Hafnium-Zirconium Carbonitride (Hf,Zr)(C,N) by One Step Mechanically Induced Self-Sustaining Reaction: Powder Synthesis and Spark Plasma Sintering

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Abstract: Nanostructured single-phase hafnium-zirconium carbonitride powders were synthesized using a simple and fast mechanochemical synthesis approach. The critical milling duration, after which a (Hf,Zr)(C,N) solid solution formation inside a jar occurred via mechanically induced self-sustained reaction (MSR), was 10 min. After 30 min of treatment, a solid-gas reaction was completed, and as a result, a homogeneous (Hf,Zr)(C,N) powder consisting of 10–500 nm submicron particles was obtained. The phase and structure evolution of the powders after different treatment durations allowed for the establishment of possible reaction mechanisms, which included the formation of Hf/Zr/C-layered composite particles, their interaction via MSR, and further grinding and nitridization. Spark plasma sintering (SPS) was used to produce bulk hafnium-zirconium carbonitride ceramics from nanostructured powder. The sample had higher values of relative density, hardness, and fracture toughness than those for binary compounds of a similar composition.

Keywords: ultra-high-temperature ceramics; hafnium zirconium carbonitride; high energy ball milling; mechanically induced self-sustaining reaction; spark plasma sintering; mechanical properties

1. Introduction

The development of new materials capable of withstanding high temperatures during aerodynamic heating (>2000 °C) is of particular interest among scientists involved in the research of ultra-high-temperature compounds [1–3]. Borides, carbides, and nitrides of transition metals of groups IV and V, known as ultra-high-temperature ceramics (UHTC), are typically used to create new compounds for use in extreme environments. The presence of strong atomic covalent bonds in these compounds determines their extreme melting temperatures (>3000 °C), high mechanical properties, electrical and thermal conductivity, oxidation resistance, chemical and phase stability, as well as their ability to withstand extreme temperatures [4,5].

From the standpoint of mechanical and thermophysical properties, more complex compounds, such as carbonitrides of transition metals, are advantageous due to the hybridization of electron orbitals upon the substitution of atoms in the metallic and nonmetallic sublattices. The properties of these compounds are dependent on the C/N ratio and surpass the properties of ordinary binary Me-C and Me-N compounds, including those at elevated temperatures [6,7]. For example, Lu Yang et al. [8] studied the effect of the C/N ratio in Ti(C1−x,Nx)-based cermet substrates and in TiN/Ti(C,N)/Al2O3/TiN coatings on the high-temperature frictional properties of CVD coatings. It was demonstrated that by varying the C/N ratio, it was possible to influence the structure of the substrate and
coatings, increasing their hardness and friction properties. In other words, it is possible to adjust the necessary parameters depending on the required functional characteristics. Harrison et al. reported [9] that the thermophysical properties of ZrC\textsubscript{x}N\textsubscript{y} ceramic material obtained by carbothermic reduction were superior to those of zirconium carbides and nitrides. Due to the growing contribution of the electronic part to the thermal conductivity, its value increased with the increase of the N content in the ZrC\textsubscript{x}N\textsubscript{y}, which ranged from 40–50 W·m\textsuperscript{-1}·K\textsuperscript{-1}. As well as being used as protective wear-resistant coatings [10,11], carbonitride ceramics are also used to improve the mechanical properties and oxidation resistance of carbon–carbon composites [12].

