Textured ZrB₂-based ceramics by tape casting from rod-like ZrB₂ starting powders

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Using rod-like ZrB₂ powders as starting materials, monolithic ZrB₂ ceramics and ZrB₂-20 vol % SiC composites were prepared by tape casting and then hot pressing. The obtained ceramic materials demonstrate partial textured microstructure; however, the morphologies of the ZrB₂ grains are not in rod-like but equiaxial in the final products. It is the ZrB₂ grain growth along the *a*, *b*-axis during the hot pressing process that attributes to equiaxial grains instead of rod-like morphology. On the other hand, the textured microstructures might have resulted in strong grain boundaries, which leads to a high flexural strength for monolithic ZrB₂ ceramics.

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1. Introduction

Zirconium diboride (ZrB₂) has attracted lots of attentions during recent years.^{1)–4)} Owing to a unique combination of excellent properties, including high melting point, high hardness, high electrical and thermal conductivity, and good corrosion resistance, ZrB₂-based ceramics are considered to be one important member of the ultra-high temperature ceramics (UHTCs) family, which has optimistic prospect to be used as suitable candidates for high temperature structural applications, such as sharp noses and leading edges for re-entry and hypersonic vehicles.^{3)–6)}

ZrB₂-based ceramics can be prepared by different sintering process, such as pressureless sintering (PLS),^{7,8)} spark plasma sintering (SPS)^{9,10)} and hot pressing (HP)^{11,12)} using commercial or laboratory synthesized ZrB₂ powders, and reactive hot pressing (RHP)^{1,13)} using elemental Zr and B as starting materials. Besides, there are also some microstructure tailoring methods to prepare textured ZrB₂-based ceramics with improved properties, such as hot-forging (HF),¹⁴⁾ templated grain growth (TGG)¹⁵⁾ and strong magnetic field alignment (SMFA).^{16,17)}

The crystal structure of ZrB₂ belongs to hexagonal system, so it has the tendency to form anisotropic microstructure and demonstrate anisotropic properties in ZrB₂-based ceramics with tailored microstructures, which is similar to other ceramics, such as Si₃N₄. Although there are many reports about microstructure tailored Si₃N₄,^{18)–24)} only some literature about the ZrB₂-based ceramics by microstructure tailoring can be found.^{14),16,17)} One reason is that ZrB₂ grains with anisotropic morphology are not easy to obtain, when compared with Si₃N₄. To the best of the authors' knowledge, there are only a few reports about the synthesis of anisotropic ZrB₂ grains, such as whiskers²⁵⁾ and platelet grains.²⁶⁾

In our previous work, we have successfully synthesized rod-like ZrB₂ powders.²⁷⁾ So in this study, using the rod-like ZrB₂

grains as starting materials, we first carried on tape casting process and then hot pressing to prepare ZrB₂-based ceramics with anisotropic microstructures. The microstructure evolution during the tape casting and hot pressing process and the mechanical properties of the ZrB₂-based ceramics will be discussed.

2. Experimental procedure

The main starting materials, rod-like ZrB₂ powders, were synthesized by the boro/carbothermal reduction process using commercial powders of ZrO₂, B₄C and graphite, which has been reported in our previous work;²⁷⁾ and the length of the as-obtained rod-like ZrB₂ grains is in the range of 2–5 μm, with aspect ratio ~5. The additive in the present experiment is commercial SiC powders (D₅₀ = 0.45 μm, Changle Xinyuan Carborundum Micropowder Co. Ltd., Changle, China). A mixture of butanone (67 vol %) and ethanol (33 vol %) was used as the solvent. Triolein was the dispersant, preventing coagulation and decelerates particle agglomeration. Polyvinyl butyral (PVB) was the binder, playing a role as a bridge between the powders and keeping the strength of the tape casted product. A mixture of polyethylene glycol (PEG, 50 vol %) and glycerol (50 vol %) was used as the plasticizer for increasing the fluidity of the slurry and providing flexibility for the tape casted product.

Two kinds of slurries were prepared in the present work, one was using monolithic rod-like ZrB₂ powders as starting materials and the other was rod-like ZrB₂ with 20 vol % SiC powders. 20 vol % of the starting powders (both for monolithic ZrB₂ and ZrB₂-20 vol % SiC) suspensions with 2 wt % dispersant were milled in the solvent of butanone and ethanol mixture for 8 h, then after adding the binder and plasticizer, the suspensions were milled for another 8 h. After that, the slurries were poured onto a glass sheet and spread as a thin layer via a doctor blade with a tape casting height of 300 μm at a speed of 1 cm/s. The tape casted layer is dried freely in air at room temperature for 1 h and a tape with the thickness of about 100 μm can be obtained. Then the tape was cut into small pieces and stacked. The stacked layers were cold isostatic pressed (CIP) to get a denser body and then calcinated at 800°C to remove the organic matters, which resulted

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in the green body. Then the green body was hot pressed at 2000°C with a pressure of 30 MPa to get the final products.

