. The

embodied energy of the structure (the energy needed to produce a material or a building, from the quarrying and processing of natural resources to production, transport, and product delivery) will be lowered too, as the amount of added fibers is much lower than the volume of steel used for traditional rebars. Incorporating recycled fibers from waste materials is also a possible option [32].

Different kinds of fibers such as PVA, PE, and steel (SF) fibers have been proposed alone or to be used in combination for manufacturing ECCs [6]. Recently, polyvinylpyrrolidone-modified [33] or ethylene–vinyl acetate modified [34] polyethylene fibers and aramid nanofibers derived from recycled aramid fibers [35] were also proposed. However, the cost and availability of aramid fibers should be assessed for real constructions and not only for laboratory testing. Hybrid fibers with high- and low-modulus fibers can also be employed to reach an optimal balance between ultimate strength, crack width, and strain capacity [6,26,36–40]. Carbon fibers induce a low tensile ductility in cementitious materials, as the strain capacity is below 1%. However, they can be used to develop multifunctional cementitious materials because they are electrically conducting [41].

Recycled polyethylene terephthalate (PET) fibers were also investigated; however, chemical degradation concerns in alkaline environments remain even if physical and mechanical properties of fibers can be improved [42]. Natural fibers, like banana stem, coconut, Curauá, sisal, and bagasse fibers, were also studied in cementitious materials, though their durability is expected to be weak [42–44].

In composite materials, interfaces are of paramount importance during stress transfer between the fibers and the matrix. Thus, fibers for the production of ECCs must fulfill these requirements [41]:

- Amount ≤ 2 vol%;
- Diameter from 20 to 50 μm ;
- Length from 6 to 12 mm; increasing fiber length leads to poorer printability;
- Tensile strength ≥ 800 MPa;
- Elastic tensile modulus ≥ 10 GPa;
- Tensile strain capacity $\geq 3\%$;
- Limited or no interfacial chemical bond;
- Interfacial frictional bond from 1 to 6 MPa, depending on fiber strength;
- Enough corrosion resistance and chemical stability in cementitious systems;
- Stability of properties over time.

The recommended fiber diameter values lead to high aspect ratios, which favor polymeric fibers because of their production techniques. Lower diameter values limit too large aspect ratios (~ 300) that would reduce workability and hamper fiber dispersion. The fiber tensile strength governs fiber rupture and the maximum bridging stress σ_0 (initial crack sizes must be smaller than the fiber bridging capacity, σ_0) [45,46], while the fiber tensile modulus is less important in the ECC's mechanical properties before cracking. However, this modulus is important to limit the crack aperture in damaged materials [45,46]. Another critical feature is the fiber tensile strain capacity to prevent failure when mixing [47]. Fiber rupture during the mixing step reduces the fiber length and aspect ratio and limits the ECC's reinforcing performance. Moreover, fiber breakage in hardened composites is challenging for randomly oriented low-shear-strain fibers when they need to bend during microcrack bridging. For example, when forming a certain angle, most carbon fibers with a low shear strain capacity can break. Therefore, metallic and polymeric fibers perform better in this particular condition [48–50].

Fiber/matrix interfacial bonding is a key point to ensure the mechanical performance of ECCs. With a limited interfacial bond, the crack bridging ability is reduced, allowing fibers to slip out, conferring to the composite low tensile ductility and large crack widths.

On the contrary, if the bond is too strong, fibers have a tendency to break instead of sliding out, decreasing the energy absorption and strain capacity of the composite [51]. Polymeric fibers usually have low bond strengths (below 1 MPa), with the exception of PVA fibers that present a frictional bond ranging from 2 to 5 MPa. This high interfacial bond can be reduced by coating them with oil.

PVA fibers can be used to limit an excessive fiber breakage and loss of tensile ductility [27]. The targeted range of the interfacial bond is also a function of the fiber length, diameter and strength [47].

Fibers also contribute to increasing the surface area to be wet, thereby decreasing the availability of free water to lubricate cement grains, specifically for PVA fibers that are hydrophilic and have low density. On the contrary, PE fibers are usually hydrophobic and do not reduce the amount of free water in the mix, displaying a different behavior [52].

In general, lower fiber volume fractions, shorter fibers, lower w/b ratios, or nanoclay addition improve the printability of ECCs [53].

Finally, the chemical stability of fibers is of paramount importance to maintain the composites' performance over time. It is obvious that carbon and polymeric fibers are much more corrosion-resistant than steel fibers, especially if stainless or galvanized steel fibers are not used [54]. Concerning chemical stability, carbon fibers are usually inert, while some polymeric and glass fibers can degrade or undergo aging phenomena due to the high basicity of the cement paste [54]. Fibers density is not crucial due to the rather low fiber volume fraction in ECC [47]. However, since the cost of fibers is based on a unit mass, while their reinforcing effectiveness is estimated in volume [10], considering the same fiber volume fraction, high-density fibers tend to weigh and cost more than a corresponding low-density fibers.

To sum up, the key points related to fiber properties and contents for ECC production are as follows:

- PE and PVA fibers that are 20–50 μm in $\varnothing$ are commonly used for ECC manufacturing;
- Recycled aramid nanofibers seem promising as well;
- High aspect ratios are needed;
- A high tensile strength and a rather low bond strength with the cementitious matrix are desirable;
- Common dosages are 1–2 vol%;
- Chemical stability in high-pH environments is mandatory.

3. Printing Processes with Concrete

Nowadays, the use of 3D-printed concrete technology is mostly restricted to formwork printing (i.e., contouring process [55]) because of concrete's low tensile strength, poor ductility, and brittleness [56]. Thus, reinforcing techniques, such as prestressing, wire mesh, and simultaneous printing of steel bars, have been investigated [57–59]. However, all these techniques require additional labor and energy input, which is inefficient and incoherent with the 3D printing process of concrete (3DPC). Therefore, fiber addition before printing allows for self-reinforcement of the composite and makes ECCs highly compatible with 3DPC [52].

Common concrete printing methods include extrusion- and powder-based methods. In the extrusion-based technique, the raw materials are pre-mixed and extruded layer-by-layer. A high viscosity is required to confer low slump and self-support abilities, which makes this process close to extrusion. The mix must be extrudable and robust enough to maintain its shape during printing. In the powder-based technique, the raw materials are divided into two parts: on one side are the liquids, and on the other side are the powders. The liquids are dripped to the desired position by the printer layer-by-layer on the powder

bed made of cement, fly ash, sand, etc. Thus, the liquid and powder parts are printed alternatively, which is another difference between the two techniques [60–64]. Optimal contact between the liquid and the powder parts is crucial for the quality of the printed parts. In the case of 3D-printed ECCs, only the extrusion-based method is used due to the presence of fibers.

The 3DPC process is shown in Figure 2.

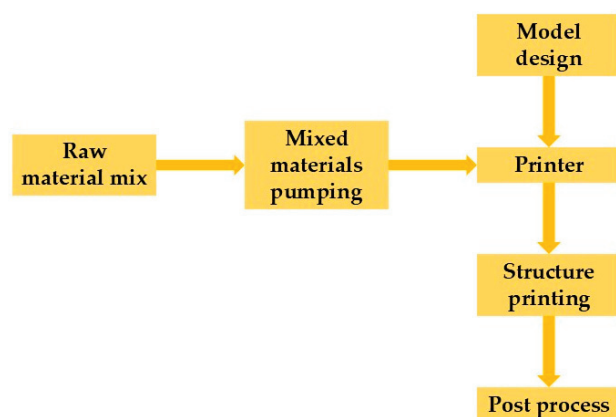


Figure 2. Flow chart of 3DPC. Figure adapted from ref. [60]. Licensed under CC BY 4.0.

In addition to the features of the printed mix, the ability of the printers and printing parameters are also important. For example, the extrusion speed should match the printing speed to control the shape and quality of printed filaments [65]. A reduced extrusion rate can produce thin layers, or even worse, discontinuous layers, while a very high speed can lead to hose blockage. In addition, waiting for a long time between printed layers allows the layer below to become too stiff to support the layers printed above, but this also decreases the bond strength between the layers [66]. Generally, printing directions show limited influence, but the distance between the nozzle and printed filaments is important [67]. A shorter distance decreases the time and space for gravity to deform filaments before encountering the bed. The accumulative deformation of each layer reduces the total height and also increases the distance between the nozzle and the last printed filament (standoff distance). Thus, the printing toolpath must be modified periodically to compensate for dynamic errors and maintain this distance. Many printing parameters of extrusion-based printing are reported in [60]. Printed filaments can have a height of 5–25 mm and a width of 30–65 mm. Meanwhile, the printing speed is different in the horizontal (H) and vertical (V) directions. These rates can vary from 20 to 157 mm/s (H) and from 1 to 13 mm/s (V). Finally, the volume of extruded material is in the range from 1 to 29 L/min, or if expressed in mass, it can reach up to 850 kg/h [60].

Several papers have studied the 3D printing process of ECCs [68–71], evidencing the strong potential of these composites as self-reinforcing printable materials [13]. However, some technical problems have still to be solved, as detailed below [21].

The key points when dealing with concrete 3D printing are as follows:

- The extrusion speed should match the printing speed to control the shape and quality of printed filaments;
- Long delays between printing one filament above an existing are not advisable;
- The standoff distance should be kept constant throughout the process.

4. Extrusion Process and Fresh State Properties

4.1. Mixing Procedure

Figure 3 shows the mix preparation procedure of a 3D-printed ECC (3DP-ECC) [72]. All the solids (binder, sand, fly ash (FA), silica fume (SF), and superplasticizer (SP)) were first premixed for 1 min. Then, 90% of the mixing water was added, and the mix was stirred for 2 min. The PE fibers were divided into three equal amounts, each one added after a 3 min mixing time step. The remaining part of the water was finally added to the mix once a uniform fiber dispersion was reached. The mixing speed was maintained constant at 48 rpm during the whole process. The fresh mixture of PE-ECC was transferred directly from the mixer to the material hopper of the 3D printer at a time of 20 min after the addition of the first batch of water.

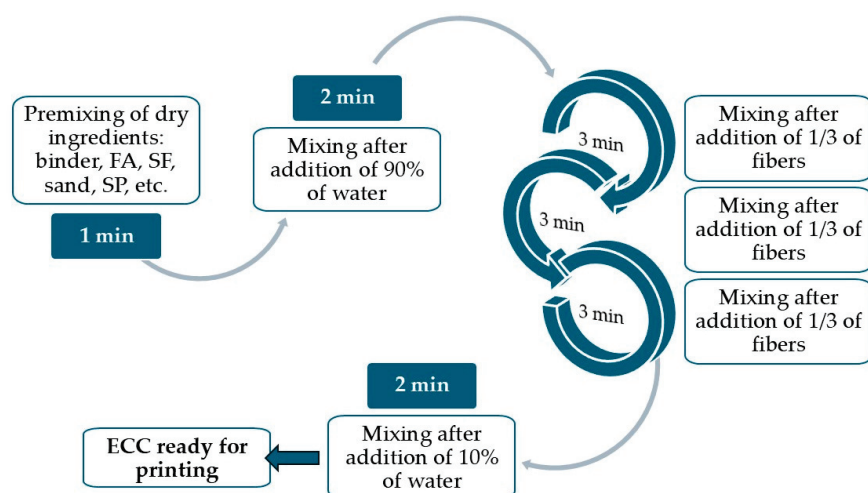


Figure 3. Mix preparation procedure of 3DP-ECC. Figure adapted from ref. [72].