Unlike traditional methods of synthesis [13–15], which require long-duration and energy-consuming treatment, mechanochemical synthesis (MS) is a fast and simple method for obtaining various compounds with the required composition. This process typically involves the mechanical activation of a ‘solid–solid’ reaction between components of a powder mixture during its treatment in different ball mills. However, the process can be conducted in a reactive gas atmosphere (e.g., N\textsubscript{2}, NH\textsubscript{3}, H\textsubscript{2}), allowing for a ‘solid–gas’ interaction and the formation of nitrides and hydrates. For example, plasma-assisted ball milling was used to rapidly obtain Mg\textsubscript{3}N\textsubscript{2}, TiH\textsubscript{2}, and TiN powders [16], as well as more complex HfC\textsubscript{x}N\textsubscript{y} compounds [17]. Alternatively, with the participation of a gaseous reagent, MS can be carried out in a high-energy planetary ball mill, which allows for the shortening of the processing duration to up to 30–90 min [18]. During the high-energy ball milling (HEBM) of reactive compounds, two types of reaction may occur: in the first case, the chemical interaction between the components proceeds gradually over time, leading to the slow formation of a product. In the second case, the HEBM of exothermic powder mixtures leads to the initiation of a fast combustion reaction in a jar—a mechanically induced self-propagating reaction (MSR). With the appropriate synthesis parameters, MSR can be used to obtain single-phase complex compounds of carbonitrides as well as double and more complex carbides [19–21]. One advantage of the MSR synthesis method is the possibility for a precise morphology and structure control of the synthesized powders. This approach was used to synthesize nanocrystalline titanium-niobium carbonitride Ti\textsubscript{y}Nb\textsubscript{1−y}C\textsubscript{x}N\textsubscript{1−x} powders with a uniform chemical composition [22].

In this work, hafnium-zirconium carbonitride (Hf,Zr)(C,N) powders were synthesized by MSR via treatment in a high-energy planetary ball mill of elementary hafnium, zirconium, and carbon powders in a nitrogen atmosphere. The evolution of the phase composition and microstructure of the powders was studied as a function of the HEBM duration. The bulk hafnium-zirconium carbonitride was produced by spark plasma sintering (SPS) method, and its physical and mechanical properties were also studied.

2. Materials and Methods

The experiments were carried out with hafnium (purity 98.7%), zirconium (purity 99.9%), and carbon black (purity 99.5%) powders, which were treated in gaseous nitrogen (purity 99.5%). The HEBM of the Hf + Zr + C powder mixture (85.5 wt% Hf, 10.89 wt% Zr, and 3.61 wt% C) was carried out in an “Activator-2S” high-energy planetary ball mill (LLC Activator, Novosibirsk, Russia) in steel jars with steel grinding media. The jar rotation speed was 694 rpm, the rotation coefficient K = 1.0, and the duration t was 5, 9, 10, 15, 20, and 30 min. Nitrogen pressure was 0.6 MPa in the jars, and the ball-to-powder ratio was 20:1.

Bulk (Hf,Zr)(C,N) samples with a diameter of 12.7 ± 1 mm and a thickness of 2–3 mm were obtained by SPS on a Labox 650 setup (SinterLand, Nagaoka, Japan). The sintering was carried out in an argon atmosphere (0.08 MPa) at a heating rate of 100 °C/min to a maximum temperature of 1900 °C with a holding time of 20 min. Throughout the entire SPS process, an external load of 50 MPa was applied.

The microstructure of powder samples was studied using scanning electron microscopy (SEM) on a JEOL JSM7600F (JEOL Ltd., Tokio, Japan) device equipped with an X-MAX 80 mm\textsuperscript{2} (Oxford Instruments, Abingdon, UK) detector for energy-dispersive
X-ray spectroscopy (EDS) and AZtec software (Oxford Instruments, Abingdon, UK) to build element distribution maps and composition profiles. The shooting was carried out in the secondary electrons SE and backscattering BSE regimes at an accelerating voltage of 15 kV.

The phase composition of the powders after different HEBM durations as well as of the consolidated samples was studied by X-ray phase analysis (XRD) on a Difrey-401 diffractometer (JSC Scientific Instruments, Saint Petersburg, Russia). The samples were analyzed using the Bragg–Brentano focusing geometry without monochromatization of the incident and reflected radiation. The X-ray diffraction patterns were recorded using the Cr-Kα wavelength (λ = 0.22909 nm). The analysis was carried out in the 2θ range from 30° to 140°, and the patterns were recorded with a step Δ2θ = 0.1° and a signal accumulation time t = 2 s. The identification of the phases present in the samples was carried out based on the ICDD PDF-4 database using the Match-3 and Maud software package version 2.94 [23].

