Brief Report

Fabrication of Reaction-Bonded Boron Carbide-Based Composites by Binder Jetting 3D Printing

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Abstract: In this work, the binder jetting 3D printing of boron carbide was combined with a subsequent liquid silicon infiltration procedure to produce reaction-bonded boron carbide (RBBC)-based structures. After printing, the samples were isostatically pressed to obtain more homogeneous and denser microstructures while maintaining their complex shapes. The RBBC bodies were successfully fabricated, and the influence of the binder content on the amount of residual silicon was studied. By increasing the binder content from 10 to 22.5 vol.%, the Si content decreased from ~28 to ~12 vol.%. The mechanical properties dependent on the Si content were additionally investigated. The measured average values for the bending strength (~355 MPa), Young’s modulus (~348 GPa), and hardness (~20 GPa) are comparable to those reported in the literature for RBBC-based materials.

Keywords: 3D printing; additive manufacturing; boron carbide; liquid silicon infiltration; mechanical properties

1. Introduction

Boron carbide (B₄C) is one of the most important engineering ceramics due to its excellent properties. The specific weight is low (2.52 g/cm³), the material is chemically inert, and it has a high hardness (29.1 GPa). B₄C also has the ability to absorb neutrons without forming long-lived radionuclides [1–4]. Thus, it is an attractive material for numerous industrial applications [5,6]. However, the production of dense boron carbide parts requires high temperatures, and it must also be hot pressed during sintering to achieve sufficient densification [7–9]. This significantly complicates the usage of the material. The infiltration of a porous preform consisting of B₄C and/or carbon with liquid silicon (LSI), which was first developed for the production of reaction-bonded silicon carbide [10], offers an interesting alternative [11]. The carbon present in the sample reacts with the liquid silicon to form silicon carbide, and the remaining silicon then fills the larger pores. This allows the fabrication of dense B₄C-based materials with a high strength without the need for high sintering temperatures [12]. This study demonstrated the production of the parts from boron carbide using binder jetting 3D printing. In this process, a powder bed consisting of the starting material or a material mixture is solidified selectively by a binder solution. Depending on the desired shape, droplets of the binder solution are sprayed using printheads onto the powder bed. After one layer is finished, a new powder layer is applied, and the next layer is solidified. This layer-by-layer build-up process makes the production of complex structures possible. In addition, the loose powder, which is removed after the printing process, supports the printed part [13–16]. Various material classes can be produced using this additive manufacturing process, and a wide variety of ceramics, e.g., hydroxyapatite (HA) or alumina (Al₂O₃), have already been investigated [16–19]. The printed green bodies exhibit a porous microstructure, which is beneficial for
subsequent infiltrations, which have already been used for different combinations such as reaction-bonded silicon carbide and B4C-Al [20–22].

In this work, binder jetting was combined with LSI for the first time to produce reaction-bonded boron carbide. Bending bars, plates, and curved plates were successfully printed, thermally treated, and subsequently, infiltrated with molten Si. In our case, the dextrin in the powder bed serves as a binder and a carbon source for Si infiltration. Although other starting materials, such as polyvinyl butyral (PVB), phenyl silicone resin, phenolic resin, etc., were used in our studies to increase the carbon content and decrease the porosity in the printed bodies, the focus of this article is solely on the influence of the dextrin content. The influence of the additional sources will be the focus of further publication. To reduce the amount of free silicon in the final product and thus improve the mechanical properties, the bulk density of the green samples was increased by cold isostatic pressing [12,23]. All of the parts could be post-processed in the pyrolyzed state, e.g., by grinding or milling. This step was essential because the processing of the pyrolyzed samples was much faster and easier than that of the siliconized samples.

2. Materials and Methods

2.1. Sample Preparation

Boron carbide powder (F1200, 3M Technical Ceramics, Germany) with a particle size of 1-7 µm and a dextrin binder powder ((C₆H₁₀O₅)n, Superior Gelbmittel F, Suedstaerke, Germany, MW: 1600–32000 g/mol) were used to obtain a powder bed suitable for the 3D printing process. To obtain a homogenous powder mixture without agglomerates, SiC milling balls with a diameter of 10 mm were added, and the mixture was dry tumbled for 24 h in a 2 L-polyethylene bottle using a tumbling mixer (Reax 20, Heidolph, Schwabach, Germany). Since the binder content greatly influences the properties of the printed parts and the mechanical properties of the final products [24–26], the dextrin amount in the powder mixtures was varied between 10.0 vol.% and 22.5 vol.%. The 3D printing was carried out on a powder-bed-based 3D printer (Zprinter 510, Z-Corporation, Burlington, VT, USA) using a water-based printing solution containing 12.5 vol.% glycerin (Sigma Aldrich Chemie, Steinheim, Germany) [27,28]. Bar- and plate-shaped samples with dimensions of 60.5 × 6.5 × 6.5 mm³, 70.5 × 70.5 × 5.5 mm³, and 70.5 × 70.5 × 7.5 mm³, respectively, were printed with a layer thickness of 100 µm. The printed samples were dried in the powder bed at room temperature for 24 h prior to dedusting. Subsequently, the samples were pressed using a cold isostatic press (Loomis Products Kahlefeld GmbH, Kaiserslautern, Germany) at a pressure of 150 MPa to reduce the porosity and obtain a more homogeneous microstructure. The advantage here is that even more complex structures could be post-compacted without incurring damage while also retaining their shape.

