Processing and Properties of Laminated ZrB$_2$-Mo$_5$SiB$_2$ Ceramic Composites Fabricated by Tape Casting and Hot Pressing Sintering

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Abstract. The slurry of ZrB$_2$-Mo-Si-B have been prepared using the polyethylene glycol-800 (PEG800) and polyvinyl butyral (PVB) as dispersant and binder respectively. The effects of different additive concentration on the fluidity of the slurry were studied. When the amount of dispersant and binder were 0.2wt%, 4wt% and R value were 1.0, the slurry was most suitable for casting, and the green tape were smooth and flexible. ZrB$_2$-Mo-Si-Blaminated structure ceramics have been successfully prepared by tape casting and hot-pressure sintering at 1900°C for 1h under a pressure of 30 MPa in argon gas. The highest flexural strength and fracture toughness of sintered samples at room temperature were 490±10 MPa and 7.73 ± 0.56 MPa·m$^{1/2}$, respectively.

1. Introduction

Ultra-high temperature ceramics (UHTCs) are a kind of ceramics material used above 2000°C, mainly concentrated in borides, carbides and nitrides of transition metals[1]. They were applied in aerospace engineering and airframe leading edges on hypersonic aircraft and sharp body re-entry vehicles due to their excellent mechanical properties and oxidation resistance under high temperature [2-4]. ZrB$_2$ have attracted significant attention due to low dense (6.09g/cm$^3$), high melting point (3245°C), high flexural strength (460MPa), high thermal conductivity (60w/(m·k)) and the other excellent properties [5]. All of these excellent properties make ZrB$_2$ the most promising candidate for ultra-high temperature applications, such as sharp leading edges and nosecones, and thermal protection systems for reusable atmosphere re-entry vehicles, hypersonic flight, and rocket propulsion systems [6]. However, the inherent brittleness of ceramic directly limited them to be used widely, especially for structural applications in severe environments [7].

The way to solve the problem of poor fracture of ceramic materials is adding some secondary phase to ceramic matrix e.g. particles, whiskers, fibers and so on[8]. But the effectiveness of these methods is still limited. Recently, domestic and overseas scholars have taken up large-scale research on laminated structure of natural biomaterials, such as bamboos, trees and nacres, they have the special laminated structure which can improve toughness to a certain extent. The study found that nacre is composed of 99vol.% aragonite wafers and 1vol.% organic matter [9]. This structure was called “brick-and-mortar” [10,11] and the flexural strength and fracture toughness increase one order than aragonite. Inspired by these natural biomaterials, researchers introduced this concept of shell-like to prepare layered composite ceramics, allowing it to withstand extreme mechanical force [12].
In last thirty years, scholars at home and abroad have been studying the layered structure to improve the comprehensive properties of ZrB2 ceramic. ZrB2/SiC[13-16], ZrB2–SiC/BN[8], ZrB2–SiC-MoSi2 [17] etc. were successfully prepared, and the results showed that the flexural strength and fracture toughness were greatly improved. But, the improvement of the mechanical property is limited. Lü [5] found that interlaminar residual stress can effectively improve the mechanical properties of materials.

In this work, the Mo5SiB2 was obtained by in situ hot pressure. Mo5SiB2 not only has good toughness, but also can form compact silicate glass phase at high temperature, thus exhibiting excellent high temperature oxidation resistance [18-20]. Since Mo5SiB2 are potential high-temperature structural materials with good high temperature strength and creep strength [21], it can be used as a soft phase material for layered ceramics. Based on the above consideration, 20wt.% and 30wt.% Mo5SiB2 were introduced into ZrB2 matrix layers respectively. laminated ZrB2–Mo5SiB2 ceramics were formed by tape casting. The effect of organic additives on tape casting slurry was studied.