In ref. [73], all the solids (binders + sand) are mixed at 140 rpm for 120 s, then water and SP are added, and the wet mix is stirred at 140 rpm for 180 s. At this point, the HPMC powder is poured and mixed for 60 s. PE fibers are added gradually while the stirring speed is raised to 420 rpm. A similar procedure was also used in ref. [69] with PVA fibers.

A slightly different mixing sequence is shown in [74], where presoaked pumice lightweight aggregates are proposed as internal curing agents. Mixing was performed in four steps (Figure 4). First, the solids (binders (cement + GGBFS) and fine aggregates) were mixed for 5 min at a low speed (140 ± 5) rpm. Then, a solution of water and SP (high-range water-reducing agent, HRWRA) was poured into the dry mix and mixed for 3 more min. At this point, presoaked pumice aggregates were added into the wet mix. Finally, PE fibers were supplemented, and mixing went on for 5 min at a low speed, (140 ± 5) rpm, before switching to a high speed, (285 ± 10) rpm, for 5 min.

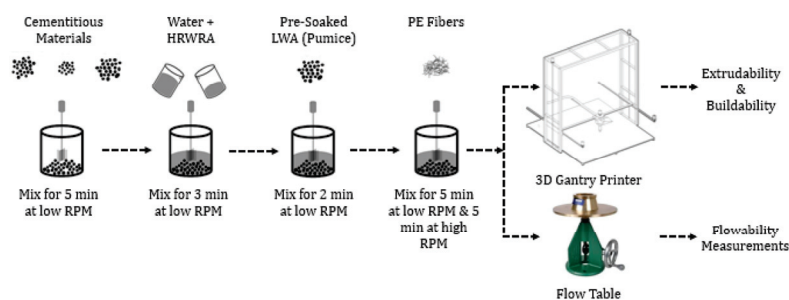


Figure 4. Mix preparation procedure of 3DP-ECCs with presoaked pumice aggregates. Reproduced from Zafar et al., 2025, licensed under CC BY 4.0 [74].

In any case, a common denominator can be found throughout the different mixing procedures: solids are first dry-mixed for 1–2 min, then water and SP are added (totally or only 90% of liquids) and mixed for 2–3 min, while fibers are progressively supplemented and mixed for several minutes at the end of the process. Finally, if remaining liquids are available, they are introduced into the mix.

4.2. Material Features

As for normal concrete, the printing process requires specific features of the material, specifically, the pumpability, extrudability, buildability, and open time (Figure 5). When printing, the material's properties evolve due to hydration reactions; thus, the strength and stiffness of the material continuously increase over time, decreasing its fluidity and increasing its bearing capacity. First, the mix should have a low initial stiffness to be pumped through the printing system and extruded, while the buildability requirement needs a material that is strong enough to bear its own weight, as well as the weight of all the successive layers on top. These two requirements are clearly in conflict from the point of view of the fresh material's properties [21].

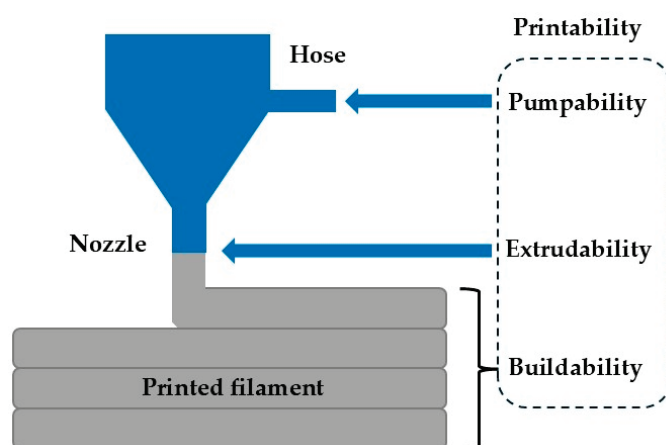


Figure 5. Workability requirements with 3D-printed concrete. Figure adapted from ref. [75]. Licensed under CC BY 4.0.

The open time should be at least 30 min, but several papers have evidenced successful printability for more than 60 min, keeping in mind that 3D printing is a time-sensitive process. The optimal open time is a balance between keeping sufficient flowability for extrusion and satisfying stiffness for buildability and shape retention of each deposited filament [76].

The open time is sometimes defined in two ways:

- Dynamic open time: The material is in the mixer at 140 rpm, simulating its movement in the hopper during the printing process.
- Dynamic–static open time: The material is kept without agitation in the mixer, and agitation is applied at 140 rpm for 30 s before measuring the consistency.

The rheological behavior of the mix is important, as well as its thixotropic character, to better understand what happens during its stay in the hopper [77]. Thixotropic materials present a reduced viscosity under shear stress (during pumping) to guarantee flowability, which suddenly increases when the stress stops (rebuilding process). The thixotropy of the mix is intimately related to its buildability [78]. The complexity of fulfilling all the requirements is well illustrated in the study by Figueiredo et al. [69,79]. The authors first adjusted the fresh material properties by means of admixtures and by varying the water-to-cement (w/c) ratio to meet the requirements of pumpability, extrudability, and open

time. However, this was not sufficient regarding the buildability. Moreover, because of the adaptation of the mechanical properties in the fresh state, the strain-hardening capacity of the ECC was compromised. This was also highlighted by van Overmeir et al. [71], who pointed out the difficulty in satisfying all the requested mechanical properties. In their research, these authors designed ECC mixes with an optimized particle size distribution to guarantee a good packing of particles and sufficient buildability and used a gantry system printing facility with a nozzle with a rectangular cross-section of $40 \times 14 \text{ mm}^2$. However, even if some samples possessed a strain-hardening capacity, mechanical tests evidenced that the composites' matrix was too strong to guarantee enough strain-hardening capacity. In general, PVA-reinforced ECCs have a compressive strength of about 40 MPa after 28 days of curing [13,68,80–82]. However, the two studied mix designs showed an average compressive strength of 51 and 56 MPa. Additionally, better buildability led to a reduction in pumpability and print quality, probably due to the arching phenomenon [83,84] in the hopper of the pump. In fact, an arch-like supported mass of bulk material formed in the reservoir pump during gravitational flow, probably due to a high initial yield stress or high thixotropic behavior of the mix. These features did not let the material flow down in the reservoir when the mix underneath was transported by the transport screw. On the contrary, the bulk material formed a self-supported arch, and no material was transferred towards the rotor–stator, producing large air voids [21].

A lack of buildability can reduce the stability and reliability of printed elements: an insufficient buildability can lead to the local failure of the material and overall collapse of the structure [85]. At the material scale, the printed filaments must withstand their own weight and the increasing weight of the successive layers placed on them. Therefore, fast development of the strength and stiffness capacity is needed after filaments are placed [85–88]. Limited and controllable deformation under load facilitates the freshly printed filament to stick to the previous layer and to have sufficient adhesion with it [89]. However, excessive deformation undermines the stability of the structure and results in overall failure. Once the vertical stress in the filament exceeds its capacity, the filament will yield or deform significantly, producing a change in its cross-sectional shape and instability of the structure. At the structural scale, even if the stress in a filament is maintained below the stress threshold, without causing any rupture, the cumulative strain and stress due to all the layers may weaken the shape control and structural stability of the printed part, leading to the collapse of the element, especially in slender structures sensitive to self-buckling [85,89–92]. To estimate the structural failure, Suiker [93] proposed mechanical models that take into consideration elastic buckling failure of printed structures. Roussel [85] calculated the critical height, H_c , at which self-buckling can occur in a slender structure by means of Equation (1):

$$H_c \approx \left(\frac{8EI}{\rho g A} \right)^{\frac{1}{3}} \quad (1)$$

where E is the elastic modulus of the fresh material, I is the moment of inertia, ρ is the density of the fresh material, g is the acceleration of gravity, and A is the horizontal cross-sectional area. The estimated height value can be used to set the nozzle standoff distance when printing and avoid structural instability problems [64].

The simplest method to assess buildability consists of comparing the maximum height or number of filaments that can be piled up under the same printing job settings [94–99]. Nevertheless, printing is needed to assess the buildability of the mix, which consumes time and material. At the same time, vertical strain or deformation of printed filaments also serves as an indirect evaluation index [100–102]. Another strategy is to indirectly estimate the buildability of materials by measuring some of their properties, like green strength [90,

103–108], yield stress [109–112], penetration resistance [111,113] of wet material, etc. The cylinder stability test, where a concrete cylinder is deformed after dynamic tamping or under static loading, has also been proposed to assess shape stability [96]. In ref. [114], the slump value determined according to the ASTM standard C1437–15 (Standard Test Method for Flow of Hydraulic Cement Mortar) was used to assess the buildability of LC3-ECC mixes and was related to the shape retention capacity of a large structure without collapsing during the 3DP process. However, these indicators can only give information at certain time frames, independently from printing parameters [76]. Thus, a quantitative evaluation approach for buildability of 3DP-ECC, considering both the material and the structural scale, is described in [76]. At the material scale, a constant-shear-rate test, incremental loading test, and green strength test were used and showed that the risk of material failure was low, at least for the investigated material compositions [76]. These authors used the following printing parameters: when the structure buildup speed was 3 layers/min over a 0.5 m straight line printed with a nozzle travelling speed of 1.5 m/min, the corresponding uniaxial loading rate was 1.5 N/min. At the same time, for a 10 layers/min buildup rate, the loading speed was around 5 N/min. The mix design was based on 605 kg/m³ of ordinary Portland cement (OPC), 678 kg/m³ of FA, 372 kg/m³ of sand, 1.8 kg/m³ of SP, a water-to-binder (w/b) ratio of 0.24, and 1.5 vol% of PVA fibers.

At the structural scale, the critical height for self-buckling can be estimated based on the evolution of stiffness over time. Premature self-buckling can be limited by proper design and printing parameters for a given material behavior evolution. The critical height of a printed structure at self-buckling is a function of time (Equation (1)), considering that the elastic modulus of the material can be estimated according to Equation (2):

$$E(t) \approx 2.65 \cdot t + 43 \quad (2)$$

where $E(t)$ is the elastic modulus of the material as a function of time in kPa, and t is the time in min.

According to Kruger et al. [115], printed cementitious materials should have an initial strength in the range from 1 to 10 kPa and a stress development ranging from 0.05 to 0.5 kPa/min during the first 60 min.

A change in printing parameters leads to variation in the microstructure of 3DP-ECC, which, in turn, influences the material's properties (Figure 6).