As B₄C is oxygen- and nitrogen-sensitive [29], the thermal treatments were carried out under an Ar atmosphere. Pyrolysis took place at 700 °C for 60 min with a heating rate from 1 to 5 K/min to ensure the decomposition of the dextrin, and thus, the formation of the residual carbon. Then, a sintering step was performed at 1900 °C with a holding time of 60 min and a heating rate of 10 K/min (FCT Systeme GmbH, Frankenblick, Germany), which was followed by infiltration with liquid silicon to obtain reaction-bonded B₄C-based material [30]. For this, the samples were placed in a boron nitride-coated graphite crucible, embedded into Si powder (Silgrain HQ, Elkem, Norway), and infiltrated at 1550°C under vacuum with a holding time of 60 min.

2.2. Sample Characterization

Laser granulometry was performed to determine the particle size distribution of the starting powders (Mastersizer 2000 APA 2000, Malvern Instruments, UK). The true density of the silicon-infiltrated samples was analyzed by helium pycnometry (Accupyc 1330, Micromeretics, Norcross, GE, USA). The open porosity in the different processing steps...
was calculated from the measured geometrical and pycnometric densities. The phase analysis of the final samples after liquid Si infiltration and of the raw powder was performed by X-ray diffraction (XRD, Kristalloflex D 500, Siemens, Karlsruhe, Germany) using monochromatic Cu-Kα radiation at a scanning rate of 1°/min over a 2θ range of 20–70°. The microstructure of the cross-sections of the infiltrated samples polished up to 1 µm were investigated by scanning electron microscopy (SEM, Quanta 200, FEI, Bmo, Czech Republic). The volume fraction of different phases in siliconized B:C-Si-SiC samples was derived from the SEM micrographs by applying a free image analysis software (ImageJ, Wayne Rasband). The bending strength was measured by a 4-point bending method. The tensile surfaces of the samples were polished up to 6 µm prior to bending. The tests were performed using a testing machine (Instron 4204, Instron Corporation, Canton, Norwood, MA, USA) with a crosshead speed of 0.5 mm/min according to DIN EN 843-5. The Young’s modulus was analyzed using the impulse excitation technique (Buzz-O-Sonic, BuzzMac International LLC, Portland, ME, USA) according to EN 843-2. The average values of these mechanical properties were calculated from at least eight measurements. The Vickers hardness (Zwick 3212, Zwick, Ulm, Germany) of the specimens polished up to 1 µm was measured at a load of 49 N which was applied for 15 s.

3. Results

3.1. Raw Materials

B:C and dextrin powder were used as the ceramic filler and binder for the 3D printing process, respectively. The measured average particle size of the B:C powder was ~4 µm, which is relatively small compared to the dextrin powder with a diameter of ~142 µm. The dextrin was converted to carbon during pyrolysis, which led to the formation of additional porosity in addition to the porosity already originating from the printing process. In spontaneous liquid Si infiltration without additional external pressure, the pore sizes are crucial for the infiltration result; large pores with a diameter of more than 150 µm can hardly be filled, and they have a negative effect on infiltration [27,31]. Therefore, the 3D printing powder blends were sieved with a 150 µm mesh screen before printing to remove the larger particles.

3.2. Properties of Reaction-Bonded B:C-SiC-Si

The binder content in the powder mixture was varied to determine the best formulation. The samples with 10.0, 18.6, and 22.5 vol.% dextrin based on the amount of B:C powder were printed, heat treated, and infiltrated with liquid silicon. The results of the physical and mechanical measurements of the samples are shown in Table 1.

<table>
<thead>
<tr>
<th>Binder Content in the Starting Powder Mixture</th>
<th>Phase Composition B:C/Si/SiC [vol.%]</th>
<th>True Density After Si Infiltration [g/cm³]</th>
<th>Young’s Modulus [GPa]</th>
<th>Hardness HV5 [GPa]</th>
<th>Bending Strength σ05 [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0 vol.%</td>
<td>57.1/28.2/14.7</td>
<td>2.58 ± 0.21</td>
<td>339 ± 25</td>
<td>18.6 ± 1.1</td>
<td>372 ± 74</td>
</tr>
<tr>
<td>18.6 vol.%</td>
<td>59.1/15.3/25.6</td>
<td>2.62 ± 0.25</td>
<td>343 ± 10</td>
<td>20.9 ± 2.6</td>
<td>392 ± 52</td>
</tr>
<tr>
<td>22.5 vol.%</td>
<td>56.6/12.3/31.1</td>
<td>2.68 ± 0.32</td>
<td>361 ± 39</td>
<td>21.1 ± 1.9</td>
<td>300 ± 47</td>
</tr>
</tbody>
</table>