2. Experimental

Commercially available ZrB2 powder (1-5μm, 99.5%purity, Zhongnuo New Material Technology Co., Ltd, China), Mo powder (0.5μm, 99.0% purity, Sinopharm Chemical Reagent Co., Ltd, China), Si powder (0.5μm, 99.0% purity, Sinopharm Chemical Reagent Co., Ltd, China) and B powder (1-5μm, 99.5%purity, Zhongnuo New Material Technology Co., Ltd, China) were used as raw material. Polyethylene glycol (PEG, Shanghai Macklin Biochemical Co., Ltd, China) was dispersants. Polyvinyl butyral (PVB, MW25000-40000, Shanghai Macklin Biochemical Co., Ltd, China) and Trimethylphenyl phosphate (TTP, 99% purity, MW368.36, Shanghai Macklin Biochemical Co., Ltd, China) were binders and plasticizers, respectively.

In order to obtain Mo5SiB2, the mixture of Mo, Si and B(mole ratio:5:1:2) was ball-milled for 24 h in a steel jar with ZrO2 balls in argon. The mass radio of ball to power weight was 15:1. Then the mixture of ZrB2, Mo5SiB2 and PEG was first ball-milled for 12h in a steel jar using ethanol as the grinding media and zirconia balls as grinding balls. Then PVB and TTP were added into the slurry and the ball-milling for 4h was continued to obtain a uniform slurry. The ZM20 (80 wt.%ZrB2+ 20 wt.% Mo5SiB2) and the ZM30 (70 wt.%ZrB2+ 30 wt.%Mo5SiB2) green sheets were subsequently formed by tape casting from the as-prepared ZrB2–Mo5SiB2 slurry and then dried in air. After that, ZM20 and the ZM30 green sheets were cut into 30mm diameter wafers. these wafers are alternately stacked and hot pressed at 1900°C for 1 hour in argon at a pressure of 30 MPa to obtain laminated ZM20/ZM30 ceramics.

The rheological curve of casting slurry was characterized by rotating viscometer (DV-1, Shanghai Pingxuan Scientific Instrument Co., Ltd, China). Microstructures of the ceramics were observed by scanning electron microscopy (JSM-7500F, Japan Electron Optics Laboratory Co., Ltd, Japan). Flexural strength (s) was tested in three-point bending on 2 mm×3 mm×16 mm bars, using a span of 10 mm and a crosshead speed of 0.5 mm/min by Universal mechanical testing machine (WD-P4504, Jinan Test machine Co., Ltd, China). Each specimen was polished with diamond grinding disc. Fracture toughness (KIC) was evaluated by a single edge notched beam (SENB) test with a span of 16 mm and a crosshead speed of 0.05 mm/min, using 2 mm×4 mm×16 mm bars with pre-fabricated cracks of 0.2 mm wide and 2 mm deep by Universal mechanical testing machine (WD-P4504, Jinan Test machine Co., Ltd, China).

3. Results and discussion

Figure1 shows that the influence of the amount of dispersant additive and process conditions on the rheological properties of the slurry. It can be found that the viscosity of the slurry was lowest when the content of PEG was 0.2 wt.%, which indicated that the solid phase particles have the best dispersion effect (showed in Figure 1(a)). When the dispersant content was less than 0.2wt.%, the particles cannot be completely dispersed. However, if the content of PEG was more than 0.2wt.%, the particles were agglomerated due to the colloidal interaction between organic dispersants. (b) and (c)
respectively show the influence of binder and plasticizer on rheological property of slurry. The viscosity of slurry was stable when the content of PVB is lower than 4 wt%. But it increased at the content of binder reached 5wt.% (showed in Figure. 1(b)). It can be found from Figure. 1 (d) that the viscosity of slurry was the lowest and the ductility of tape was the best when R was 1.0. Finally, on the premise of guaranteeing the casting effect, the influence of the solid content on the rheological properties of the slurry. The viscosity of slurry was lower when the solid content was 30 vol.% and 50 vol.%. However, the green tape of the former was more easily broken than that of the latter. Thus, the best of the solid content was 50 vol.%.

