Preparation and Microstructure of Laminated ZrB$_2$-SiC Ceramics with Porous ZrB$_2$ Interlayers

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Abstract. Laminated ZrB$_2$–SiC ceramics with porous ZrB$_2$ interlayers were successfully prepared by Spark plasma Sintering (SPS)/tape casting, laminating and Reactive Spark Plasma Sintering (RSPS). ZrB$_2$–SiC plates were sintered by SPS. And ZrO$_2$-B$_4$C sheets were prepared by tape casting, which will undergo reducing reaction that produces porous ZrB$_2$ interlayers during SPS processing. The ZrB$_2$-SiC plates and ZrO$_2$-B$_4$C sheets were laminated alternately and reactive sintered to laminated ceramics with porous ZrB$_2$ interlayers. The porosity and thickness of the porous layers were controlled by the tape casting processing and sintering pressure. The microstructure of the laminated ZrB$_2$-SiC ceramics was analysed and discussed in details.

Introduction

Zirconium diboride (ZrB$_2$) is a member of a family of materials known as ultra-high-temperature ceramics (UHTCs) [1-4]. Several carbides and nitrides of the group IVB and VB transition metals are also considered UHTCs based on melting temperatures in excess of 3000 °C and other properties [1, 5-7]. In addition to high melting temperatures, ZrB$_2$ has a unique combination of chemical stability, high electrical and thermal conductivities, and resistance to erosion/corrosion that makes it suitable for the extreme chemical and thermal environments associated with hypersonic flight, atmospheric re-entry, and rocket propulsion [8-11].

Thermal conductivity value of single-crystal ZrB$_2$ is 140 W·m$^{-1}$·K$^{-1}$ in the basal direction and 100 W·m$^{-1}$·K$^{-1}$ along the c-axis [1, 2]. High thermal conductivity, which leads to low temperature difference between the surface and the bottom of ceramic components, is important for applications such as thermal insulation [12]. In addition to thermal properties, the low fracture toughness directly related to the limited mechanical reliability has long prevented ZrB$_2$ ceramic from being used in wide structural applications. [13, 14]

Porous materials have advantages, for example, low thermal mass, low thermal conductivity, low density and high specific strength [15-20]. Porous ZrB$_2$ ceramics are expected to have low density and thermal conductivities. Ronald Loehmen et al. [21] reported that porosity had the greatest effect on the thermal diffusivity and thermal conductivity. In comparison with the ZrB$_2$-SiC ceramics, the diffusivities of the porous samples are very small. Based on these results, the ceramics designed with low porosity may present low thermal conductivity, and good thermal shock resistance. According to

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Chen Yuan et al. [22], the pores appear to improve the resistance to thermal shock, because porosity decreases the elastic modulus of the material and hence reduces the driving force for cracking.

The design of ceramic laminate to enhance the fracture toughness of ceramics is considered one of the effective strategies. [13, 14] Previous work has demonstrated the benefits of laminating either strong ceramic layers or fibers with crack deflecting interlayers to produce ceramic components with enhanced resistance in application where there are high thermal loads. [23] In the case of layered ceramics, the low-energy paths for crack propagation in the porous interlayers can be controlled to improve their mechanical properties. [24, 25] In our former work, Zirconium oxide (ZrO$_2$) and boron carbide (B$_4$C) were used to produce ZrB$_2$ porous ceramic, and the reaction process was investigated in details [26]. And then ZrO$_2$ and B$_4$C were added to ZrB$_2$ raw powders to prepare ZrB$_2$ porous ceramics by Reactive Spark Plasma Sintering (RSPS). The porosity could be controlled by changing the ratio of synthesized ZrB$_2$ to raw ZrB$_2$ powders [27].

In the present work, ZrB$_2$–SiC plates were sintered by SPS. And ZrO$_2$–B$_4$C sheets were prepared by tape casting. Laminated ZrB$_2$–SiC ceramics with porous ZrB$_2$ interlayers were successfully prepared by ZrB$_2$–SiC plates and ZrO$_2$–B$_4$C sheets, which will undergo reducing reaction that produces porous ZrB$_2$ interlayers during SSPS processing. The Microstructure of the laminated ZrB$_2$–SiC ceramics was investigated in details.

