Microstructure control and toughening of ZrB$_2$–SiC/Zr–Al–C composite ceramics by selecting additional powders mixed with ZrB$_2$ in ball milling for spark plasma sintering

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ZrB$_2$–SiC composite ceramics were fabricated by spark plasma sintering SiC powders with various mixtures of ZrB$_2$, Zr, Al and graphite components, toughening the ceramics through the in-situ synthesis of Zr–Al–C microstructures. Different microstructures of Zr–Al–C toughened ZrB$_2$–SiC (ZSA) composite ceramics were formed during the sintering process by varying the components ball milled with the ZrB$_2$ powders prior to sintering. When the milled ZrB$_2$-based powders contained Al, the major Zr–Al–C phase changed into Zr$_3$Al$_2$C$_6$ from the designed Zr$_2$Al$_4$C$_5$, and the layered Zr–Al–C grains formed with a large aspect ratio in the ZSA ceramics due to the formation of an Al-based coating layer covering the ZrB$_2$ powders during milling process. The Zr and Al co-milled ZrB$_2$-based powders further improved the toughness of composite ceramics through a more uniform distribution and the larger aspect ratio of Zr–Al–C grains. As a result, the ZSA ceramic made using the milled powders of ZrB$_2$, Zr and Al showed the highest fracture toughness of 5.96 MPa·m$^{1/2}$, about 10% higher than that of the ceramic made using milled ZrB$_2$ and Zr powders. The toughening mechanisms are shown to be crack deflection and bridging caused by Zr–Al–C grains. This work points to a possible pathway to control the microstructure of Zr–Al–C grains for toughening ZrB$_2$–SiC composite ceramics.

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1. Introduction

Recently, ZrB$_2$–SiC composite ceramics have attracted increased interest due to their superior oxidation resistance and mechanical properties in comparison to well-known, ultrahigh-temperature monolithic ZrB$_2$ ceramics.$^{1-14}$ The low fracture toughness of ZrB$_2$–SiC composite ceramics is one of the major barriers for practical applications. The addition of components with a large aspect ratio is a widely used approach to improve the fracture toughness of a ceramic matrix. Layer-structured Zr–Al–C compounds have attracted significant research interest due to their superior strength, high fracture toughness and excellent oxidation resistance.$^{15-18}$ The Zr–Al–C compounds have been used to improve the sinterability and toughness of ZrB$_2$–SiC composite ceramics as well as ZrB$_2$ ceramics.$^{19-23}$

Spark plasma sintering (SPS) is a well-known rapid sintering technique for nearly full densification of compound ceramics and thermoelectric bulk materials at a relatively low temperature.$^{24-30}$ The ZrB$_2$–SiC composite ceramics have been rapidly sintered by SPS.$^{3,4}$ In our previous works, we used the SPS method to in-situ synthesize Zr–Al–C grains for toughening ZrB$_2$–SiC ceramics.$^{21,23}$ It was found that milling ZrB$_2$-based composite powders for a moderate time led to a more uniform distribution and a longer slenderness ratio of Zr–Al–C grains in the sintered composite ceramics, leading to increased toughness.$^{23}$ However, the impact of the composition of the ball-milled ZrB$_2$-based composite powders on the sintered composite ceramics was unknown. Discovering a relationship between the composition of the raw ball-milled powders and the microstructure of resulting composite ceramics is significant for optimizing preparation processing and improving performance.

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In this study, we used SiC powders in conjunction with various ZrB$_2$-based composite powders to fabricate Zr–Al–C toughened ZrB$_2$–SiC (ZSA) composite ceramics by SPS. The four different ZrB$_2$-based composite powders were prepared through mixing the selected additional components—Zr (Z), Al (A), Zr and Al (ZA), and Zr, Al and graphite (ZAC)—with ZrB$_2$ powders by using ball milling. An optimal ball milling time of 4 h was used as found in previous work. The microstructure evolution and toughening mechanism of the ZSA composite ceramics prepared through the addition of different ZrB$_2$-based composite powders were identified and evaluated.