The pycnometric density (ρp) of the consolidated samples was measured by gas pycnometry using an AccuPyc 1340 setup (Micromeritics, Norcross, GA, USA). The hydrostatic density (ρh) of the samples was determined by hydrostatic weighing. The corresponding masses were obtained by weighing the samples on an analytical balance in air and in distilled water (ρw = 0.9978 g/cm³) after applying a thin layer of Vaseline to the surface to cover open porosity (ρl = 0.870 g/cm³). The relative density of the samples after SPS ρ (%) was determined as the ratio of hydrostatic density (ρh) to pycnometric density (ρp).

The microhardness (HV) and fracture toughness (KIC) of sintered samples were measured by the Vickers method using a Durascan 70 digital hardness tester (Struers ApS, Ballerup, Denmark) with a diamond indenter in the form of a tetrahedral pyramid with an apex angle of 136°. The maximum load was 30 N, and the exposure time was 20 s. When the load was removed, the diagonals of the imprint remaining on the surface of the sample were measured along with the length of the cracks.

To determine the Young’s modulus, the sintered sample was indented under an applied load of 100 mN and an exposure time of 10 s on a Micro-Hardness Tester (CSM Instruments, Peseux, Switzerland). After measurements, the numerical value of the Young’s modulus was determined by the slope of the unloading curve. The fracture resistance is calculated using the Anstis formula [24].

3. Results and Discussion

A high-energy mechanical treatment of a hafnium, zirconium, and carbon powder mixture was carried out for 5–30 min in a nitrogen atmosphere. Figure 1 shows the diffraction patterns of the initial mixture and the powders after different HEBM durations. Based on the XRD results, the powder mixture consisted of individual Hf and Zr after 5 min of HEBM.

After 9 min of HEBM, low-intensity peaks of a NaCl-type solid solution were detected on the diffraction pattern, which indicated the beginning of a chemical interaction between the components of the mixture and the formation of a new-phase nucleus. The phase composition changed drastically after 10 min of HEBM due to the mechanically induced reaction. The powder consisted predominantly of hafnium-zirconium carbonitride (Hf,Zr)(C,N), while some Hf and Zr remained unreacted after the reaction. After 20 min of HEBM, individual peaks of hafnium and zirconium were still present in the diffraction pattern, and only an increase in the mechanical treatment duration to 30 min allowed for a complete reaction and the formation of a single-phase (Hf,Zr)(C,N) carbonitride.
The dependence of the (Hf,Zr)(C,N) lattice parameter $a$ (nm) on the HEBM duration was studied (Table 1). The lattice parameter decreased over the entire treatment interval from 10 to 30 min, indicating that nitrogen atoms were introduced into the (Hf,Zr)(C,N) lattice and that the nitridation degree increased with the increase of the HEBM duration.