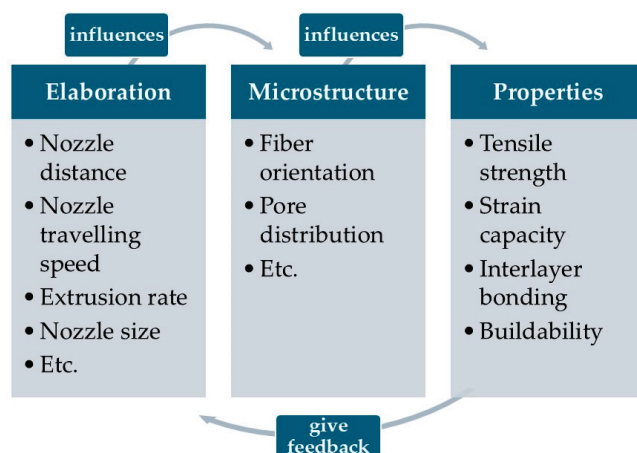


Figure 6. Influence of printing parameters on ECC's microstructure and properties. Figure adapted from ref. [72].

In [77], apart from extrudability and buildability, the workability, another crucial parameter in 3D printing, was evaluated by means of the consistency table according to the

EN 1015–3 standard [10] at 0, 10, 20, 35, 45, and 60 min. A shape retention test was carried out as follows: the freshly extruded mixture was introduced into a mini-slump cone, which was lifted after 1 min. Then, a weight of 465 g was placed on top, and the material was allowed to deform under the load for 45 s. Then, another weight was added to the previous one to reach a final mass of 700 g, and the material was allowed to deform for another 45 s. After each rest time of the mix, the expansion of the material was measured in two directions at 90°. The smaller the diameters, the higher the shape holding capacity of the material [77].

The layer-by-layer printing process produces weak interfaces, which result in a pronounced anisotropy of the structures [5]. Nonetheless, the fibers in 3DP-ECC materials tend to be aligned according to the printing direction, leading to the absence of fiber penetration between layers [6,7]. This anisotropy is higher than in 3DPC. The influence of mix compositions on the fresh properties and anisotropy of 3DP-ECCs, the shape retention ability, and the anisotropy of the compressive strength of 3DP-ECCs with different amounts of fly ash (FA) and hydroxypropyl methyl cellulose (HPMC) were investigated in [116]. HPMC allowed the shape of the printed filaments to be maintained: an addition of 0.35% resulted in a total deformation of 2.67%. HPMC also increased the viscosity and the thixotropy and prevented segregation when pumping [68]. In addition, it acted as a water reservoir when the mix was still fresh and also contributed to the internal curing effect of cementitious composites [79]. Contrarily, when the content of FA increased, the shape retention decreased from 5.3 to 45%. 3DP-ECC materials presented significant anisotropy in terms of compressive strength in different directions according to the following order: $z > y > x$, with the z direction showing the highest compressive strength, while the x direction had the lowest one [116].

Microsilica, ground silica flour, and attapulgite nanoclay can also be added to improve early strength and thixotropy and enhance cohesion [68]. The silica fume content and the water-to-solid ratio are also important parameters to optimize fresh properties and strain-hardening behavior [117]. Calcium aluminate and sulphoaluminate (CSA) cements can increase the early flowability and the early strength [68]. Sodium silicate can also be used in place of CSA cement, even if its cost is higher, but the effect is strong, and a reduced amount is required to make OPC rapidly set after deposition.

4.3. Influence of Nozzle Size

In [53], three rectangular nozzles with the same cross-sectional area of 150 mm² were tested to investigate the effect of the extrusion nozzle size on the 3D printability of a mix made with 0.6 OPC, 0.3 FA, 0.1 microsilica, 0.2 sand, 0–0.5% nanoclay, a 0.325–0.375 w/b and 1–2 vol% PE fibers that were 24 µm in diameter and 9, 12, and 18 mm in length. The nozzle with a smaller width-to-height ratio (5 × 30 mm²) showed a higher probability of smooth printing with a continuous and non-cracked layer. However, the nozzle size had less influence on fiber agglomeration and clogging in the pump screw.

4.4. Rheological Properties

ECC pastes behave as non-Newtonian fluids. Usually, the Bingham model finds agreement for describing the non-Newtonian fluid rheology of cement pastes (Equation (3)) [117–119]:

$$\tau = \tau_0 + \eta \dot{\gamma} \quad (3)$$

where τ_0 and τ are the yield stress and shear stress, respectively, in Pa; η is the plastic viscosity, in Pa.s; and $\dot{\gamma}$ is the shear rate, in s^{−1}.

Rheological properties can be determined by means of a rheometer. However, the fiber dispersion of ECC significantly impacts its rheological properties. Fibers also increase

the yield stress at rest times, as well as the plastic viscosity and the dynamic yield stress of cementitious composites [52]. Therefore, the printability and fiber dispersion of 3DP-ECC need to be evaluated in a different way.

The yield stress should be lower than the maximum shear force exerted by the extrusion system to guarantee a smooth extrusion process of the mix during printing. At the same time, it should be higher than the weight of the upper extruded filament to maintain its shape. Thus, these two requirements must be fulfilled by the yield stress (Equation (4)) [118]:

$$\rho gh(t) \leq \tau_0 \leq P_{extrusion} \quad (4)$$

where ρ is the density of the mix, in g/cm³, g is the gravity constant, equal to 9.8 N/kg, $h(t)$ is the height of printed layers, in mm, and $P_{extrusion}$ is the maximum shear force of the printer extrusion system, in Pa. It is also worth mentioning that printed materials commonly contain accelerating agents like sulphate aluminum cement to rapidly confer the extruded filaments enough strength and stiffness. The self-weight pressure of two printed layers can be set as the lower boundary (Equation (5)):

$$\rho gh(2) \leq \tau_0 \leq P_{extrusion} \quad (5)$$

where $h(2)$ is the height of two printed layers, in mm. The theoretical relationship between slump and yield stress was proposed by Hu et al. [120] and is described by Equation (6):

$$\tau_0 = \frac{\rho(H-s)}{0.27} = 3.7 \cdot \rho(H-s) \quad (6)$$

In this way, the yield stress can be related to the slump (Equation (7)):

$$s_1 \leq s \leq s_2 \quad (7)$$

where H is the slump cone's height, in mm; s is the slump, in mm; s_1 represents the lower boundary of the slump, in mm; and s_2 represents the upper boundary of the slump, in mm [121].

In [122], the highest flowability in ECC is achieved with a sand-to-binder (s/b) ratio of 0.35 and a superplasticizer-to-binder (SP/b) ratio of 0.30. The ECC mix with PVA fibers reached a compressive strength of 41.71 MPa after 28 days. This result was due to the good dispersion of fibers within the cementitious matrix during the mixing step thanks to the use of a superplasticizer [122].

To adapt the workability and homogeneity of the fresh mix, two admixtures, i.e., superplasticizer and thickener (or viscosity modifier), must be used [68,123,124]. The thickener changes the rheology of the material and contributes to dispersing the fibers. Then, its influence on tensile properties is high. A high thixotropy is helpful to guarantee that the extruded layers firmly stack up [13]. Therefore, thixotropic additives, like HPMC, can influence printability [73]. The thickener retains water and reduces capillary water absorption [125]. However, its use causes an increase in the void content of about 20 vol% in mortars, which obviously decreases the mechanical properties [126,127]. For example, in [128], the tensile strength and the tensile strain capacity first increased and then decreased with the addition of HPMC, and the optimum value was 0.05%. However, HPMC addition had negative effects on the initial cracking strength and the elastic modulus. When the HPMC content reached 0.05%, the ECC samples showed the ability to saturate multiple cracking, and the crack number, the average crack size, and the average crack spacing almost reached the optimal level. Nevertheless, due to the entrapped air effect of HPMC, the matrix compactness was altered, and the density gradually decreased when increasing

the HPMC content. The matrix fracture toughness was in line with the variations in the initial cracking strength and the compressive strength. The addition of HPMC weakened the frictional bond strength as well as the slip-hardening coefficient during the slippage of fibers from matrix. The effective fiber-bridging effect was the reason for the observed improved tensile properties [128].

Pretreated incinerator bottom ash (IBA) was also used for preparing 3DP-ECCs and showed a positive effect on the fresh properties of the material by decreasing the spreading diameter and the dynamic stress, while the plastic viscosity increased, indicating a better printability [129]. The pretreated IBA led to an increase in tensile strength by 7%, while the compressive strength decreased by 22%. The early-age shrinkage of 3DP-ECC was significantly decreased by adding pretreated IBA. The autogenous shrinkage at 7 days and the plastic shrinkage at 24 h were decreased by 56% and 30%, respectively. The substitution of IBA influenced the hydration products and pore structure of 3DP-ECC mainly at the early age: for example, the content of portlandite at 3 days and the content of calcium carbonate at 7 days were decreased by 30.9% and 29.9%, respectively. The volume fraction of macropores increased by approximately 300% and 500% at 3 days and 7 days, respectively, which caused a reduction in compressive strength as well as early-age shrinkage. Due to the lack of formworks, once printed, 3DP-ECC is directly exposed to the environment and undergoes a higher shrinkage compared to traditional concrete. Thus, IBA can mitigate the risk of cracking due to shrinkage, especially for on-site 3D printing applications in real environmental conditions [129].

4.5. Printing Parameters with ECCs

For printing, pumpable mixtures with the requirement of the highest bulk yield stress and extrudability (i.e., below the shear yield stress limit) should be preferred because they should result in excellent buildability [69]. Thus, the use of rheology-modifying agents is of paramount importance for the development of ECC composites with dough-like texture in the fresh state [69]. Among the influencing parameters, the liquid-to-solid ratio of the mix is highly pertinent to the shape stability of printable mixtures, rather than the superplasticizer content. The particle size distribution and the ratio of liquid to total surface area of all solids are also more pertinent than the addition of rheology-modifying agents. In addition, these agents do not significantly influence the mechanical properties of printed composites [69]. Mixtures with a 2 vol% of PVA fibers with a bulk yield stress of 34.26 kPa could pass through a 5 m hose in ref. [69].

In [119], the fresh ECC mix (20 min after water addition) with a w/b of 0.24 and 1.2 vol% of PVA fibers and an initial spread diameter of 132 mm was filled into a cone and showed, after cone removal, a spread diameter under a weight of 600 g equal to 106 mm. This mix was used to print a 1.5 m high twisted column with 150 printed layers of 10 mm.

For buildability measurements, a 10-layer structure was printed with a rectangular printing nozzle ($10 \times 100 \text{ mm}^2$) in [114]. Each layer was theoretically 10 mm in height (h_d) and 100 mm in width (w_d), and the real height (h_p) and width (w_p) of each printed layer were measured by means of a ruler and compared with the theoretical ones. Then, the relative deviation in height (d_h) and width (d_w) were calculated by means of Equations (8) and (9), respectively:

$$d_h(\%) = \frac{|h_d - h_p|}{h_d} \times 100 \quad (8)$$

$$d_w(\%) = \frac{|wh_d - wp|}{w_d} \times 100 \quad (9)$$

The total height of the 10 printed layers was 99 mm, 98 mm, and 97 mm for mixes with 2.0%, 1.5%, and 1.0% PE fibers, respectively. The corresponding deviation value, d_h , was equal to 2% at maximum, while the deviation width, d_w , was no more than 6%. All the prepared mixes in [114] showed excellent buildability and shape-retention ability when printing 10 layers at a time.