**Experimental**

The raw materials used in the present study are as follows: commercial monolithic ZrO$_2$ (monolithic ZrO$_2$, no stabilizers, particle size ~0.1 μm, Jiaozuo Weina Co., Ltd, Henan, China), B$_4$C (particle size <10 μm, Alfa Aesar Co., Ltd.), ZrB$_2$ (particle size ~3 μm, Alfa Aesar Co., Ltd.), and SiC (particle size 5.5 μm, Shandong Weifang Huamei Co., Ltd, Shandong, China).

The designed compositions of the laminated ZrB$_2$–SiC ceramics with porous ZrB$_2$ interlayers were 80 vol.% ZrB$_2$ and 20 vol.% SiC. The powder mixtures of ZrB$_2$ and SiC were ground using alcohol as the solvent in agate mortar, followed by rotating evaporation to remove the solvent. After evaporation, the obtained mixtures were sintered to ZrB$_2$–SiC ceramic plates in graphite die under vacuum (~10 Pa) by SPS (Model SPS-1050, Sojitz Machinery Corporation, Japan). The sintering temperature is 1800°C at a heating rate of 100 °C per minute from 600–1800 °C, and a hold time of 3 min at 1800 °C with 30 MPa Pressure, and the heat treatment temperature is 1600 °C with a hold time of 10 min, as seen in Figure 1. The pressure of ~30 MPa at 1800 °C and ~2 MPa at 1600 °C was applied during the sintering processing. Changes in the vacuum level of the chamber and shrinkage of the powder were monitored and recorded during the sintering.

![Figure 1. SPS sintering of ZrB$_2$-SiC ceramic plates](image)

The powder mixtures of ZrO$_2$ and B$_4$C (with the mole ratio of 7:5 according to reaction (1)) were ball-mixed for 2 h in a polyethylene bottle using agate balls and ethanol as the grinding media, followed by
adding polyvinyl butyral resin (PVB), polyethylene glycol-6000 (PEG-6000), EYPS-3 and acetone as adhesive, plasticizer, disperser and solvent. Then the slurries were ball milled for another 10 h. The mass ratio of ZrO$_2$-B$_4$C mixture to PVB, PEG-6000, EYPS-3, ethanol and acetone is 10:1:1:0.4:6:6 in slurries. The ZrO$_2$-B$_4$C sheets were formed by tape casting.

\[ 7 \text{ZrO}_2 + 5 \text{B}_4\text{C} \rightarrow 7 \text{ZrB}_2 + 3 \text{B}_2\text{O}_3 (\ell) + 5 \text{CO (g)} \]  

(1)

The ZrB$_2$-SiC ceramic plates and ZrO$_2$-B$_4$C sheets were alternately stacked in a graphite die and sintered to laminated ZrB$_2$-SiC ceramics with porous ZrB$_2$ layers by SPS at 1600 °C for 10 min. Different sintering pressure was applied to control the thickness and porosity of the porous ZrB$_2$ layers. The phase analysis of the ZrB$_2$-SiC ceramic plates, ZrO$_2$-B$_4$C sheet and laminated ZrB$_2$-SiC ceramics with porous interlayers was carried out using X-Ray Diffraction (XRD, Model Ultima I11, Rigaku, Japan). The microstructure features of laminated ZrB$_2$-SiC ceramics were observed by Scanning Electron Microscope (SEM, Model 4300N, Hitachi, Japan) with simultaneous chemical analysis by energy dispersive spectroscopy (EDS, Hitachi, Japan).

**Results and discussion**

1.1. Preparation

![Figure 2. XRD spectra of ZrB$_2$-SiC powders, ZrO$_2$-B$_4$C sheet (a) and the side of the laminated ZrB$_2$-SiC ceramics with porous ZrB$_2$ interlayers (b).](image-url)

The laminated ZrB$_2$-SiC ceramics were prepared from stacked ZrB$_2$-SiC plates/ZrO$_2$-B$_4$C sheets body. Figure 1 shows the XRD patterns of the ZrB$_2$-SiC powders, ZrO$_2$-B$_4$C and laminated ZrB$_2$-SiC. According to the XRD results, only the ZrB$_2$ and SiC phases were detected in the laminated ceramics. The EDS results show that there exists B, Zr, Si and C on the surface that perpendicular to the laminas. It is obvious that the reduction between ZrO$_2$ and B$_4$C (reaction (1)) was complicated after the RSPS process at 1600 °C [26].
1.2. Microstructure

Figure 2. EDS of ZrB$_2$ porous interlayer and ZrB$_2$-SiC laminates.