### Table 1. The interplanar distances and lattice parameters of reference binary compounds and hafnium-zirconium carbonitride after different HEBM durations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>HEBM Duration, min</th>
<th>(111)</th>
<th>(200)</th>
<th>(220)</th>
<th>(311)</th>
<th>(222)</th>
<th>$a$, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>HfC (#39-1491)</td>
<td></td>
<td>2.6776</td>
<td>2.3189</td>
<td>1.6401</td>
<td>1.3983</td>
<td>1.3389</td>
<td>0.4638</td>
</tr>
<tr>
<td>ZrC (#35-0784)</td>
<td></td>
<td>2.7089</td>
<td>2.3459</td>
<td>1.6592</td>
<td>1.4149</td>
<td>1.3547</td>
<td>0.4693</td>
</tr>
<tr>
<td>HfN (#33-0592)</td>
<td></td>
<td>2.6120</td>
<td>2.2620</td>
<td>1.6002</td>
<td>1.3641</td>
<td>1.3061</td>
<td>0.456</td>
</tr>
<tr>
<td>ZrN (#02-0956)</td>
<td></td>
<td>2.64</td>
<td>2.29</td>
<td>1.62</td>
<td>1.38</td>
<td>1.32</td>
<td>0.46</td>
</tr>
<tr>
<td>(Hf,Zr)(C,N)</td>
<td>10</td>
<td>2.6342</td>
<td>2.2817</td>
<td>1.6273</td>
<td>1.3889</td>
<td>1.3296</td>
<td>0.4588</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>2.6332</td>
<td>2.2803</td>
<td>1.6268</td>
<td>1.3871</td>
<td>1.3289</td>
<td>0.4585</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>2.6330</td>
<td>2.2801</td>
<td>1.6245</td>
<td>1.3863</td>
<td>1.3283</td>
<td>0.4583</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>2.6328</td>
<td>2.2792</td>
<td>1.6225</td>
<td>1.3838</td>
<td>1.3268</td>
<td>0.4578</td>
</tr>
</tbody>
</table>

The microstructures of the samples and the distribution of elements after different HEBM durations are shown in Figure 2. The initial Hf + Zr + C mixture (Figure 2a) consisted of individual particles of hafnium, zirconium, and carbon black with different morphologies. Carbon black was found in the form of agglomerates of up to 200 µm, and hafnium and zirconium particles were in the range of 20 to 250 µm. The short-term mechanical treatment (Figure 2b) contributed to the grinding of the initial components of the mixture, their flattening, and the cleaning of the surfaces from the oxide films. Through HEBM, atomically clean planes were formed, through which the flattened particles welded to each other, creating layered Hf/Zr/C composite particles. With an increase in the HEBM duration to 9 min (Figure 2c), the tendency for grinding remained, and the thickness of the layers in the Hf/Zr/C composite particles decreased to 0.2–2 µm. It is clear from the structure of the powder that the mechanically induced self-sustained reaction occurred between 9 and 10 min of HEBM. Figure 2d shows that the powder consisted mainly of agglomerates of submicron rounded particles after 10 min, which indicated the occurrence of a combustion reaction and crystallization from the melt [25,26].

![Figure 1. X-ray diffraction patterns of the initial Hf + Zr + C powder mixture and after HEBM in a nitrogen atmosphere, depending on the different treatment durations.](image-url)
Figure 2. SEM images and distribution of elements for the Hf + Zr + C powder mixtures after (a) 0, (b) 5, (c) 9, (d) 10, and (e) 30 min of HEBM in a nitrogen atmosphere.

Apparently, repeated processes of destruction and cold welding [27] during HEBM led to the accumulation of defects as well as to a decrease in the diffusion distance between Hf, Zr, and C in Hf/Zr/C composite particles and, consequently, to a decrease in the activation energy and increase in the reactivity of the mixture. Intense local heating due to friction forces, accumulated defects, and high exothermicity of the powder mixture [28,29] contributed to the initiation of a self-propagating reaction inside the jars, as a result of which the (Hf,Zr)(C,N) product was formed instantly. However, it should be noted that after 10 min, the reaction was incomplete. There were still agglomerates with a layered structure in the powder, which consisted mainly of submicron particles. A solid solution was found along the edges of the particles, and hafnium and zirconium layers about 5 µm thick were found in the central part of a submicron particle (Figure 2d). With an increase in the duration of the HEBM, the grinding of unreacted metals and solid-solution particles was promoted, resulting in the creation of new active surfaces capable of forming (Hf,Zr)(C,N) (Figure 2e). According to the EDS analysis, the synthesis product (Figure 2b–e) contained iron inclusions, which can be explained by the interaction of the mixture with the material of the steel jars and balls. After 30 min, the powder consisted of agglomerates (Figure 3a) of submicron (Hf,Zr)(C,N) particles ranging in size 10–500 nm (Figure 3b).