The bulk densities were measured by Archimedes technique. Examination of phase composition was carried out via X-ray diffractometry (XRD, D/max 2250V, Rigaku, Tokyo, Japan) using Cu K α radiation. The microstructures of the samples were analyzed using scanning electron microscopy (SEM, TM3000, Tokyo, Japan). Three-point bending strength was measured on bars with dimensions of 2 mm $\times$ 2.5 mm $\times$ 30 mm using a span of 20 mm and a crosshead speed of 0.5 mm $\cdot$ min⁻¹ (INSTRON-5566, America), and each value was obtained at least 5 measurements.

3. Results and discussion

The starting powders of rod-like ZrB₂ grains, the ZrB₂ tape after tape casting and its microstructure are shown in Fig. 1. Using the rod-like ZrB₂ grains [Fig. 1(a)] together with dispersant, binder and plasticizer, homogenous, continuous and flexible tapes can be obtained [Fig. 1(b)]. After dried freely in air, we can get a thin layer with thickness of 105 μ m [Fig. 1(c)]. SEM image with high magnification shows that during the tape casting process, under the shear force of the doctor blade, the rod-like ZrB₂ grains have the tendency to align along the tape casting direction [Fig. 1(d)]. But it should be noted that owing to the difference between the tape casted layer thickness ($\sim$ 100 μ m) and the length of the rod-like ZrB₂ grains (2–5 μ m), the alignment is not perfect.

XRD patterns of the starting rod-like grains, the tape after tape casting and the final ceramics were shown in Fig. 2, respectively. From Fig. 2, it can be seen that the pattern peaks on different crystal planes of ZrB₂ are changing. From the starting powder to tape casted layer, then to the final ceramics, the (001) and (101) peaks are decreasing while the (100) peak is increasing. The Lotgering orientation factor, $f(hk0)$, which is used to evaluate the degree of orientation and texture, shows that the $f(hk0)$ are 0.010, 0.138 and 0.448 for the three patterns, respectively. For the starting powders, the rod-like ZrB₂ grains arrange randomly, certainly resulting in a low orientation factor. While after tape casting, as discussed above, by the shear force during the tape casting process, the orientation factor increased. It is known that hot pressing is an effective method to densify ceramics and prepare textured microstructure. So after hot pressing, fully

densified ceramics, for both monolithic ZrB₂ and ZrB₂-20 vol% SiC, were realized with relative density $>99\%$. Besides, from the XRD pattern in Fig. 2, it can be seen that the orientation factor has increased remarkably compared with the tape casted layer, which demonstrates that hot pressing is one kind of effective sintering methods to realize textured microstructure as well as SPS and pulsed electric current sintering (PECS).^{28,29)}

SEM images of the fracture and polished surfaces for both monolithic ZrB₂ and ZrB₂-20 vol% SiC were shown in Fig. 3, respectively. The fracture mode of the monolithic ZrB₂ ceramics is mainly transgranular, while for ZrB₂-20 vol% SiC composites, the fracture is mixtures of intergranular and transgranular. For the ZrB₂-20 vol% SiC ceramics, it can be seen that the SiC particles distributed in the grain boundary, especially in the triangular grain boundary, playing a role to hinder the grain growth of ZrB₂, so the ZrB₂ grains in the ZrB₂-SiC composites are smaller than those of monolithic ZrB₂, resulting in a fine and homogeneous microstructure. As demonstrated above, the rod-like ZrB₂ powders were used to prepare the tape casted and hot

Fig. 2. XRD patterns of the starting rod-like ZrB₂ powders, the top surface of ZrB₂ tape after tape casting and the top surface of hot pressed monolithic ZrB₂ ceramics, compared with the standard JCPDS card (34-0423) of ZrB₂.

Fig. 1. (a) SEM image of rod-like ZrB₂ powders as the starting materials, (b) photo of the ZrB₂ tape after tape casting, (c, d) SEM images of the cross section of the ZrB₂ tape in (b) with different magnifications.

Fig. 3. SEM images of the fracture surfaces for (a) monolithic ZrB₂ ceramics and (b) ZrB₂-20 vol% SiC composites, respectively; and polished surfaces for (c) monolithic ZrB₂ and (d) ZrB₂-20 vol% SiC, respectively.

Fig. 4. Schematic diagram of a proposed microstructure evolution process of the rod-like ZrB_2 grains during the tape casting and hot pressing process: (a) rod-like ZrB_2 starting powders; (b) stacking ZrB_2 layers after tape casting; (c) rod-like ZrB_2 grains grow along a , b -axis during the hot pressing process and (d) final ZrB_2 ceramics after hot pressing.

pressed ceramics, however, there occurred an interesting phenomenon that we could not find the rod-like ZrB_2 grains in the final products, either on the fracture or polished surfaces. By analyzing the grain sizes between the starting powders and the final ceramics, it is found that the length (c -axis direction) of the starting rod-like ZrB_2 grains seemed not to increase, but the diameter (a , b -axis direction) of the rod-like grains enlarged obviously, which results in nearly equiaxial grains in the microstructure of final product.