A uniaxial unconfined compression test (UUCT), on a cylinder with a diameter of 70 mm and a height of 140 mm, was also proposed to evaluate the green compression strength of printable mortars in [71]. When the UUCT is performed at different time intervals after mixing, it can determine the initial yield strength and apparent Young's modulus as well as their evolution over time. Young's modulus appeared to be the critical fresh mechanical parameter for the two developed mixes and was equal to 209.3 kPa (mix A) and 54.6 kPa (mix B). Both mixes had high initial yield stress and presented no plastic failure during buildability tests.

Another way of assessing buildability was illustrated in [130]: a 24-layer structure with a height of 120 mm and a horizontal width of 28 mm was printed, and the slump ratio (β) of the total stacking height after 48 h of printing was calculated. When β was higher than 9%, the buildability was considered unacceptable, while if β was below 3%, the proposed lightweight ECC possessed ideal buildability and maintained stability without huge deformation during the printing process.

In [131], a six-axis robotic arm with an extruder and a nozzle of $5 \times 30 \text{ mm}^2$ printed with a linear speed of 15 mm/s. The mix was made of 0.6 OPC, 0.3 FA, and 0.1 SF, the sand-to-binder ratio was 0.2, and the nanoclay-to-binder ratio was equal to 0.005, while the water-to-binder ratio was 0.3. Finally, a 1 vol% of PE fibers with a diameter of 24 μm and a length of 12 mm was added. The printing process was strictly controlled, and the distance between the nozzle and the printed layers was minimized to improve the interface between the layers as well as the quality of printing.

A mix made with 656 kg/m³ of OPC 52.5, 118 kg/m³ of SF, 604 kg/m³ FA, 410 kg/m³ of sand with a maximum size of 1.18 mm and a fineness of 1.62, 1.5 vol% of ultra-high-molecular-weight PE fibers, and a water-to-binder ratio of 0.26 was extruded through a 30 mm diameter nozzle and used as a formwork for casting concrete in [132]. The printed filament height was in the range from 10 to 30 mm, and the speed rate of the nozzle was 40 mm/s. The interfacial bond strength between the 3DP-ECC and cast concrete was influenced by the fiber content and filament printing height, showing an improvement and then a reduction. It was then also observed that there was a limited difference in the width of the interfacial transition zone between the printed and cast concrete when the filament printing height was 15 mm and 20 mm, while the width was reduced when the filament printing height was 10 mm. The same mix design and printing conditions were then used to investigate the interlayer bonding properties in [133]. Elliptical and flattened pores were observed within the interfaces, and their sphericity was influenced by the printing height of the filaments: a higher thickness increased the pore sphericity. When the fiber content was equal to 1.5 vol% and the printing filament height was 15 mm, the porosity at the interface was reduced. When the fiber content increased and the filament printing height rose, the interlayer interface bonding strength first increased and then decreased, evidencing the importance of an appropriate filament printing height and fiber volume content.

A mix based on 259.2 kg/m³ of CEM I 42.5, 604.9 kg/m³ of blast furnace slag, 864.1 kg/m³ of limestone powder, 26 kg/m³ of PVA fibers (2 vol%), 5.1 kg/m³ of HPMC, 17.3 kg/m³ of SP, and 345.6 kg/m³ of water was printed in filaments that were 10 mm in thickness and 50 mm in width at 100 mm/s in [79]. The initial bulk and shear yield stress was equal to (34.74 ± 5.20) kPa and (4.41 ± 0.18) kPa, respectively. The time interval between two contiguous filaments was 3, 2, and 4.5 min, respectively, for samples

printed with two, three, and four layers. After 28 days of curing, a compressive strength of (44.09 ± 4.33) MPa was reached by the printed layers perpendicular to the load, while it was equal to (41.93 ± 1.88) MPa for the printed layers parallel to the load. Moreover, these average compressive strength values were close to that of cast samples. Extruding a filament against the previous one was a good strategy to increase its bond strength as well as to orient the fibers perpendicular to the printing direction.

To sum up, the key points related to the fresh mix properties are as follows:

- The order of mixing the products is fundamental in 3DP-ECC: First, solids are dry-mixed, then water and SP are added, and fibers are progressively introduced in the mix. Finally, the VMA is supplemented;
- The open time should be 30–60 min and should be compatible with buildability;
- An optimized particle size distribution guarantees a good packing of particles and contributes to buildability;
- The mix should have a low initial stiffness to be pumped and extruded, while the buildability requirement requires a stiff material able to bear its own weight;
- Fibers increase the yield stress at rest times, as well as the plastic viscosity and the dynamic yield stress;
- HPMC increases the viscosity and the thixotropy and prevents segregation when pumping as well as favors the internal curing effect;
- A high thixotropy is helpful to guarantee that the extruded layers firmly stack up;
- Microsilica, ground silica flour, and attapulgite nanoclay improve early strength and thixotropy and enhance cohesion. The silica fume content and the water-to-solid ratio are important parameters to optimize the fresh properties and strain-hardening behavior. Calcium aluminate and sulphoaluminate cements increase the early flowability and the early strength;
- The liquid-to-solid ratio of the mix is fundamental for the shape stability of printable mixtures, rather than the superplasticizer content;
- A nozzle with a smaller width-to-height ratio has a higher probability of smooth printing;
- The maximum printable height value can be estimated and used to set the nozzle standoff distance when printing to avoid structural instability problems;
- ECC pastes behave as non-Newtonian fluids, whose behavior is usually described by the Bingham model;
- The yield stress of the mix should be lower than the maximum shear force exerted by the extrusion system;
- The yield stress can be related to the slump value.

5. New Compositions

5.1. Use of Limestone-Calcined Clay Cement

Manufacturing ECC requires a high cement content because of the absence of coarse aggregates, contributing to high carbon emissions and energy consumption. Thus, more sustainable ECC compositions must be developed for the 3D printing process [52]. To this aim, limestone-calcined clay cement (LC3), a new cement based on limestone, calcined clay, and cement, appears to be a sustainable alternative to ordinary Portland cement (OPC) [134–136]. The tensile strain capacity of LC3-based ECC reached 6%, with an average residual crack width below 50 μm , and the compressive strength reached 32 MPa [137]. Lightweight engineered cementitious composites with LC3 cement (LL-ECC) and polyethylene (PE) fibers were studied in [52]. The optimal mixture for 3D printing due to rheological properties and suitable open time range was the LL-ECC with a 1.25% PE fiber content. Moreover, the compressive strength and fracture toughness of the printed LL-ECC-1.25% showed weak anisotropy. Additionally, the printed LL-ECC-1.25% evi-

denced a higher shear strength and energy dissipation ability with respect to mold-cast LL-ECC-1.25%. These results were attributed to the relatively high interlayer bond strength (2.62 ± 0.18) MPa, the fiber orientation, and the piling up of layers due to the printing procedure. Moreover, printed LL-ECC-1.25% beams presented 40% higher flexural strength than cast samples with close damage patterns and a limited anisotropy. The cracks in the printed beams were fully developed and spread throughout the section. A gantry-type 3D printer was used with an extrusion rate of 0.9 L/min and a nozzle travel speed of 30 mm/s. Finally, LL-ECC-1.25% was more sustainable than regular OPC-ECC: its embodied energy was equal to 3.952 MJ/kg, while the carbon footprint was 483 kg/m³ [52].

On the contrary, in [138], the tensile strength and strain capacity of printed LC3-ECC decreased by 16.6–22.7% and 43.3–54.6%, respectively, compared to that of cast specimens. This was mainly due to a heterogeneous orientation of the PVA fibers during printing. The loss in strain capacity was more pronounced than that of the tensile strength, highlighting that the bridging ability of the fibers was decreased. Moreover, the compressive and flexural strengths presented significant anisotropy, which became more prominent at 28 days with respect to 7 days. Moreover, the x/y/z compressive strengths and y/z flexural strengths of the printed LC3-ECC were higher than those of the cast specimens. A lower flexural strength was noted in the x-direction and was attributed to the presence of the printed interfaces. SEM observations and X-CT scan images evidenced that the pore structure of the printed LC3-ECC was denser than that of the cast specimens. The number of pores bigger than 0.25 mm in the printed LC3-ECC was relatively lower than that of the cast specimen, but the pores in the printed samples were rather ellipsoidal, resulting in anisotropic properties of LC3-ECC. Compared to the mold-cast samples, 3DP improved either the compressive and the flexural strength of LC3-ECC, as well as its strain-hardening and multiple cracking behaviors. The 3D concrete printer head moved with a speed of 50 mm/s, and the extrusion rate was 1.5 L/min, while the nozzle had a diameter of 15 mm. The printed layers had a height of around 7.0–7.2 mm.

In [139], two ECC formulations, LC3-ECC and calcium sulphoaluminate–ECC (CSA-ECC), were designed to be printed and compared with cast materials. Cast LC3-ECC showed a gradual stabilization of shrinkage during the 28-day air-curing period, while CSA-ECC evidenced an expansion behavior either under air-curing or wet-curing conditions. Moreover, 3-day wet curing after demolding led to a consistent expansion of CSA-ECC. The experimental results highlighted that when keeping the same compositions and curing conditions compared with that of cast ECC, printed ECC had a greater shrinkage or a decreased expansion. The main reason was the exposition of the material to an external environment at an early stage. On the contrary, wet curing or water spraying during the first hours after printing CSA-ECC led to an expansion of the material. Considering the important expansion observed in cast CSA-ECC, the increase in the wet-curing time after printing guaranteed a certain expansion. The designed LC3-ECC and CSA-ECC materials had a much lower carbon footprint (by 75% and 59%, respectively) than the concrete reference and lower embodied energy than classic M45-ECC (by 73% and 67%, respectively; M45-ECC had a tensile strength of 4.5 MPa and a strain capacity of 3% at 28 days). In addition, when taking into consideration the higher mechanical properties of ECCs to reduce the size of the structure with the aim of reducing material consumption, the embodied carbon and energy in printed ECC structures will be significantly reduced with respect to that of concrete structures. The mechanical properties of printed ECC surpassed those of cast specimens, and printed CSA-ECC samples demonstrated similar or even higher mechanical properties than printed LC3-ECC. However, when carbonation was actuated, the flexural performance of printed ECCs decreased. Thus, carbonation curing used to mitigate the carbon footprint of materials should be performed with care.

Moreover, the open time of a fresh mixture can change when using different printing setups, requiring the adjustment of the proportion (or CSA dosage) to satisfy specific printability requirements. Finally, the impact of a prolonged wet-curing time on the expansion behavior of CSA-ECC requires further investigation [139]. A rectangular nozzle was mounted on a six-axis robotic arm which moved at 3 m/min. The layers were 10 mm in height and 30 mm in width.

5.2. Strain-Sensing Cements

Recently, functionalized cementitious materials with strain-sensing ability were also 3D-printed [140]. The cementitious materials were made by adding graphite (G), milled carbon microfibers (MCMFs), and/or chopped carbon microfibers (CCMFs) to reach electrical percolation and activate a piezoresistive effect. The results showed that electrical percolation was reached by using a mix of G and CMFs. In particular, with respect to the weight-to-cement percentage (wt%), optimal mixtures were obtained when adding 10 wt% G and 0.5 wt% MCMF for G+MCMF specimens, 10 wt% G and 0.125 wt% CCMF for G+CCMF specimens, and 10 wt% G, 0.250 wt% MCMF, and 0.125 wt% CCMF for hybrid filled G+MCMF+CCMF specimens. The 10G250M125CCMF mixture (10 wt% G, 0.25 wt% MCMF and 0.125 wt% CCMF) demonstrated optimal sensing performance and mechanical strength. Specifically, a static gauge factor of 622, a resolution of $167 \mu\epsilon$, an accuracy of $19.24 \mu\epsilon$, and a Young's modulus of 798 MPa were measured [140]. The gauge factor is the ratio of the relative change in resistance divided by the strain.