Figure 3. SEM images of (Hf,Zr)(C,N) powder after 30 min of HEBM at different magnifications of (a) ×3500 and (b) ×50,000.

The EDS results showed that the nitrogen N atomic content was dependent on the HEBM duration (min) (Figure 4). After 5 min of HEBM, no nitrogen was found in the composite particles. During the interval between 5 and 15 min of HEBM, the amount of
nitrogen in the system began to gradually increase from 0 to 4 at%. With a further increase in the treatment duration from 15 to 30 min, the nitrogen content continued to grow, which was in good agreement with the XRD results (Table 1). After 30 min of HEBM, the nitrogen content in the powder was ~12 at%.

![Figure 4. Dependence of the nitrogen content on the HEBM duration.](image)

Considering the XRD and SEM results, it can be concluded that during the HEBM process of a Hf + Zr + C powder mixture in a nitrogen atmosphere, the formation of a solid solution proceeded according to several stages (Figure 5). In the first stage, due to the grinding and plastic deformation of the precursor powders (Figure 5a), layered Hf/Zr/C composite particles were formed, in which the diffusion distances between Hf, Zr, and C were decreased (Figure 5b). At the second stage (Figure 5c), intense local heating led to the occurrence of a mechanically induced self-sustaining reaction. As a result, (Hf,Zr)(C,N) particles with a low nitridation degree (~1 at% N) and partially unreacted hafnium and zirconium were formed. The final stage (Figure 5d) was characterized by the formation of fully reacted submicron (Hf,Zr)(C,N) particles ranging in size 10–500 nm.

![Figure 5. Possible formation mechanism of the (Hf,Zr)(C,N) solid solution during HEBM process: (a) initial powders, (b) 1st stage: formation of composite particles, (c) 2nd stage: mechanically induced self-sustaining reaction, formation of partially reacted (Hf,Zr)(C,N) particles, (d) 3rd stage: formation of fully reacted (Hf,Zr)(C,N) particles.](image)

The synthesized submicron hafnium-zirconium carbonitride powder was consolidated by SPS at a temperature of 1900 °C, a constant pressure of 50 MPa, and a holding time of 20 min. The diffraction patterns of the MS product (30 min) and consolidated sample are shown in Figure 6. After SPS, the hafnium-zirconium carbonitride peaks became more
The synthesized submicron hafnium-zirconium carbonitride powder was consolidated by spark plasma sintering (SPS) at a temperature of 1900 °C, a constant pressure of 50 MPa, and a holding time of 20 min. The dihedral angle of the obtained (Hf,Zr)(C,N) compound was 0.4578 nm.

\[
\rho = \frac{V}{m}
\]

where \(\rho\) is the density, \(V\) is the volume, and \(m\) is the mass. The oxygen content did not exceed 2 wt%.

\[
\text{Hardness} = \frac{F}{A}
\]

where \(F\) is the load and \(A\) is the contact area. The hardness, fracture toughness, and Young’s modulus of the obtained (Hf,Zr)(C,N) are comparable to those of binary and multicomponent carbides and carbonitrides.

Figure 6. X-ray diffraction patterns of the mechanically synthesized (Hf,Zr)(C,N) powder and corresponding bulk ceramics.

Figure 7 illustrates the microstructure of the sintered sample and the distribution of the elements. The bulk material consists of (Hf,Zr)(C,N) grains (gray areas, Figure 7b) ranging in size 3–15 μm (Figure 7a). The dark areas on the micrograph correspond to ZrO2 (Figure 7b). The oxygen content did not exceed 2 wt%.

Figure 7. (a) Microstructure and (b) elemental map distribution of the consolidated (Hf,Zr)(C,N) ceramics.