All of the samples, independent of the amount of added binder, showed a high porosity of about 63% after pyrolysis and sintering. When the additional pressing step (150 MPa) was performed, the samples showed suitable properties for the subsequent liquid silicon infiltration, with a porosity of about 39%. After infiltration, the samples exhibited a density of ~2.6 g/cm³ and a residual porosity of <1%, indicating successful infiltration. The density slightly increased with an increasing binder content due to the increasing amount of SiC in the final product. Figure 1a shows a representative homogeneous
The higher magnified SEM image (Figure 1b) shows three distinct phases, which were analyzed by EDX (Energy-dispersive X-ray spectroscopy): (i) the dark B₄C-phase, (ii) the bright Si-phase, and (iii) the brighter and needle-shaped secondary β-SiC phase formed in situ during the silicon infiltration by the reaction between the residual carbon and the molten silicon [3,32]. The phase composition of the samples with a varying binder content was additionally analyzed by image analysis (Table 1). As the binder content increases, the amount of residual Si decreases from ~28 vol.% to ~12 vol.%, which can be explained by the higher amount of carbon available for the reaction with the silicon, leading to a simultaneous increase of the SiC content (from ~15 vol.% to ~31 vol.%). The volume fraction of the B₄C phase remains constant (~58 vol.%) since it was not varied in this study.

**Figure 1.** (a) Representative SEM images of a siliconized B₄C-based sample with an initial binder content of 18.6 vol.%. (b) Higher magnified SEM image with detected phases: B₄C, reaction-formed SiC, and Si.

Furthermore, the composition of the reaction-bonded B₄C-based samples was investigated by XRD. According to the XRD analysis, no significant influence of the binder content on the phase composition could be detected. As an example, the XRD spectrum of the sample with 10.0 vol.% binder content is shown in Figure 2.

As already analyzed by EDX, all of the siliconized samples, independent of the binder content, consist of B₄C, β-SiC, and Si. Hayun et al. reported that during Si infiltration, B₄C reacts with molten silicon to form a ternary B₁₂(C, Si, B)₃ phase that precipitates in the rim region of the initial boron carbide [32]. However, in the XRD pattern B₁₂(C, Si, B)₃ shows the same peak position as the B₄C phase, making it difficult to distinguish between these phases [33,34]. A complete reaction of the carbon, which was added in the form of the binder, to SiC can be assumed since no carbon could be detected in the infiltrated samples.

The mechanical properties of the reaction-bonded B₄C-based samples after liquid silicon infiltration were investigated, and they are shown in Table 1. Compared to hot-pressed B₄C, the obtained hardness values of ~20 GPa are lower due to the presence of Si and SiC phases in the matrix [33,34]. Increasing the binder content, and thus, the carbon content, leads to an increase of the SiC content and a decrease of the Si content, which are beneficial for mechanical properties, and can explain the slight increase in hardness (Table 1) [7,35]. Compared to traditional fabricated RBBC samples, the additively manufactured ones in this work show comparable hardness values [7,10]. Additionally, the measured values of ~390 MPa and ~340 GPa for the bending strength and Young’s modulus, respectively, are comparable to literature data for the conventionally fabricated RBBC [7,11,12]. The formation of residual micro-stresses due to the thermal and elastic mismatches
between the phases, the volume expansion (58 vol.%) during the reaction of silicon with carbon leading to the formation of silicon carbide, and the expansion of the residual silicon during its solidification may explain the relatively small differences between the measured values of the mechanical properties and their deviations [36].

Figure 2. XRD spectrum of the infiltrated sample consisting of SiC, B₄C, and Si.

In addition to the fabrication of the samples to characterize the manufactured material, this work also demonstrated the feasibility of fabricating large B₄C plates by 3D printing and the subsequent Si infiltration (Figure 3). Defect-free reaction-bonded B₄C plates with a final dimension of 70 × 70 × 5 mm³, 70 × 70 × 7 mm³, as well as curved plates, were successfully fabricated with an initial binder content of 18.6 vol.% in the starting powder blend.

Figure 3. Siliconized and ground RBBC plates with varying thicknesses and a curved plate.

4. Conclusions
This study demonstrated for the first time that nearly dense reaction-bonded boron carbide samples can be produced by binder jetting 3D printing in combination with liquid silicon infiltration. The samples were printed, cold isostatically pressed to obtain a more homogenous microstructure, and successfully infiltrated with liquid silicon. The obtained mechanical properties are promising and comparable to those of conventionally manufactured RBBC-based materials. At the same time, the demonstrated process offers the possibility to create more complex structures.

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References


