Preparation and properties of ZrB$_2$-YAG-Al$_2$O$_3$ ceramics

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ZrB$_2$, YAG and Al$_2$O$_3$ are widely applied because of some excellent properties, but ZrB$_2$ is easily oxidized in high-temperature air. To achieve better properties in ZrB$_2$ ceramics, high-density ZrB$_2$-YAG-Al$_2$O$_3$ ceramics were prepared. Below 1000 °C, the shrinkage of ZrB$_2$-YAG-Al$_2$O$_3$ ceramics is less than that of ZrB$_2$-YAG ceramics. From 1000 °C to 1600 °C, the second largest shrinkage occurs. Above 1600 °C, the shrinkage of ZrB$_2$-YAG-Al$_2$O$_3$ ceramics is more than that of ZrB$_2$-YAG ceramics. The fracture toughness of sintered ceramics from coated raw materials is higher than that of sintered ceramics with mixed raw materials with the same phases and phase content, the fracture toughness of ZrB$_2$-YAG-Al$_2$O$_3$ ceramics is higher than that of ZrB$_2$-YAG ceramics with the same raw materials. The weight gain of all types of ceramics is increased with all increase in the oxidation temperature, the weight gain of ceramics is reduced with all increase in the YAG-Al$_2$O$_3$ content and Al$_2$O$_3$ proportion, especially above 1500 °C.

Key words: ZrB$_2$ ceramics, Sintering shrinkage, Fracture toughness, Oxidation.

Introduction

Zirconium diboride (ZrB$_2$) has attracted substantial interest because of its extreme chemical and physical properties, such as, high melting point, superior hardness and low electrical resistance. ZrB$_2$ has several applications such as in Hall-Heroult cell cathodes for electrochemical processing of aluminium, evaporation boats, crucibles for handling molten metals, thermowell tubes for steel refining, thermocouple sleeves for high-temperature use, nozzles, plasma electrodes, or as dispersoid in metal and ceramic-matrix composites for heaters and igniters [1-4]. However, ZrB$_2$ is easily oxidized in high-temperature air which impacts its high-temperature strength, restricts its applied range [5, 6]. Some excellent oxidation-resistance materials are considered as assistant phases for ZrB$_2$ materials to improve the high-temperature performance of ZrB$_2$ materials, such as Al$_2$O$_3$-ZrB$_2$, SiC-ZrB$_2$, LaB$_6$-ZrB$_2$, and ZrO$_2$-ZrB$_2$ [7-9].

Yttrium aluminium garnet (YAG or Y$_3$Al$_5$O$_{12}$) has a cubic garnet structure and is of great interest as a high-temperature engineering material, due to its high-temperature strength coupled with low creep rate [10-14], which indicates that YAG ought to be a suitable matrix or reinforcing phase [15, 16].

To give ZrB$_2$ ceramics better oxidation resistance, in this paper, high-density ZrB$_2$-YAG-Al$_2$O$_3$ ceramics were prepared and the properties of these ceramics were investigated.

Materials and Experiment

Analytical grade aluminum nitrate, yttrium nitrate, ammonia and commercially available ZrB$_2$ powder (99.5% in purity) were used. ZrB$_2$ coated with Al$_2$O$_3$-Y$_2$O$_3$ composite powder was synthesized by a co-precipitation method [17]. Superfine Al$_2$O$_3$-Y$_2$O$_3$ composite powder was synthesized with aluminum nitrate, yttrium nitrate and ammonia via a co-precipitation method. Superfine Al$_2$O$_3$-Y$_2$O$_3$ composite powder was calcined at 1000 to obtain superfine YAG powder. YAG was mixed into ZrB$_2$ powder to form a mixed raw material. Then the composite raw materials were encased in a graphite mould, sintered, demoulded and tested. Different ceramics were prepared with spark plasma sintering (SPS) (Table 1). A process flow diagram is shown in Fig. 1.