Figure 3. Macro- and microstructure of cross-section of the laminated ZrB$_2$-SiC ceramic (a-b), ZrB$_2$-SiC lamina (c) and the ZrB$_2$ porous interlayer (d).

Figure 3 (a) shows the cross-section of the laminated ZrB$_2$-SiC ceramic. The uniform, aligned layers in the ceramics are perpendicular to the sintering direction. The alternating interlayers between the ZrB$_2$-SiC layers and porous ZrB$_2$ layers are readily observed and the uniform thickness of the different layers is also detected. The porous ZrB$_2$ layers are bright and thin, while the ZrB$_2$-SiC layers appear as thick and dark layers separating as the porous layers. It is confirmed by SEM analysis that the thickness of porous layers is about 36 $\mu$m.

The microstructure of the ZrB$_2$-SiC layers is shown in figure 3 (c). The grey phase and black phase is ZrB$_2$ and SiC, respectively. The SEM image indicates that the SiC grains have been homogeneously
dispersed in the layers. The average thickness and relative density of the ZrB$_2$-SiC layers is about 245 μm and 92.07%, respectively.

The thickness of ZrO$_2$-B$_4$C tape can be controlled by the tape casting process. The average thickness of ZrO$_2$-B$_4$C tape used in this research is 192 μm, and the average mass of ZrO$_2$-B$_4$C sheets is 28.1 mg. The mass and the porosity of the porous interlayers can be calculated from the mass of the ZrO$_2$-B$_4$C sheet according to reaction (1) and the thickness of the porous layers. The porosity of the ZrB$_2$ interlayers in figure 3 is ~42%, as seen in Figure 3 (b). The grain size of the ZrB$_2$ in the porous interlayers is about 1–2 μm, figure 3 (d), which is much smaller than that of ZrB$_2$-SiC laminas, because the ZrB$_2$ from the reaction between ZrO$_2$ and B$_4$C is small than the commercial ZrB$_2$ particles in the ZrB$_2$-SiC laminas. This is investigated in our former work [26, 27].

Higher sintering pressure was applied during the RSPS process to adjust the microstructure of the porous interlayers. The thickness and porosity of the porous layers of the samples in figure 4 is ~21 μm and 69%, which is thinner and lower than that of figure 3. The thickness and porosity of the ZrB$_2$ porous interlayers can be controlled by the pressure during the RSPS process. The thickness of the porous layers decreases with the increase of sintering pressure.

![Figure 4](image.png)

**Figure 4.** Microstructure of cross-section of the laminated ZrB$_2$-SiC ceramic (a-b) and ZrB$_2$-SiC lamina (c-d).

**Conclusions**

Laminated ZrB$_2$-SiC ceramics with porous ZrB$_2$ interlayers were prepared successfully by Reactive Spark Plasma Sintering using the stacking ZrB$_2$-SiC plates/ZrO$_2$-B$_4$C sheets body at 1600 °C 10 minutes holding. The ZrB$_2$-SiC plates were prepared by Spark Plasma Sintering at 1800 °C, and the ZrO$_2$-B$_4$C sheets were prepared by tape casting from slurry, respectively. ZrO$_2$-B$_4$C sheets transferred to porous ZrB$_2$ interlayers in laminated ZrB$_2$-SiC ceramics, because ZrO$_2$ react with B$_4$C to produce ZrB$_2$ during the RSPS process. The laminated ZrB$_2$-SiC ceramics with porous ZrB$_2$ interlayers have uniform thickness of the different layers. The average thickness and relative density of the ZrB$_2$-SiC layers is about 245 μm and 92.07%, respectively, and the SiC grains have been homogeneously dispersed in the layers. Laminated ZrB$_2$-SiC ceramics with porosity ZrB$_2$ interlayers of 42% and 69% relative density were prepared in this research. The thickness and porosity of ZrB$_2$ interlayers can be
controlled by the sintering pressure. As the sintering pressure increase, the thickness of the porous layers decreased and the porosity increased.

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