2. Experimental details

2.1 Preparation

The raw materials used in the preparation of the ZSA ceramics were SiC (purity >99.95%, 6 μm), ZrB$_2$ (purity >99.5%, 10 μm), Zr (purity >99.9%, 10 μm), Al (purity >99.99%, 8 μm), and graphite (purity >99.9%, 1 μm) powders. The selected additional components—Zr (Z), Al (A), Zr and Al (ZA), and Zr, Al and graphite (ZAC)—were mixed with ZrB$_2$ powders to prepare four different ZrB$_2$-based composite powders (Z, A, ZA, and ZAC composite powders) by using high-energy ball milling (Vario-Planetary Mill, Fritsch Pulverisette 4, Germany) at a constant frequency of 350 Hz for 4 h in a steel tank with WC balls and a protective Ar gas atmosphere. The weight ratio of powders to balls was 1:10. Additionally, Si powders (4 wt. % of the total weight of ZrB$_2$, Zr and Al powders) were added into ZrB$_2$-based mixture powders for ball milling. The molar ratio of ZrB$_2$:Zr:Al:C in raw powders for sintering was 3.5:1:3:1:4:8. The designed component of composite ceramics was 50 vol. % ZrB$_2$, 20 vol. % SiC and 30 vol. % Zr$_2$Al$_4$C$_3$. The SiC powders, four different ball-milled ZrB$_2$-based composite powders, and the other raw powders were sufficiently mixed in an agate mortar for sintering.

The detailed SPS process was reported in previous works. The temperature was measured by an optical pyrometer focused on the surface of the graphite die. The samples were heated to 600°C at a rate of 300°C/min, after which an average heating rate of 100°C/min was maintained up to 1800°C where the it was held constant for 3 min. The sample was cooled naturally after the sintering period was completed. A uniaxial pressure of 20 MPa and a vacuum atmosphere were applied from the start to the end of the sintering cycle.

2.2 Characterization and measurement

An oxygen and nitrogen analyzer (Leco TC600, USA) was used to analyze the oxygen content in the powder samples. The bulk density and porosity of the ceramic samples were measured through the Archimedes’ immersion method using water as the immersion medium. The phase composition of samples was analyzed by X-ray diffraction (XRD) using a Rigaku Ultima III diffractometer (Cu Kα radiation, operation at 40 KV and 40 mA). The surface and fracture morphologies of bulk ceramics were observed using a scanning electron microscopy (SEM, Hitachi S-3400, Japan). A software program (Image-Pro Plus 6.0, Media Cybernetics, USA) was used to determine the slenderness ratio of Zr–Al–C grains and the grain size of ZrB$_2$ in bulk ceramics through image analysis of SEM micrographs.

A detailed description of the measurement of mechanical properties, including Young’s modulus (E), Vickers hardness (HV) and fracture toughness (K$_\text{IC}$), was reported in previous work. The Young’s modulus of the composites was determined by using an ultrasonic equipment (Panametrics 5072PR) with a fundamental frequency of 20 MHz. The Vickers hardness and fracture toughness were measured using a Vickers indenter (Wolpert 430SVD, USA). Each polished sample was indented at five locations with a 98N load for 15s. The fracture toughness was calculated using the following equation:

$$K_{\text{IC}} = \frac{0.026\sqrt{a}}{E} \left(\frac{P}{c^3}\right)^{1/2}$$  \hspace{1cm} (1)

where $E$ is Young’s modulus, $P$ the load, $2a$ the indentation diagonal length, and $2c$ the crack length. If the ratio of crack length to indentation length ($c/a$) is smaller than 2.3, or if crack branching occurs, the data are rejected.

3. Results and discussion

The mechanochemical process of ball milling causes chemical adsorption of oxygen on the surface of the milled powders. During the SPS process, only chemically adsorbed oxygen can affect the microstructure of the resulting composite ceramics as the physically adsorbed oxygen is removed during the heating process. Because a large portion of the detected oxygen represents the physically adsorbed surface oxygen, it is expected that the actual content of chemically adsorbed oxygen is much lower than the measured value. As shown in Table 1, the oxygen content (molar ratio) of sample A is very close to that of sample ZA, and there is only a slight increase in the oxygen content for sample ZAC while a much lower oxygen content was detected in sample Z. Normally, Al powders adsorb oxygen and form chemical bonds during ball milling, which could explain why substantially more oxygen was detected in the milled powders containing an Al component. The further increase in the oxygen content of ZAC sample probably resulted from the physically adsorbed oxygen on the flake graphite powders. The graphite powders could adsorb oxygen from the other powders during ball milling and prevent the oxidation of milled powders, hence, the chemically adsorbed oxygen

| Table 1. Oxygen content of milled ZrB$_2$-based composite powders with different additional powders |
|-------------------------------------------------|--------|-----|------|-----|
| **Item** | **Z** | **A** | **ZA** | **ZAC** |
| Additional powder | Zr | Al | Zr and Al | Zr, Al and C |
| Oxygen content (wt.%) | 2.92 | 4.32 | 3.80 | 3.65 |
| Molar ratio of Zr:Al:O | 1:~0.46 | ~3:1.0:0.68 | 1:3:1.0:70 | 1:3:1.0:86 |
in the milled powders would be reduced. The physically adsorbed oxygen on graphite powders would be removed during the SPS process. Therefore, it can be concluded that the content of chemically adsorbed oxygen in the ZAC sample is lower than that in the A and ZA samples, and that some of the oxygen detected in the ZAC sample exists in the form of carbon oxides.