ZrB$_2$-YAG-Al$_2$O$_3$ ceramics were prepared by SPS (Mode: SPS-1050, Japan) and oxidation treated in a furnace (Mode: Nabertherm LHT04, Germany). Phase analysis was performed by X-ray powder diffraction (XRD) (Model: D/Max-RB, Japan). Microstructure analysis was performed by scanning electron microscopy (SEM) (Model: JSM-5610LV, Japan). Element analysis was performed.

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<th>Table 1. Types of ceramics</th>
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with an electron probe microanalysis system (EPMA) (Model: JXA-880R, Japan).

**Results and Discussion**

**Sintering behavior of ZrB$_2$-YAG-Al$_2$O$_3$ ceramics**

The sintering curve of the ceramics prepared by SPS is shown in Fig. 2. The Z-axis displacement shows the shrinkage state of the ceramic body during the sintering process, the value of the Z-axis displacement increases, which indicates the ceramic body is shrinking, on the contrary, the ceramic body is expanding. The Z-axis displacement (1) and Z-axis displacement (2) show the shrinkage state of sintered Z-YA ceramics and Z-Y ceramics, respectively. The shrinkage curves (1) and (2) are similar, however, there are differences. Below 1000°C, the shrinkage of Z-YA ceramics is less than that of Z-Y ceramics, because the shrinkage is caused by forming YAG from Al$_2$O$_3$ and Y$_2$O$_3$ from 700°C to 950°C [18]. From 1000°C to 1600°C, YAG melts and fills the space between ZrB$_2$ particles in the SPS system [19, 20], which brings about the second large shrinkage. Above 1600°C, the shrinkage of Z-YA ceramics is more than that of Z-Y ceramics, because the shrinkage is caused by Al$_2$O$_3$ diffusion [21]. The XRD of ZrB$_2$-YAG-Al$_2$O$_3$ ceramics prepared with the SPS process at 1700°C is shown in Fig. 3. The relative densities of ceramics are shown in Fig. 4, which indicate that the relative density is increased with an increase in the sintering temperature, the phase type and the proportion of Al$_2$O$_3$. The effect of the YA content on the microstructure of Z-YA ceramics is shown in Fig. 5.

**Mechanical property of ZrB$_2$-YAG-Al$_2$O$_3$ ceramics**

The fracture toughness of sintered ceramics from coated ZrB$_2$ powder and mixed ZrB$_2$ powder at a sintering temperature of 1700°C, a sintering pressure for 20 MPa and a holding time for 4 minutes is shown in Fig. 6, which indicates that the fracture toughness of sintered ceramics with coated raw materials is higher than that of sintered ceramics with mixed raw materials with the
same phases and phase contents, the fracture toughness of Z-Y A ceramics is higher than that of Z-Y ceramics. Because the YAG phase is situated in the space between the ZrB$_2$ particles after sintering with mixed raw materials by SPS (Fig. 7(a) and (b)), however, the YAG phase is situated on the crystal boundaries among the ZrB$_2$ particles after sintering the coated raw materials (Fig. 7(c) and (d)). In the later case YAG as the reinforce phase is homogeneously dispersed, which makes the reinforce effect with coated raw materials better than that with mixed raw materials. From Fig. 7, the ZrB$_2$ grain size is apparent, the ZrB$_2$ grain size is more homogeneous and finer with coated raw materials than that with mixed raw materials, because the reinforced phase may arrest the growth of

![Fig. 5. Effect of YA content on microstructure of Z-Y A ceramics (a-10 wt%, b-20 wt%, c-30 wt% and d-40 wt%).](image)

![Fig. 6. Effect of raw materials on fracture toughness of ceramics (1-Mixing 30 wt%Y, 2-Mixing 30 wt%Y$_6$A, 3-Coating 30 wt%Y and 4-Coating 30 wt%Y$_6$A).](image)

![Fig. 7. Effect of raw materials on the microstructure of ceramics (a-Mixing 30 wt%Y, b-Mixing 30 wt%Y$_6$A, c-Coating 30 wt%Y and d-Coating 30 wt%Y$_6$A).](image)

![Fig. 8. Effect of oxidation temperature on weight gain of ceramics (a-Z-YA, b-Z-Y3A and c-Z-Y6A).](image)
the ZrB$_2$ grains during the sintering process [22]. The fine grain size helps to increase the mechanical properties of YAG-ZrB$_2$ multi-phase ceramics. The mechanical properties of YAG-Al$_2$O$_3$ composite materials are higher than that of single phase YAG and Al$_2$O$_3$ materials [23].