5.3. Rubberized ECCs

In recent times, rubberized ECCs were proposed in [141]. All the compositions investigated reached a compressive strength of 25 MPa, required for structural applications, except for the one with 15% rubber. Rubberized ECC containing 5% waste crumb rubber (CR) was 3D-printed and showed strong anisotropy, highly evident during flexural tests. Testing in parallel to the fiber direction resulted in 3 and 4% higher early-age and lateral compressive strengths, respectively, compared to the z direction, perpendicular to the fiber direction. In addition, the printed specimens showed less stiffness, more deflection capacity, a prolonged strain-hardening region, higher peak stress, and higher post-peak stress compared to the mold-cast ones. Moreover, flexural tests revealed that when loaded according to the z direction, where the fibers were parallel to the longitudinal axis of the printed sample, increases of 104% and 47% in the 7- and 28-day flexural strengths, respectively, were evidenced with respect to the specimen printed in the z' direction, where the fibers were mostly perpendicular to the longitudinal axis of the printed specimen. This could be due to the ability of the fibers to resist tensile stresses parallel to the longitudinal axis of the sample when undergoing flexural tests, along their length. Compared to the mold-cast specimen, 158% and 75% higher 28-day flexural strengths were noted for the printed specimens in the z and z' directions, respectively, which were due to the alignment of the fibers during the extrusion from the nozzle and to their uniform distribution within the specimens. In addition, the samples printed in the direction parallel to the fiber orientation revealed 27% less drying shrinkage compared to the perpendicular direction after 56 days of printing. Finally, shrinkage strains decreased by 64% and 74% for the perpendicular and parallel printing directions, respectively, when compared to the mold-casted samples. The reasons were a higher number of voids due to the CR aggregates and the presence of weak joints between printed layers that could block water [141]. The samples were printed with a HC1008 Desktop Concrete 3D Printer and a 20 mm nozzle.

5.4. Carbonation Curing

Carbonation curing was proposed with ECCs to reduce their carbon emissions. This process has the advantage of rapidly leading to high-strength cementitious products when carried out at an early age. In addition to cement, alkaline industrial by-products rich in Ca^{2+} , Al^{3+} , Mg^{2+} , etc., can be carbonated if present in the mix and contribute to the formation of stable carbonates that improve the fiber–matrix interface and the mechanical properties of ECCs [142]. However, the CO_2 concentration (20%) and pressure need to be high, which limits the use of this technique to prefabrication plants.

Carbonation curing was also associated with the use of sisal fibers in [44]. The selection of sisal fiber for low-carbon ECC manufacturing targeted several purposes. First, from a sustainability point of view, sisal fiber increased carbon sequestration by 10% by favoring diffusion transport of CO_2 into the samples during carbonation curing due to their hollow structure. Then, from a mechanical performance point of view, sisal fibers enhanced the tensile ductility of the ECC by acting as artificial flaws and triggering a larger number of microcracks in the matrix during tensile strain hardening. The cast specimens were demolded 18 h after manufacturing and dried with a fan for 4 h to remove water from capillary pores and enhance CO_2 diffusion. Then, the samples were cured for 24 h under 5 bars of CO_2 (99.8%purity) at room temperature (23 ± 2) °C. The addition of 0.5% sisal fibers led to an ultimate tensile strength of (6.14 ± 0.02) MPa with an ultimate tensile strain of $(8.62 \pm 1.28)\%$ after carbonation curing. The lowered alkalinity due to carbonation curing is also expected to mitigate the well-known degradation problem of sisal fiber in cementitious composites [44].

To sum up, the following are observed:

- More sustainable ECC compositions based on limestone-calcined clay cement (LC3) can be successfully developed and printed;
- New mixes containing crumb rubber, recycled aggregates [118], and conducting fillers can be printed to produce more sustainable and self-sensing concretes;
- Carbon curing can be actuated on ECCs, which can lower the pH of the matrix and make it more compatible with natural fibers.

6. Mechanical Properties and Durability of Printed ECCs

6.1. Anisotropy of Mechanical Properties

Several papers [20–22] evidenced that the mechanical strength of the interfaces between deposited layers is significantly influenced by the material composition, print time interval, surface moisture, and physical layer interlock, as well as extrusion speed. However, no systematic characterization of interface toughness has ever been performed. These interfaces may also influence the compressive strength, resulting in anisotropic compressive strength and different stress–strain relationships in the parallel and perpendicular directions to the printing direction. While anisotropic compressive strength [23–25] is well known, the constitutive stress–strain laws in the longitudinal and transverse directions necessary for the structural design of 3DP-ECC elements have not yet been investigated [119].

Printed ECCs show anisotropic properties, maintaining the tensile strain-hardening features in the printed filaments according to the printing direction, while the ductility in the filament in the perpendicular directions is much lower, specifically in the vertical direction across the interfaces. This anisotropic behavior is not surprising due to the fiber alignment in the printing direction during the extrusion process, although the magnitude of fiber alignment depends on various printing parameters. Surprisingly, a minimal toughness across the interface between superposed filaments is observed, probably due to fibers crossing the filaments when printed layers are deposited while still in the fresh state. The weaker interfaces between printed filaments remain a bottleneck that needs further efforts

by researchers to ensure structural reliability and robustness for full-scale structures. Other research areas should be studied as well, like, for example, the curing of printed structures, long-term durability under various environmental exposures, and the response to different loading types (static, impact, creep, etc.). In addition, the quantitative determination of fiber distribution and orientation due to the extrusion step and the way these have to be incorporated into mechanical models appear also as a major research topic priority. Once these studies are completed and validated by large-scale structural tests, the emergence of 3DP-ECC structures will be possible [13].

The mechanical anisotropy coefficient (I_a) can be calculated according to Equation (10), as proposed in [142]:

$$I_a = \frac{\sqrt{(f_x - f_c)^2 + (f_y - f_c)^2 + (f_z - f_c)^2}}{f_c} \quad (10)$$

where, f_x, f_y, f_z are the compressive, tensile, and bending strengths, etc., of printed materials tested in the x, y, and z directions, respectively. f_c is the strength of mold-cast samples. For cast samples, considered as homogeneous materials, $I_a = 0$.

In [119], as expected, an increase in the compressive strengths of 3DP-ECC samples with curing ages from 1 day to 28 days was observed, as well as anisotropic behavior. The specimen cut perpendicular to the printing direction (Prism-Per) had a more ductile failure mode together with a higher compressive strength and strain and a gentler descending branch compared to those cut parallel to the printing direction (Prism-Par) specimen. However, due to the closing of the space at layer interfaces, the elastic modulus of the Prism-Per specimen was 16% lower than that of the Prism-Par one, which could potentially induce a larger deformation of the 3DP-ECC element and needs a special attention in the design of 3DP structural elements. Under uniaxial tensile load, the 3DP-ECC showed multiple microcracking and strain-hardening performance, with a strain capacity of 3.0%. For printed samples with a smooth interface, a fiber-bridging effect was noted in broken samples, contributing to a limited increase in the load–displacement curve after an initial decrease, when a crack grows along with the interface from the notch tip. This effect was due to fiber interpenetration across the deposited filaments while in the green state. However, the interface remained quasi-brittle. To overcome this drawback, grooved layers were printed by means of a shaped nozzle (groove depth and width were about $3 \times 3 \text{ mm}^2$). Then, mechanical interlocking between the deposited filaments was observed, and this led to a non-brittle failure response associated with a higher loading capacity. Groove printing seems to be a promising solution to produce tougher filament-to-filament interfaces and limit the delamination failure tendency of 3DP-ECC structures [119]. A six-axis robotic arm with a pump installed on a linear gantry was used to print the samples. The nozzle had a cross-section of $30 \times 10 \text{ mm}^2$, and the printing speed was 50 mm/s (extrusion speed equal to 0.9 L/min).

6.2. Patterned Structures

The flexibility and precision of the 3D printing technique were fully exploited to design personalized and customized structures able to mimic complex biological structures with high performance in [143] (Figure 7). Then, investigations on the fracture behavior of 3DP-ECC with Bouligand structures replicating a mantis shrimp shell were conducted.

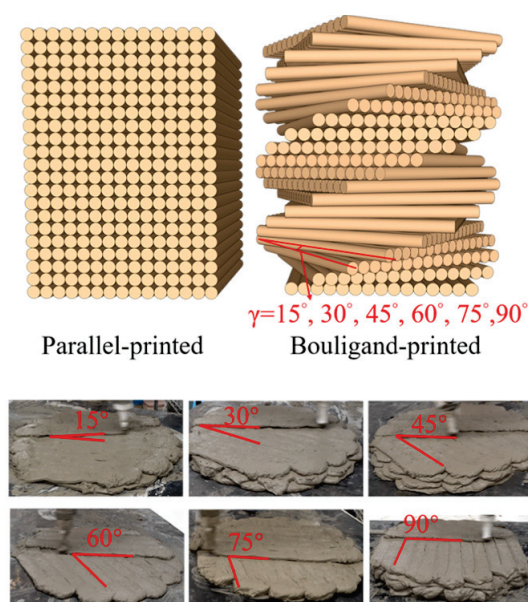


Figure 7. Parallel- and Bouligand-printed structures with different pitch angles (γ). Reproduced from ref. [143]; published by Elsevier, 2025.

Three groups of samples, including parallel-printed, Bouligand-printed, and mold-cast notched beam specimens, were manufactured and tested in three-point bending. A six-axis robotic arm alimented with a pump was used with a rectangular nozzle ($3 \times 50 \text{ mm}^2$). The flow rate was set to 0.02 L/s, while the nozzle travel speed was 100 mm/s. The influence of different pitch angles (15° , 30° , 45° , 60° , 75° , and 90°) on the fracture behavior of the 3DP-ECC specimens was studied too. The parallel-printed specimens presented a more uniform and brittle failure mode, while the Bouligand-printed samples showed different fracture patterns, characterized by microcracking, crack delamination, crack branching, crack bridging, and crack twisting. Contrarily, the cast samples evidenced a singular, almost linear crack propagation path with microcracking and fiber bridging. The parallel-printed specimens evidenced a flexural strength and fracture energy of 33% and 67% lower than those of the cast samples, respectively, while the Bouligand-printed specimens showed a flexural strength ranging from 0.97 to 1.29 times and a fracture energy ranging from 0.99 to 1.63 times that of cast specimens. The Bouligand-printed samples with a 30° pitch angle gave the highest values. The parallel-printed specimens presented a fracture toughness 60% lower than that of the cast specimens. On the contrary, the Bouligand-printed samples showed a toughness ranging from 2.24 to 3.76 times that of the parallel-printed specimens and 0.87 to 1.47 times that of the cast specimens, with, again, the highest toughness for a 30° pitch angle. Finally, the fracture behavior of 3DP-ECC with Bouligand structures was simulated by means of a combination of the concrete plastic damage model and cohesive elements. The simulation results were in good accordance with the experimental data, with errors ranging from 1.45% to 7.16%. Cohesive elements underwent shear and tensile failure, which was consistent with experimental observations. The synergistic effects of crack twisting and bridging in the Bouligand-printed samples were able to enhance the toughness, in agreement with natural toughening mechanisms. A 30° pitch angle provided optimal energy absorption, maximizing the crack bridging and twisting effects and resistance to crack propagation. A nonlinear regression analysis method was also used to model the relationships between pitch angles, flexural strength, fracture energy, and toughness. The maximum flexural strength was obtained with a pitch angle of 31.44° , while the highest fracture toughness occurred at 30° , and the maximum fracture energy was reached for a pitch angle equal to 23.56° . These results evidenced that

the optimization of the pitch angle of 3DP-ECC with Bouligand structures could improve fracture performance for specific applications [143].