Table 2 presents the densities measured by hydrostatic weighing (\(\rho_h\)) and helium pycnometry (\(\rho_p\)), as well as the calculated relative density, which was 97 ± 1%. In addition, Table 2 shows the mechanical properties of bulk hafnium-zirconium carbonitride, as well as that of more complex compounds. The hardness, fracture toughness, and Young’s modulus of the obtained (Hf,Zr)(C,N) are comparable to those of binary and multicomponent carbides and carbonitrides.
Table 2. Mechanical properties of consolidated (Hf,Zr)(C,N) ceramics in comparison with other ceramic materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho_{h}$ g/cm³</th>
<th>$\rho_{p}$ g/cm³</th>
<th>$\rho$, %</th>
<th>HV, GPa</th>
<th>Fracture Toughness $K_{1C}$ MPa m¹/²</th>
<th>Young’s Modulus, GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Hf,Zr)(C,N)</td>
<td>10.9</td>
<td>11.3</td>
<td>97 ± 1</td>
<td>17.3 ± 0.5 (30 N)</td>
<td>4.5 ± 0.4</td>
<td>450 ± 20</td>
</tr>
<tr>
<td>ZrC [30]</td>
<td>–</td>
<td>–</td>
<td>98.2</td>
<td>16.4 ± 1.3</td>
<td>3.1 ± 0.7</td>
<td>210 ± 19</td>
</tr>
<tr>
<td>HfZrC₂ [31]</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>19 ± 1.6 (100 mN)</td>
<td>3.82</td>
<td>466 ± 81</td>
</tr>
<tr>
<td>HfCo₅N₀₂ [32]</td>
<td>–</td>
<td>–</td>
<td>95.6 ± 1</td>
<td>20.8 ± 1 (10 N)</td>
<td>3.5 ± 0.2</td>
<td>~460</td>
</tr>
<tr>
<td>(Ta,Hf)CN [33]</td>
<td>–</td>
<td>–</td>
<td>98 ± 1</td>
<td>19.4 ± 0.2 (30 N)</td>
<td>5.4 ± 0.4</td>
<td>591</td>
</tr>
<tr>
<td>(Ti,V,Nb,Ta,Mo)(C,N) [34]</td>
<td>–</td>
<td>–</td>
<td>99.8</td>
<td>24.0 ± 0.7 (9.8 N)</td>
<td>4.87 ± 0.25</td>
<td>–</td>
</tr>
<tr>
<td>(Zr,Ti)(C,N)–SiC [35]</td>
<td>–</td>
<td>–</td>
<td>98.5 ± 1</td>
<td>17.7–22.4 (9.8 N)</td>
<td>3.0–4.4</td>
<td>–</td>
</tr>
<tr>
<td>(Ti,W)(C,N) [36]</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>15.9–17.8 (30 N)</td>
<td>4.0–4.57</td>
<td>429–481</td>
</tr>
</tbody>
</table>

4. Conclusions

Single-phase hafnium-zirconium carbonitride powders were mechanochemically synthesized in a planetary ball mill by treating elemental Hf, Zr, and C powders in a nitrogen atmosphere. A study of the phase evolution and structure formation, as well as the nitridization kinetics during HEBM, allowed us to establish the formation mechanism of hafnium-zirconium carbonitride powder. It was possible to obtain a solid solution of (Hf,Zr)(C,N) after short-term (10 min) HEBM due to a mechanically induced self-sustaining reaction occurring in the jars. An increase in the HEBM duration promoted further grinding of the powder media and stimulated the formation of new active surfaces that were able to interact with gaseous nitrogen. Following the above-mentioned processes, a single-phase powder with a characteristic grain size in the range of 10–500 nm was formed after 30 min of HEBM.

The consolidation of the (Hf,Zr)(C,N) samples by SPS at a temperature of 1900 °C, an external load of 50 MPa, and a holding time of 20 min led to the production of bulk high-density ceramic material. Carbonitride exhibited a relative density of 97% with a high hardness of 17 ± 0.2 GPa and fracture toughness of 4.5 ± 0.4 MPa·m¹/². The mechanical properties of the (Hf,Zr)(C,N) ceramics were comparable to or even higher than those of binary precursor compounds and double carbides.

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