**Oxidation resistance of ZrB$_2$-YAG-Al$_2$O$_3$ ceramics**

The weight gain of different ceramics after being oxidized at different oxidation temperatures for 1 hour is shown in Fig. 8, which indicates the weight gain of all types of ceramics is increased with an increase in the oxidation temperature. Also, the weight gain of ceramics is reduced with an increase in the YAG-Al$_2$O$_3$ content and Al$_2$O$_3$ proportion, especially above 1500°C. The effect of the oxidation temperature on the weight gain of ceramics is decided by the relative density of ceramics. However, factors such as the effect of YAG-Al$_2$O$_3$ content and YAG: Al$_2$O$_3$ ratio on the weight gain of ceramics are not just on the relative density of ceramics, but also on the chemical reaction of ZrB$_2$ reactions with O$_2$ to form B$_2$O$_3$ [24], B$_2$O$_3$ reacts with Al$_2$O$_3$ to form Al$_{18}$B$_4$O$_{33}$ (Fig. 9). Al$_{18}$B$_4$O$_{33}$ melts and coats the surfaces of the ceramics to form a protection layer giving oxidation resistance of the ceramics at high temperatures [25] (Fig. 10). XRD patterns of ceramics with different Al$_2$O$_3$ contents after being oxidized at 1600°C for 1 hour are shown in Fig. 11, which indicates the Al$_{18}$B$_4$O$_{33}$ content of the oxidized surfaces of ceramics are increased with an increase in the proportion of Al$_2$O$_3$, which means the thickness of oxidation resistance layer is increased. SEM of an oxidized Z-40 wt%Y6A ceramic sample is shown in Fig. 12.

**Conclusion**

(a) The shrinkage of ZrB$_2$-YAG-Al$_2$O$_3$ ceramics and ZrB$_2$-YAG ceramics is similar, however, there are differences.

![Fig. 9. Effect of oxidation temperature on the phase production in of Z-40 wt%YA ceramics (a-1100°C, b-1200°C, c-1300°C, d-1400°C, e-1500°C and f-1600°C).](image)

![Fig. 10. Element distribution of ZrB$_2$-40 wt%Y6A ceramics after being oxidized at 1600°C for 1 hour.](image)

![Fig. 11. XRD of surfaces of different ceramics after being oxidized at 1600°C for 1 hour (a-Z-40 wt%YA, b-Z-40 wt%Y3A and c-Z-40 wt%Y6A).](image)

![Fig. 12. Effect of oxidation temperature on the oxidation layer of ZrB$_2$-40 wt%Y6A ceramic sample after being oxidized at 1600°C for 1 hour.](image)
Below 1000 °C, the shrinkage of ZrB$_2$-YAG -Al$_2$O$_3$ ceramics is less than that of ZrB$_2$-YAG ceramics. From 1000 °C to 1600 °C, a second large shrinkage occurs is caused. Above 1600 °C, the shrinkage of ZrB$_2$-YAG-Al$_2$O$_3$ ceramics is more than that of ZrB$_2$-YAG ceramics.

(b) The fracture toughness of sintered ceramics from coated raw materials is higher than that of sintered ceramics with mixed raw materials with the same phases and phase content, and the fracture toughness of ZrB$_2$-YAG-Al$_2$O$_3$ ceramics is higher than that of ZrB$_2$-YAG ceramics with the same raw materials.

(c) The weight gain of all type of ceramics is increased with an increase of the oxidation temperature, the weight gain of ceramics is reduced with an increase of the YAG-Al$_2$O$_3$ content and Al$_2$O$_3$ proportion, especially above 1500 °C.

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