Knitted and tilted filaments were also designed to mimic the crossed-lamellar microstructure of conch shells and were printed in [144] (Figure 8). Their features were compared with filaments classically printed parallel each other. The fresh mix was put into a hopper connected to a peristaltic pump and transported through a 5 m long tube to a six-axis robotic arm.

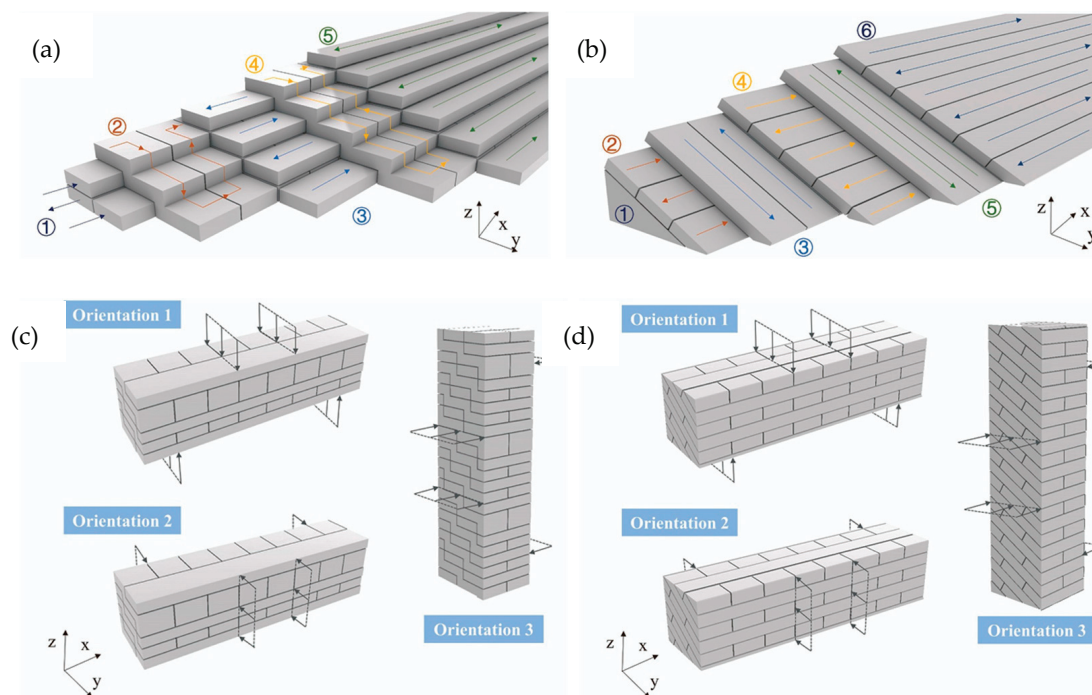


Figure 8. Schematic diagrams of filaments: knitted (a) and tilted (b); loading modes for filaments: knitted (c) and tilted (d). Arrows indicate loading directions. Reproduced from ref. [144]; published by Elsevier, 2023.

These patterns introduced a complex 3D interface system exploiting the original weak interfaces as a structural strengthening method. In four-point bending tests, parallel printed filaments loaded perpendicularly and parallel to the printing direction evidenced excellent flexural strengths and strain-hardening behavior, significantly higher than the cast specimens. These results were explained based on the fiber alignment in the extruded ECC filaments, the crack branching and deflection in the laminate structure, and crack trapping by the fibers. Knitted and tilted filaments had a bending strength higher than or comparable to cast ECC samples when tested according to orientations 1 and 2. Moreover, knitting and tilting filaments led to a unique failure mode: multiple cracks occurred from the bottom of the samples (tensioned zone) and rose in the loading direction. Further deflection and bifurcation then happened when the cracks met the filament interfaces, causing energy dissipation and delaying failure to increase ductility. Thus, anisotropy was notably reduced due to these innovative printing patterns. Moreover, when the specimens were tested according to orientation 3, a strong increase in flexural strength was noted in knitted and tilted filaments compared to parallel ones. An increase of up to 179% was measured in the tilted filaments, and the strength of the knitted filaments also increased compared to that of parallel filaments by 116%. The ratio of the strength in orientation 3 relative to orientation 1 was enhanced from 8.6% to 30%, indicating a notable reduction in anisotropy in 3DP-ECC.

Finally, without steel reinforcement in 3DP-ECC, durability concerns due to steel corrosion should be null. However, because of complex interfaces between the printed filaments, further research should be carried out to study the ingress and diffusion transport mechanisms of aggressive agents inside 3DP-ECC in harsh environments and the eventual damages to fibers and the matrix [144].

Table 2 reports the results of the best mixes reported in literature.

Table 2. Comparative results on 3DP-ECC.

Composition (In kg/m ³ If No Other Information)	Additives SP	w/b	Fiber Type and Content	Open Time Window	Slump/Thixotropy Index	Mechanical Strength	Ref.
259.2 CEM I 42.5, 604.9 BFS, 864.1 limestone powder, 26 PVA	5.1 kg/m ³ methylcellulose (201,000 mPa.s), 17.3 g/m ³ SP (BASF Glenium 51)	0.41	PVA 2 vol%	n.d.	Mixture could pass through a 5 m hose	6–10 MPa peak flexural strength // to printing direction ≈2–3 MPa tensile strength	[69]
480.2 CEM I 42.5, 567.6 FA, 109.1 limestone powder, 186.3 sand (125–250 µm), 294 sand (250–500 µm), 26 PVA	6.5 kg/m ³ methylcellulose (201,000 mPa.s), 13 g/m ³ SP (BASF Glenium 51)	0.31	PVA 2 vol%	n.d.	Mixture could pass through a 5 m hose	≈1.6–3.1 MPa peak tensile strength	[69]
309 CEM I 52.5R, 1026 FA, 345 sand (50–550 µm), 26 PVA	2 kg/m ³ HPMC 7500–14,000 mPa.s (2% aqueous solution at 20 °C), 3 kg/m ³ SP polycarboxylate- based	0.24	PVA with 1.2% oil (by mass) 39 µm in Ø	70 min	Spread diameter from ≈132 to 123 mm after 20 and 60 min, respectively, in the flow table test. The mixture did not flow before the flow table drop was applied	31.2 MPa 28 d compressive strength //, 30.6 MPa ⊥ to printing direction on cubes (3.38 ± 0.03) MPa peak stress 28 d tensile stress with (3.09 ± 0.25)% strain capacity	[119]
656 CEM I 52.5, 118 FA, 246 SF, 604 sand, 57,120 mesh crumb rubber	3 kg/m ³ SP	0.27	1–2% PE 25 µm in Ø	n.d.	Spread diameter of 162 mm with 1.5% of fibers	19.4 MPa flexural strength with 1.5% fiber // to printing direction and 22 MPa ⊥ to printing direction	[114]
0.38 CEM II 52.5, 0.05 SAC, 0.09 SF, 0.48 FA, 0.26 sand * (<300 µm),	0.0004 HPMC * (viscosity of 38,000–42,000 mPa.s), 0.01 SP * polycarboxylate- based	0.26 water *	0.018 PE * 24 µm in Ø	n.d.	n.d.	62.8 kN peak load four-point bending test // to printing direction and 32.3 kN ⊥ to printing direction on 500 mm long and 100 mm high beams	[145]
0.4 CEM II 52.5, 0.03 SAC, 0.57 FA, 0.4 sand	0.001 HPMC°, 0.005 ANC°, 0.012 SP°	0.28 water°	1.5 PE° 24 µm in Ø	n.d.	Slump flow = 55 mm and spread flow = 155 mm; shear thinning behavior and dynamic yield stress of ≈550 Pa; and plastic viscosity of ≈11.7 Pa.s with 2% of PE fibers	(5.68 ± 0.4) MPa ultimate tensile strength with (9.57 ± 1.01)% tensile strain capacity	[78]
0.38 CEM II 52.5, 0.05 SAC, 0.09 SF, 0.48 FA, 0.26 sand	0.0004 HPMC (viscosity of 38,000–42,000 mPa.s), 0.001 SP polycarboxylate- based	0.26 water	0.018 PE 24 µm in Ø	n.d.	n.d.	(6.15 ± 0.15) MPa ultimate tensile strength with (7.31 ± 1.83)% tensile strain capacity	[73]
72 CEM I, 23 FA, 5 CAC, 45 sand, 10 MS, 5 GS, 5 ANC,	0.4 HPMC°, 0.8 SP°	43 water° (w/b = 0.36)	2 vol% PVA	n.d.	n.d.	≈6 MPa tensile strength with ≈4% tensile strain capacity	[68]

Table 2. Cont.