The XRD patterns of sintered ZSA ceramics are shown in Fig. 1. The Zr$_3$Al$_4$C$_6$ and Zr$_2$Al$_4$C$_5$ belonging to Zr–Al–C compounds are considered to have the same influence on the ZSA composite ceramics. Zr$_2$Al$_4$C$_5$ is the major Zr–Al–C phase in the ZSA–Z sample while Zr$_3$Al$_4$C$_6$ becomes the major Zr–Al–C phase in the ZSA–A and ZSA–ZA samples. Furthermore, an apparent mixed phase of major Zr$_3$Al$_4$C$_6$ and partial Zr$_2$Al$_4$C$_5$ was observed in the ZSA–ZAC sample. It is indicated that adding Al into the ball-milled ZrB$_2$–based powders led to the apparent phase transition from Zr$_2$Al$_4$C$_5$ to Zr$_3$Al$_4$C$_6$ in the composite ceramics during sintering process. The different milled ZrB$_2$–based composite powders have different compositions, leading to different reaction processes in the SPS sintering process and different resulting phase compositions in the composite ceramics. It is clearly apparent from Fig. 1 that there are Al$_2$O$_3$ peaks in the ZSA–A and ZSA–ZA samples, which is probably attributed to the reaction of Al with the chemically adsorbed oxygen in the composite powders during the sintering process.

Figure 2 shows the open porosity and density of the ZSA composite ceramics. The very small changes in the density are likely a result of the difference in the composition of the mixed phases of the ZSA ceramics. The increase in the open porosity is mainly attributed to the increase in oxygen content of the milled powders. On one hand, the existence of Al$_2$O$_3$ hindered the sintering and densification of the composite ceramics and resulted in the formation of open pores inside the sintered ceramics. On the other hand, the removal of carbon oxides included in ZAC powders during the sintering process caused pore formation which increases the open porosity of the ZSA–ZAC sample.

As shown in Fig. 3, in combination with EDS analysis, it is clear that Zr–Al–C grains are the columnar or plate-like gray grains while the bright particles and dark phases correspond to ZrB$_2$ and SiC, respectively. The different grains disperse more homogenously in the ZSA–ZA sample showing agglomeration-free, and uniform distribution of the Zr–Al–C grains. There is obvious agglomeration observed in ZSA–A and ZSA–ZAC samples, while no clear layered structure of Zr–Al–C grains is observed in ZSA–Z sample.

Table 2 shows the average grain size of ZrB$_2$ and aspect ratio of Zr–Al–C in ZSA composite ceramics.

| Sample   | ZSA–Z | ZSA–A | ZSA–ZA | ZSA–ZAC |
|----------|-------|-------|--------|---------|
| Grain size of ZrB$_2$ (µm) | 3.8 ± 2.1 | 3.6 ± 1.4 | 2.9 ± 1.5 | 3.2 ± 1.7 |
| Aspect ratio of Zr–Al–C | 3     | 6     | 7      | 6.5     |

Fig. 1. XRD patterns of ZSA composite ceramics by using different milled ZrB$_2$–based composite powders: (a) ZSA–Z, (b) ZSA–A, (c) ZSA–ZA, (d) ZSA–ZAC.

Fig. 2. The curve of the open porosity and density of ZSA composite ceramics made by using different milled ZrB$_2$–based composite powders.

Fig. 3. BESEM images of the polished surfaces of ZSA composite ceramics: (a) ZSA–Z, (b) ZSA–A, (c) ZSA–ZA, (d) ZSA–ZAC.
which can be attributed to the formation of an Al coating layer covering ZrB₂ particles during ball milling. In addition, the sufficient mixing and combination of Zr, Al, and ZrB₂ in the milling process caused a more uniform distribution of the ZrB₂-based composite powders, resulting in the larger aspect ratio of Zr–Al–C grains and the more uniform distribution of the different components in the ZSA–ZA sample.