The ZrB_2 is primitive hexagonal (AlB_2 -type, $P6/mmm$ space group),³⁾ so it seems possible to form anisotropic morphology, either platelet or rod-like grains. During the synthesis process of the rod-like ZrB_2 grains, the ZrB_2 grains has the tendency to grow along the c -axis to form an anisotropic rod-like morphology, however, during the hot pressing process after tape casting, the anisotropic rod-like grains grow along the a , b -axis. With the grain growth along the a , b -axis during sintering process, when the diameter of the rod-like grains is more or less the same with the grain length, particles with equiaxial morphology will be formed. Here we will discuss the microstructure evolution in the hot pressing process.

As is shown in Fig. 1(d), after tape casting, the rod-like ZrB_2 grains will align along the tape casting direction to form a partial textured microstructure [Fig. 4(b)]. The following cold isostatic pressing will result in a compact green body with the texture microstructure. Then during the hot pressing process, the ZrB_2 grains can easily contact to each other. Because the length of starting rod-like ZrB_2 grains is in some large distribution range from 2 to 5 μm , there will be an Ostwald ripening phenomenon during the sintering process. The surface energy on the c -planes of ZrB_2 crystal is higher than other planes, such as a , b -plane, so activation energy diffusion paths along a , b -axis direction is lower than that along the c -axis.^{30),31)} Besides, owing to the anisotropic morphology and the alignment effect of the tape casting, the most possible contact mode between the rod-like ZrB_2 grains is a , b -plane connection. Therefore, under the high temperature sintering and applied pressing, the relative smaller rod-like grains will diffuse to and recrystallize onto larger grains along the a , b -axis, which is attributed to the radial direction growth of the rod-like grains [Fig. 4(c)]. As a result with this mechanism, equiaxial morphology with larger grain size in the final ceramics after hot pressing was obtained [Fig. 4(d)].

Three-point flexural strengths for both the samples were tested. The results show that flexural strengths for monolithic ZrB_2 ceramics is 738 ± 7 MPa, while for ZrB_2 -20 vol % SiC is 790 ± 33 MPa. Compared with the data in previous literature,^{11),32)} the present monolithic ZrB_2 has a high flexural strength. For ZrB_2 -20 vol % SiC, however, the addition of SiC did not improve the flexural strength remarkably, although the ZrB_2 grain growth has been hindered, resulting in a finer microstructure. It is thought that finer grain size leads to higher strength; while in the present work, the grain size of the two specimen were different, but the flexural strengths are nearly the same. So there must exist another factor which compensate the negative effect of the large grain size in the monolithic ZrB_2 ceramics and improve their strengths. As describe above [Fig. 3(a)], for monolithic ZrB_2 ceramics, transgranular fracture is the dominating mode on the fracture surface, which means that the monolithic ZrB_2 ceramics have strong grain boundaries. From the schematic diagram in Fig. 4, it can be concluded that owing to the orderly arranged and contact of the final equiaxial ZrB_2 grains, there exist strong grain boundaries among the grains, which should have improved the flexural strength and compensate the negative effect cause by the larger ZrB_2 grain size for monolithic ceramics. On the other hand, for ZrB_2 -20 vol % SiC composites, the SiC can act as a sintering aid to enhance the densification process, and lead to a finer microstructure, but in the present work, it can also lead to a weak connection between the ZrB_2 grains, resulting in grain boundaries not as strong as monolithic ZrB_2 grains. So, there is a mixture of intergranular and transgranular modes on the fracture surfaces of ZrB_2 -20 vol % SiC composites; and the flexural strengths have not been improved too much compared with the monolithic ZrB_2 ceramics in the present work.

4. Conclusions

In summary, using rod-like ZrB_2 powders as starting materials, monolithic ZrB_2 ceramics and ZrB_2 -20 vol % SiC composites were prepared by tape casting and hot pressing. The rod-like ZrB_2 grains can realign to form a partial texture microstructure during the tape casting process and then, after hot pressing, the extent of texture can be improved further. For the microstructure of the final product after hot pressing, however, there were no rod-like ZrB_2 grains left, which is attributed to the ZrB_2 grain growth along the a , b -axis to result in an equiaxial morphology. Owing to the finer microstructure, the ZrB_2 -20 vol % SiC composites have a flexural strength of 790 ± 33 MPa, while for monolithic ZrB_2 ceramics, although the grain size is large, they can also obtain a high flexural strength of 738 ± 7 MPa, which thanks to the strong grain boundaries by the compact contact of the ZrB_2 grains.

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