Composition (In kg/m ³ If No Other Information)	Additives SP	w/b	Fiber Type and Content	Open Time Window	Slump/Thixotropy Index	Mechanical Strength	Ref.
483 CEM 42.5, 314 BFS, 70 SF, 447 LS powder ($<250\ \mu\text{m}$), 284 sand ($125\text{--}250\ \mu\text{m}$),	5.2 HPMC (Tylose MHS 15002 P6), 3.47 SP		26 PVA $40\ \mu\text{m}$ in $\varnothing$	3 h 30 min, determined by Vicat penetration test	n.d.	(8.68 ± 2.00) MPa maximum flexural strength	[71]
1 OPC, 0.11 SF, 0.89 sand, 0.8 hollow glass microspheres ($20\ \mu\text{m}$ in $\varnothing$)	0.015 SP ^{..}	0.65 water ^{..} (w/b = 0.59)	0.0175 PVA ^{..} $39\ \mu\text{m}$ in $\varnothing$	n.d.	153 mm slump flow 65 min setting time	(8.46 ± 0.39) MPa flexural strength // to printing direction and 9.12 ± 0.30 MPa $\perp$ to printing direction at 28 days	[130]
656 CEM I 52.5, 118 SF, 410 sand	2 SP	363 water (w/b = 0.47)	15 PE $24\ \mu\text{m}$ in $\varnothing$ (1.5 vol%)	n.d.	≈ 167 mm initial spreading diameter, ≈ 154 mm spreading time after 100 min	7.51 MPa maximum flexural strength with a strain capacity of 5.4%	[146]
730.41 OPC 52.5, 87.65 SAC, 233.73 FA, 116.87 SF, 701.19 sand (330 μm average diameter)	0.18 HPMC, 23.4 SP	257.1 water (w/b = 0.22)	17.53 PVA $40\ \mu\text{m}$ in $\varnothing$	Open time of ≈ 40 min	Initial setting = 37 min, final setting time = 64 min, determined by isothermal calorimetry, dynamic yield stress of 2505 Pa and plastic viscosity of 140.2 Pa.s with 2% of PE fibers	1.43 kPa initial compressive strength, with a stress increase rate of 0.095 kPa/min.	[147]
1 CEM I 52.5, 1.26 FA, 0.11 densified SF, 5 vol% to FA waste aggregates (1–2 mm), 0.89 sand ($<600\ \mu\text{m}$)	6 mL SP polyether-based superplasticizer	0.65 water (w/b = 0.41)	1.75 vol% PVA $39\ \mu\text{m}$ in $\varnothing$	n.d.	240 mm slump diameter	≈ 9.3 MPa flexural strength // to printing direction, ≈ 6.2 MPa flexural strength $\perp$ to printing direction at 28 days	[141]
0.47 OPC 42.5R, 0.44 FA, 0.09 FA, 0.29 sand	0.0018 SP	0.24 water	0.01 PE $24\ \mu\text{m}$ in $\varnothing$	n.d.	≈ 136 mm spread diameter and ≈ 25 mm slump 20 min after water addition, ≈ 127 mm spread diameter and ≈ 21 mm slump 80 min after water addition	≈ 7 MPa peak tensile strength with $\approx 4\%$ tensile strain capacity	[72]
1 OPC 52.5, 1.33 FA, 0.11 SF, 0.89 sand	0.024 activated carbon powder, 0.025 VMA, 0.068 SP	0.65 water	0.021 PVA $39\ \mu\text{m}$ in $\varnothing$	n.d.	n.d.	10.81 MPa // to printing direction, 10.08 MPa flexural strength $\perp$ to printing direction at 28 days	[148]
0.6 OPC, 0.3 FA, 0.1 MS, 0.2 sand	0–0.5% nanoclay	0.325–0.375 w/b, function of fiber content	1–2 vol% PE $24\ \mu\text{m}$ in $\varnothing$	n.d.	Slump = 10.5 mm and slump flow = 198 mm for mix with 1 vol% of 12 mm in length fiber and w/b = 0.35, Static yield stress = 530.8, 809.1, 1477.3, 2552.7, and 3870.1 Pa for 0, 0.5, 1.0, 1.5, and 2.0 vol% of fibers, respectively	n.d.	[53]
75 wt% CEM II/A-M (S-LL) 52.5R, 15 wt% SF and 10 wt% FA	none	0.22–0.24 w/b	0.3–1.5 vol% HDPE $12\ \mu\text{m}$ in $\varnothing$	n.d.	119 mm spread diameter and 133 mm after shocks (w/b = 0.22, s/b = 0.2 and 1.5 vol% fibers)	5.66 MPa tensile strength with 3.21% ultimate tensile strain (w/b = 0.22, s/b = 0.2, and 1.5 vol% fibers)	[70]

Table 2. Cont.

Composition (In kg/m ³ If No Other Information)	Additives SP	w/b	Fiber Type and Content	Open Time Window	Slump/Thixotropy Index	Mechanical Strength	Ref.
360 OPC 52.5 R, 196.5 MK, 98.3 LS, 360.3 GGBFS,	1.0 HPMC, 4.0 SP	264 water	10–17.5 kg/m ³ PE fibers 24 µm in Ø	5–45 min recommended	Initial slump diameter of 115 mm and of ≈103 mm after 60 min, initial flow diameter of 130 mm and of ≈115 mm, flow table test (1.25 vol% of fibers)	Anisotropic parameter = 0.799 on nominal flexural strength and 0.067 on compressive strength (1.25 vol% of fibers)	[119]
223 PLC, 71 MK, 51 LS, 841 FA, 30 SF, 30 CR (40–80 mesh), 466 sand	4.0 SP	253 water	26 PVA 39 µm in Ø	60 min	Spread diameter = 165 mm 20 min after water addition, ≈145 mm 60 min after water addition	≈4.8 MPa tensile strength with ≈2.7% tensile strain capacity	[52]
0.6 OPC, 0.3 FA, 0.1 SF, 0.2 sand (100–300 µm)	0.005 nanoclay	0.3 water	1 vol% UHMWPE fibers 24 µm in Ø	n.d.	n.d.	17.41 MPa flexural strength Bouligand structure at 30° in the z direction	[143]
497 OPC, 781 FA, 332 sand	2.5 SP	320 water (w/b = 0.25)	26 PVA 39 µm in Ø (2 vol%)	n.d.	n.d.	21.6 MPa flexural strength // to printing direction, ≈16.5 MPa ⊥ to printing direction	[144]

(n.d.: not determined, SP: superplasticizer, SAC: sulphoaluminate cement, *: mass ratios of the binder mass (CEM+SAC+FA+SF), °: mass ratios of the binder (OPC+SAC+FA) weight, except the fiber content (volume fraction), ANC: attapulgite nanoclay, CAC: calcium aluminate cement, LS: limestone, MS: microsilica, GS: ground silica, %: % to total cementitious materials, BFS: blast furnace slag, VMA: viscosity-modifying agent, HDPE: high-density polyethylene, MK: metakaolin, SG: semi-hydrated gypsum, GGBFS: ground granulated blast furnace slag, PLC: Portland limestone cement, CR: crumb rubber, UHMWPE: ultra-high-molecular-weight polyethylene).

To summarize:

- 3DP-ECCs show anisotropic properties according to the printing direction;
- The ductility in the filament in the perpendicular direction is much lower, specifically in the vertical direction across the interfaces;
- Groove printing seems to be a promising solution to produce tougher filament-to-filament interfaces;
- Patterned structures like Bouligand ones, as well as knitted and tilted structures, can improve fracture performance for specific applications. They also fully exploit 3D printing potentialities;
- Durability aspects of 3DP-ECCs are still to be investigated.

7. Critical Steps in the Printing Process

In [72], cast specimens performed better than printed ECCs in terms of multiple cracking ability, tensile strength, and strain capacity. In fact, both the fibers and cementitious matrix were responsible for the performance decrease when printing. When the blades of the pump rotated, fresh ECC was continuously submitted to shear stress in the hopper and extruded out of the nozzle in a twisted form. As a result, the thin synthetic fibers were curled because of their flexibility. This curling effect then hampered the crack-bridging ability of the fibers, which were not totally exploited under tension. In addition, the orientation of the fibers inside the twisted filament was rather well aligned with the printing direction, while fibers in the cast specimens presented a random distribution and orientation. For example, in the filaments printed with a nozzle standoff distance of 12 mm and a speed of 8 m/min, a fiber orientation of about 45° with respect to the printing direction was noted and weakened the tensile resistance in the printing direction. Moreover, in the samples printed with a nozzle standoff distance of 12 mm and a speed of 7 m/min, the fibers were oriented almost perpendicular to the printing direction and led to

a limited tensile strength with a low printing speed. It was also expected that the extrusion step guaranteed less porous specimens than cast ones because the shear forces made the material denser [70,149]. However, this was not always what happened; in fact, cast ECCs could have a higher volume of finer pores compared with 3DP-ECCs. Thus, cast ECCs presented a higher initial cracking strength under tensile loads because of a denser matrix. The standoff distance of the nozzle strongly influenced the tensile strength of 3DP-ECC: a lower standoff distance led to a higher mechanical performance. For a lower standoff distance, the nozzle flattened the fibers and better aligned them in the horizontal plane because of an extra compressive stress. Consequently, the out-of-plane angle of the fiber was limited, and the tensile resistance in the printing direction was higher due to better fiber orientation. At the same time, as the material compacted after deposition, due to the action of the nozzle, the pore structure was slightly impacted. Thus, lower standoff distances produced a less porous matrix, and the initial cracking stress of the 3DP-ECC was in general inversely proportional to the nozzle standoff distance. For example, when the nozzle standoff distance decreased from 14 mm to 10 mm, the strain capacity of the same mixture increased by about 30%, while the tensile strength was up to 39% higher. Concerning the nozzle travelling speed, moderate printing speeds yielded superior tensile strength, demonstrating that the printing speed may be optimized to lead to optimal tensile performances. However, low printing speeds could lead to potential accumulation of an excess of material: because of a limited space for the already printed material, the newly extruded one compressed the previously deposited one, yielding more aligned fibers perpendicular to the printing direction. For high printing speeds, though the matrix was compact, the tensile strength was lower because the extruded filaments were thinner than standard ones due to the reduced material volume flow. Therefore, a gentle smaller vertical secondary compaction was caused by the additional stress of the nozzle. Consequently, a higher number of out-of-plane fibers were produced, leading to a reduction in tensile strength [72].

The interfacial bonding between 3DP-ECC filaments has two origins. On one hand, part of the adhesion is due to the contact area between the fresh materials deposited and is related to the printing job. Then, the printing speed has a notable influence on the formation of weak interfaces. On the other hand, another contribution to interfacial bonding derives from fibers bridging the interface. As previously mentioned, when an upper layer of material is printed, its own weight presses it onto the underlying layer and part of the fibers penetrate in it, contributing to inter-layer fracture resistance. During flexural tests, the load first linearly increases as a function of the displacement until the fracture toughness of the matrix is reached. Then, the brittle fracture of the matrix leads to a rapid post-peak decrease in load without reaching the null value, as in the case of brittle failure of common cementitious materials. This is due to the presence of fibers that redistribute stress after matrix cracking and fibers bridging cracks that play a fundamental role in load bearing. The load capacity increases halfway until it reaches another peak or a plateau and allows for further development of a large deflection. The second rising branch characterizes the fiber bridging capacity of ECCs, and the enhancement in overall fracture resistance ability is notable [72].

Fibers are mainly responsible for the difference in fracture resistance between inter- and intra-layer specimens: fiber bridging capacity in printed layers is usually higher because of the fiber amount. Consequently, the fracture resistance of intra-layer specimens is much higher than that of inter-layer ones. Pore distribution along the layer stacking direction was studied by μ -computer tomography scanning, and it appeared that the inter-layer porosity area did not show significant differences from intra-layer ones. More pores were introduced into the bulk of the filaments than the interface due to the agitation of

the pump. Nonetheless, the pore distribution investigation also confirmed that a nozzle standoff distance slightly lower than the filament height could effectively eliminate the formation of interlayer voids [150]. To sum up, both the inter-layer and intra-layer fracture resistance capacity are proportional to the nozzle standoff distance due to the number of fibers bridging adjacent layers as a result of the deformation of the overlapping areas in contact. A higher nozzle standoff distance generally produced more important cross-sectional deformation. In addition, because of the unavoidable weight loading from the upper layers, the printed filaments are vertically squeezed, and the contact area of adjacent layers is augmented. In the meantime, the fibers close to the surface penetrate the cementitious matrix of the filament below, raising the interfacial fracture resistance. Interlayer bonding is then increased. Contrarily, a lower nozzle standoff distance produces less rounded cross-sections during extrusion, and the deformation between two successive layers is limited. Moreover, more fibers are flattened and aligned along the printing direction, reducing the number of fibers penetrating the interface and leading to weaker interfacial fracture resistance [72].