From Table 3 it is found that Vickers hardness and Young’s modulus of the ZSA–ZA sample are not remarkably different for the ZSA ceramics. The ZSA–ZA sample exhibits relatively higher values of Vickers hardness and Young’s modulus, which is probably attributed to the more uniform distribution of different components as well as the slightly higher values of Zr₂Al₄C₆ (12.4 and 367 GPa) compared to Zr₂Al₄C₅ (11.7 and 361 GPa). As shown in Table 3, the ZSA–ZA sample exhibits a fracture toughness value of 5.96 ± 0.41 MPa.m^1/2, which is about 10% higher than that of the ZSA–Z sample. The relatively low roughness of the ZSA–ZAC sample is due to its relatively high open porosity.

Figure 4 shows the SEM fracture surface of the ZSA ceramics. There are many pits resulting from the pull-out of Zr–Al–C grains found on the fracture plane of the ZSA–Z sample. Many long fracture edges and fewer pull-out pits are also observed on the fracture plane of the ZSA–A and ZSA–ZA samples. Some pores are observed in the ZSA–ZAC sample, corresponding to the high open porosity. A mixture of transgranular and intergranular fracture modes is clearly observed for all the samples.

The quantitative metallographic technique was adopted to determine the aspect ratio of Zr–Al–C grains, and the maximum average aspect ratio of Zr–Al–C grains was estimated to be 7 for the ZSA–ZA sample, as shown in Table 2. It is generally believed that elongated grains with a high aspect ratio enhance the fracture toughness of a ceramic matrix, and the incorporation of high aspect ratio reinforcements has been used to reduce the brittleness of ZrB₂-based composites. In addition, the weak interface bonding between Zr–Al–C and matrix phases, and the weak internal layers of Zr–Al–C crystals lead to crack deflection and bridging. For the ZSA–A and ZSA–ZA samples, the Zr–Al–C grains caused apparent crack deflection and bridging that correspond to the many long fracture edges observed on the fracture surface as shown in Fig. 4. The relatively homogeneous microstructure further contributed to the improvement of fracture toughness for the ZSA–ZA sample.

The propagation paths of Vickers indentation-induced cracks in the ZSA ceramics were observed by SEM to investigate the toughening mechanisms, as shown in Fig. 5. The crack paths are lengthened in all samples as they follow a zigzag pattern. This crack pattern absorbed the energy of crack propagation during the fracture process and led to more short crack paths, extending the total path and toughening the ceramics. The arrows indicate the crack deflection and crack bridging caused by layered Zr–Al–C grains. It is clearly observed that the Zr–Al–C grains with a larger aspect ratio caused crack deflection and crack bridging due to the weak interface bonding between Zr–Al–C and matrix phases, leading to the longer crack paths and hence achieving the best toughening of ZSA composite ceramics.

Table 3. The Young’s modulus, Vickers hardness and fracture toughness of ZSA composite ceramics made by using different milled ZrB₂-based composite powders

| Sample | ZSA–Z | ZSA–A | ZSA–ZA | ZSA–ZAC |
|--------|-------|-------|--------|---------|
| Vickers hardness (GPa) | 15.02 | 15.21 | 16.14 | 15.57 |
| Young’s modulus (GPa) | 374 | 367 | 393 | 357 |
| Fracture toughness (MPa.m^1/2) | 5.42 ± 0.27 | 5.73 ± 0.29 | 5.96 ± 0.41 | 5.61 ± 0.28 |

4. Conclusions

Zr–Al–C toughened ZrB₂–SiC composite ceramics (ZSA) were prepared by spark plasma sintering SiC pow-
ners in combination with different ball-milled ZrB₂-based powders. By using four different additional components-Zr powder, Al powder, Zr and Al powders, and Zr, Al and graphite powders- mixed with ZrB₂ powders in the ball milling process, ZSA composite ceramics with different microstructures were obtained. The presence of Al in the milled powders resulted in an Al coating layer on the surface of ZrB₂ particles and led to the formation of Zr–Al–C grains with a much higher aspect ratio in the sintered ZSA ceramics. When only adding Zr powder for milling with ZrB₂, as the designed composition, the Zr–Al–C phase was Zr₂Al₄C₅ in the ZSA ceramic. While the milled powders of Zr, Al and ZrB₂ resulted in a more uniform distribution of the different components and a larger aspect ratio of Zr–Al–C grains in the ZSA ceramic, which contributed to the higher fracture toughness. A mixed fracture mode of inter- and intra-granular fractures occurred, and the toughening mechanisms of crack deflection and bridging caused by Zr–Al–C grains were found.

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