Figure 1. The influence of the process conditions on the rheological properties of the slurry.(a) dispersant PEG; (b) binder PVB; (c) R value; (d) solid content.

Figure 2(a) shows that the crack propagation between the layers of ZrB2–Mo5SiB2 ceramics and the microstructure of the laminated ceramics. It was seen that the crack passed straightly through the laminate. The layers of ZM20 and ZM30 were tightly bound together and uniformly thick, which was about 120 μm. The microstructure of the sintered ceramics is dense and homogeneous (showed in Figure 2(c)), which can improve the strength of the laminated ceramics. A small amount of crack deflection occurred, which can effectively absorb the energy of crack growth when the crack passes through the dense ZM20 and ZM30 layers. Therefore, the fracture toughness of the laminated ZrB2–Mo5SiB2 ceramics can be improved.

Table 1 shows the relationship between the thickness ratio and mechanical properties of the laminated ZrB2–Mo5SiB2 ceramics. It was observed that the flexural strength perpendicular to the layer was always higher than that parallel to the layer. This is due to the dissociation in the parallel direction, which separates the layer from the layer, resulting in the failure of the material, thus
significantly reducing the strength of the composite material. When the thickness ratio of the layers was 1:1, the flexural strength in vertical of the samples reached the maximum, which value is 756.3 MPa. Since the stress between the layers reached the maximum, which significantly offsets part of the external load, thus the flexural strength of the material was increased.

Figure 2. SEM images of polished cross-section of the laminated ZrB$_2$–Mo$_5$SiB$_2$ ceramics. (a) Crack growth path; (b) laminated structure; (c) A partial enlarged view of ZM20.

Table 1. The relation between thickness ratio and mechanical properties of the laminated ZrB$_2$–Mo$_5$SiB$_2$ ceramics

| Thickness ratio (ZM20/ZM30) | Flexural strength (MPa) | Fracture toughness (MPa·m$^{1/2}$) |
|-----------------------------|-------------------------|-----------------------------------|
|                             | Parallel | Vertical |                             |
| 1:1                         | 305.1 ± 27.6 | 756.3 ± 59.1 | 5.67 ± 0.40 |
| 6:1                         | 353.3 ± 16.6 | 362.0 ± 26.6 | 5.74 ± 0.33 |
| 8:1                         | 265.0 ± 18.0 | 378.0 ± 27.5 | 7.73 ± 0.56 |
| 10:1                        | 345.0 ± 21.8 | 490.0 ± 10.0 | 5.88 ± 0.29 |

The fracture toughness of the laminated ZrB$_2$–Mo$_5$SiB$_2$ ceramics is 7.73 MPa·m$^{1/2}$ when the thickness ratio of the layers reached to 8:1, which is more than twice of ZrB$_2$ ceramics. When the crack extends to the weak interface in the stress field, the crack tip will passivate, absorb some energy and prevent the further crack growth. Which will improve the flexural strength and fracture of laminated ceramic composites.

4. Conclusions
The ZrB$_2$–Mo$_5$SiB$_2$ ceramics with laminated structure were successfully fabricated by tape casting and hot pressing at 1900°C. When PEG and PVB content were 0.2wt.% and 4wt.% respectively, R value was 1.0 and the solid content was 50vol.%, high quality tape film was prepared. The maximum apparent fracture toughness of these laminated ZrB$_2$–Mo$_5$SiB$_2$ ceramics composites is 7.73 ± 0.56 MPa·m$^{1/2}$. It was shown that the crack deflection in laminated structure can improve fracture toughness of composites. The maximum Flexural strength of these specimens are 756.3 ± 59.1 MPa in the vertical and 353.3 ± 16.6 MPa in the parallel respectively, which was owing to the dissociation in the parallel direction. The results also showed that the stress between layers can offset part of the external load to improve the flexural strength of composites.
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