To sum up, the following observations are made:

- When the nozzle standoff distance decreases by about 30%, the strain capacity of the same mixture can be increased by about 30%, while the tensile strength can be up to 39% higher;
- Moderate printing speeds yield superior tensile strength;
- Low printing speeds could lead to potential accumulation of an excess of material and should be adapted to the feeding rate of the nozzle (better integration and interface between the hardware of the printing chain).

8. Current Technical Challenges and Limitations

Contrarily to what happens with conventional concretes, ECCs are designed and processed according to micromechanical principles [151,152] to trigger steady-state crack propagation and multiple cracking behavior [153–155]. However, as previously seen, manufacturing of these materials introduces variations in their properties, specifically in the case of a non-uniform fiber distribution within the cementitious matrix [13,76,156]. A loose fiber dispersion decreases fiber bridging abilities, potentially hampering the composite's strain-hardening capacity while also limiting tensile strength and strain capacity [157–159]. Thus, the rheological properties of ECCs in 3DPC must guarantee optimal fiber dispersion and suitable printability. This complexity shows that the rheological optimization of 3DP-ECC is much more difficult than in traditional 3D concrete printing as well as in casting common ECC mixes [121]. Thus, an innovative printability evaluation method specifically designed for 3DP-ECC that considers the impact of fiber dispersion while also emphasizing cost-effectiveness and efficiency was proposed in [121]. The method simplifies rheological parameters through slump and slump flow tests. Moreover, the determination of the printable open time is also possible, thus adjusting the mixing time of the ECC paste. The feasibility of the proposed method was validated through printing and rheological tests (the Marsh cone flow test was used as a fiber dispersion evaluation technique, and a flow time of between 24 and 33 s was set). The experimental results were in good agreement with theoretical ones. Finally, the tensile strength of 3DP-ECC was also studied, further validating this new methodology [121].

However, significant gaps in the field of 3DP-ECC structures need to be investigated deeper. Some of the parameters to take into consideration include the curing conditions of printed structures, their durability over time when exposed to different environmental conditions, and their response to diverse loads [13].

Internal curing can be actuated by means of lightweight aggregates like presoaked pumice [74]. A mix was made of 50% OPC and 50% GGBFS, 0.7 river sand, 0.01% methyl-cellulose, 0.0015% SP, 2 vol% of PE fibers that were 17.9 μm in $\varnothing$ and 6 (1 vol%)–10 (1 vol%) mm in length, and a water-to-binder ratio of 0.3. The flow diameter of ECC mixes with 2% PE fibers ranged from 14 to 15 cm. A printing speed of 1 cm/s with an extrusion rate of 0.1 rounds/s led to a smooth filament texture, dimensional consistency, and a stable extrusion process. The use of presoaked pumice aggregates caused a slight reduction in buildability (which was 16 layers with 30% of pumice aggregates). Other self-curing or internal curing agents could include polyethylene glycol (PEG) [160] or coarse biochar [161]. To the best of the author's knowledge, none of these have been used yet during ECC printing. Finally, fine biochar (10–20 wt% additions) has not only the potential to decrease the carbon footprint of cement in general but also to reduce the chemical and frictional bond strength between the fiber and matrix [162].

Possible methods to increase the tensile strength of printed ECCs include limiting the adverse impact of the progressive cavity pump and/or increasing the favorable wall effect of the extrusion nozzle. Future studies should also consider the evaluation of the fiber distribution and orientation in extruded filaments [119]. However, it should be emphasized that an extensive design based on micromechanics and fracture mechanics concepts is still needed to correctly understand the mechanical and electrical features of ECCs [163].

Moreover, due to the use of plastic microfibers, some concerns can be raised in terms of workers exposed during the preparation of the mixes as well as during the demolition of ECC structures. Cerebral and epithelial human cells exposed to 3–16 μm PE fibers under 10 ng/mL–10 $\mu\text{g/L}$ for 24–48 h during in vitro tests showed oxidative-stress-induced cytotoxicity [164]. Thus, personal protection equipment (gloves, goggles, and respiratory masks) is recommended when handling them. On the contrary, electrospun PVA nanofibers are used in tissue engineering and scaffold production because of their biocompatibility and biodegradability [165].

To summarize, the following observations are made:

- Fiber dispersion is of paramount importance, and rheological properties should be adapted;
- Internal curing should be considered to improve mechanical strength;
- Further micromechanics and fracture mechanics concepts should be studied to understand the mechanical behavior of 3DP-ECCs;
- Safety precautions should be taken by workers when handling PE fibers.

9. Advancing the Field of ECCs Through Machine Learning

In the last years, machine learning (ML) techniques have been proposed as cost-effective and efficient ways to predict the influence of materials on properties, costs, and timelines of proposed mixtures [166]. To this aim, Shi et al. [163] used the artificial neural network (ANN) method to predict the mechanical and electrical properties of ECCs. Their study evidenced good agreement between the anticipated and observed outcomes, indicating that ANN models can forecast the properties of electrically conductive composites. The ANN technique was also used by [166] to predict the compressive strength of ECCs manufactured with fly ash and ground granulated blast furnace slag. While various ML algorithms were used to forecast various features of concrete, their use to predict self-healing ECC properties is not common and is challenging. Recently, in [167], the anisotropic-mechanical properties of 3DP-ECC were experimentally investigated and examined by means of ML prediction models like the non-dominated sorting genetic algorithm II (NSGA-II) to simultaneously optimize mechanical, environmental, and economic performances. A total of 114 sets of compressive strength data and 104 sets of flexural strength data were

used. As expected, 3DP-ECC showed a mechanical anisotropy particularly during flexural tests, attributed to weak interfaces and fiber orientation effects. The highest compressive strength was observed in the z direction. Moreover, 3DP-ECC displayed a lower compressive strength than cast ECCs whatever the loading direction. However, the flexural strength between the different samples was as follows: 3DP-z > 3DP-y > cast > 3DP-x. The grey relational analysis (GRA) results showed that the critical parameters influencing the mechanical properties of 3DP-ECC were the SCM-to-binder, aggregate-to-binder, and water-to-binder ratios, the fiber reinforcing index, and the loading direction, confirming the results of the papers analyzed in the previous chapters. Back-propagation artificial neural network (BPANN) models were interpreted with Shapley additive explanations (SHAP) and partial dependence plots (PDP) analyses. The results showed that the most significant parameters that impact the compressive strength of 3DP-ECC ($R^2 = 0.999$ and RMSE = 3.817 MPa when testing) were the water-to-binder ratio as well as the loading direction during flexural strength tests ($R^2 = 0.998$ and RMSE = 1.37 MPa when testing), as also shown in the previous chapters. In addition, the PDP analysis highlighted how each parameter influenced the anisotropic-mechanical properties of 3DP-ECC. However, further studies are still needed, as the specimen size and shape, curing age, and printing process parameters are also key factors that influence the mechanical properties of 3DP-ECC. Thus, their effects should also be taken into consideration in ML property prediction. Finally, this study mainly focused on the compressive strength and flexural strength of 3DP-ECC, omitting other important features like flowability and rheology, interlayer bond strength, and durability performance.

To sum up, machine learning techniques have confirmed that the crucial parameters influencing the mechanical properties of 3DP-ECC are as follows:

- SCM-to-binder ratio;
- Aggregate-to-binder and water-to-binder ratios;
- Fiber reinforcing index;
- Loading direction.

10. Conclusions and Perspectives

3DPC technology presents several benefits for the construction sector, such as a reductions in costs because of less labor (due to a lack of formwork, it is a direct process, and there are less risks for workers), as well as a decrease in energy consumption (lower movements of materials) and pollution (less waste produced). However, transferring these advantages to 3DP-ECC is not obvious. As previously discussed, the challenge of balancing conflicting requirements such as pumpability and buildability is not immediate due to the presence of fibers that should remain aligned in the filaments and ideally penetrate between the different layers to improve the interface strength.

The crucial parameters when 3D printing ECCs are as follows:

- Chemical stability of fibers in high-pH environments is mandatory;
- PE and PVA fibers that are 20–50 μm in $\varnothing$ are commonly used for ECC manufacturing;
- Recycled aramid nanofibers seem promising as well;
- High aspect ratios are needed;
- Common dosages are 1–2 vol%;
- A high tensile strength and a rather low bond strength with the cementitious matrix are desirable;
- Fibers increase the yield stress at rest times, as well as the plastic viscosity and the dynamic yield stress;
- Fiber dispersion is of paramount importance, and rheological properties should be adapted;

- An optimized particle size distribution guarantees a good packing of particles and contributes to buildability;
- The open time should be 30-60 min and should be compatible with buildability;
- The order of mixing the products is fundamental in 3DP-ECC: first, solids are dry-mixed, then water and SP are added, and fibers are progressively introduced in the mix. Finally, the VMA is supplemented;
- The mix should have a low initial stiffness to be pumped and extruded, while the buildability requires a stiff material able to bear its own weight. Stiffness can be increased by CSA or sodium silicate additions;
- The extrusion speed should match the printing speed to control the shape and quality of printed filaments;
- Long delays between printing one filament above an existing are not advisable;
- When the nozzle standoff distance decreases by about 30%, the strain capacity of the same mixture can be increased by about 30%, while the tensile strength can be up to 39% higher;
- Internal curing should be considered to improve mechanical strength;
- Carbon curing can be actuated in ECCs, which can lower the pH of the matrix and make it more compatible with natural fibers.

Experimental tests and machine learning techniques showed that the crucial parameters influencing mechanical properties of 3DP-ECC are as follows:

- SCM-to-binder ratio;
- Aggregate-to-binder and water-to-binder ratios;
- Fiber reinforcing index;
- Loading direction.

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Abbreviations

The following abbreviations are used in this manuscript:

ECC	Engineered cementitious composite
SHCC	Strain-hardening cementitious composite
3D-SHCC	3D-printable strain-hardening cementitious composite
SCM	Supplementary cementitious material
PVA	Polyvinyl alcohol
PE	Polyethylene
PET	Polyethylene terephthalate
3DPC	3D printing process of concrete
3DP-ECC	3D-printed ECC
FA	Fly ash
SF	Silica fume
SP	Superplasticizer
HRWRA	High-range water-reducing agent
HPMC	Hydroxypropyl methyl cellulose
w/b	Water-to-binder
IBA	Incinerator bottom ash
OPC	Ordinary Portland cement
s/b	Sand-to-binder
UCCT	Uniaxial unconfined compression test
LC3	Limestone-calcined clay cement

CSA	Calcium sulphoaluminate
LL-ECC	Lightweight engineered cementitious composites
G	Graphite
MCMF	Milled carbon microfibers
CCMF	Chopped carbon microfibers
ML	Machine learning
ANN	Artificial neural network
NSGA-II	Sorting genetic algorithm II
GRA	Grey relational analysis
BPANN	Back-propagation artificial neural network
SHAP	Shapley additive explanations
PDP	Partial dependence plots
PEG	Polyethylene glycol

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