Effect of raw materials on the properties of ZrB$_2$-YAG-Al$_2$O$_3$ multi-phase ceramics

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ZrB$_2$ belongs to a class of ceramics defined ultra-high-temperature ceramics with extremely high melting temperatures, but ZrB$_2$ ceramics is difficultly sintered and easily oxidized. To make ZrB$_2$ ceramics possess the high relative density and the better oxidation resistance. The effects of raw materials on the properties of ZrB$_2$ composite were investigated. YAG and Al$_2$O$_3$ help for the densification of ZrB$_2$ ceramics. Fracture toughness of sintered ceramics with coated powder is higher than that of sintered ceramics with mixed powder. The mechanical property of ZrB$_2$-YAG-Al$_2$O$_3$ materials is higher than that of ZrB$_2$-YAG materials. Oxidation layer thickness of sintered ceramics with coated powder is thinner than that of sintered ceramics with mixed powder. These results show the sintered ZrB$_2$ based multi-phase ceramics with coated microstructure help to increase the mechanical properties and oxidation resistance. The oxidation resistance of ZrB$_2$-YAG-Al$_2$O$_3$ ceramics is better than that of ZrB$_2$-YAG materials.

Key words: ZrB$_2$-YAG-Al$_2$O$_3$ ceramics, Densification, Fracture toughness.

Introduction

ZrB$_2$ is of particular interest because of the unique property combination of high refractoriness, high-electrical and -thermal conductivity, chemical inertness against molten metals or nonbasic slags and good thermal shock resistance [1-2], which make it attractive candidates for high-temperature applications where corrosion-wear-oxidation resistance is demanded. ZrB$_2$ has several applications such as Hall-Heroult cell cathodes for electrochemical processing of aluminum, evaporation boats, crucibles for handling molten metals, thermowell tubes for steel refining, thermocouples sleeves for high-temperature uses, nozzles, plasma electrodes, or as dispersoid in metal and ceramic-matrix composites for heaters and igniters [3-5]. In addition, ZrB$_2$ is a metallic conductor with electrical resistivity comparable with those of their parent metals. This permits to produce complex components at reduced shaping costs. ZrB$_2$, because of its higher costs of production, has found a limited number of applications [6-7].

Yttrium aluminium garnet (YAG) exists in the cubic form with a garnet structure [8]. It also has been recognized that YAG may be the most creep-resistant oxide [9], which indicates that YAG ought to be a suitable matrix or renforcing materials [10-11].

To make ZrB$_2$ ceramics possess the high relative density and the better oxidation resistance in the air at high-temperature, in this paper, the effect of raw materials on the properties of ZrB$_2$ ceramics were investigated, the property includes sintering property, mechanical property and oxidation resistance property.

Materials and Experimental

Analytical grade of aluminum nitrate, yttrium nitrate, ammonia and commercially available ZrB$_2$ powder (99.5% in purity) were used. ZrB$_2$@Al$_2$O$_3$-Y$_2$O$_3$ core-shell composite particles are successfully synthesized by co-precipitation method [12-14]. TEM of the ZrB$_2$@Al$_2$O$_3$-Y$_2$O$_3$ core-shell composite particles were shown in Fig. 1. Superfine Al$_2$O$_3$-Y$_2$O$_3$ composite powder was synthesized with aluminum nitrate, yttrium nitrate and ammonia via the co-precipitation method. Superfine Al$_2$O$_3$-Y$_2$O$_3$ composite powder was calcined at 1000 °C to obtain superfine YAG powder. YAG was synthesized by a co-precipitation method. Superfine Al$_2$O$_3$-Y$_2$O$_3$ composite powder was calcined at 1000 °C to obtain superfine YAG powder. YAG was synthesized via the co-precipitation method. Superfine Al$_2$O$_3$-Y$_2$O$_3$ composite powder was calcined at 1000 °C to obtain superfine YAG powder. YAG was synthesized by a co-precipitation method. Superfine Al$_2$O$_3$-Y$_2$O$_3$ composite powder was calcined at 1000 °C to obtain superfine YAG powder. YAG was synthesized by a co-precipitation method. Superfine Al$_2$O$_3$-Y$_2$O$_3$ composite powder was calcined at 1000 °C to obtain superfine YAG powder. YAG was synthesized by a co-precipitation method. Superfine Al$_2$O$_3$-Y$_2$O$_3$ composite powder was calcined at 1000 °C to obtain superfine YAG powder. YAG was synthesized by a co-precipitation method.
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mixed into ZrB$_2$ powder to form YAG/ZrB$_2$ composite powder. Then tow sorts of composite powder were encased in the graphite mould, sintered, demoulded and tested, respectively. ZrB$_2$-YAG and ZrB$_2$-YAG-Al$_2$O$_3$ ceramics were obtained (Tab. 1). The process flow diagram is shown was Fig. 2.

ZrB$_2$-YAG and ZrB$_2$-YAG-Al$_2$O$_3$ ceramics were sintered with the spark plasma sintering (SPS) (Mode: SPS-1050, Japan). Phase was identified by X-ray powder diffraction (XRD) (Model: D/Max-RB, Japan). Microstructure was performed by scanning electron microscopy (SEM) (Model: JSM-5610LV, Japan) and transmission electron microscopy (TEM) (Model: JEM-2010, Japan).

Results and Discussion

Effect of raw materials on the densification

The sintering curve of preparing ZrB$_2$-YAG multi-phase ceramics with the SPS is shown in Fig. 3. Z-axis displacement shows the shrink state of ceramic body during the sintering process, the value of Z-axis displacement is increasing, 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 shrink state of coated ZrB$_2$ with Al$_2$O$_3$-Y$_2$O$_3$ composite powder and mixed ZrB$_2$ with YAG powder, respectively. The Z-axis displacement (2) shows the lesser shrink displacement below 950 °C, the biggish shrink displacement is shown from 950 °C to 1600 °C, Z-axis displacement is not varied basically above 1700 °C. However, the Z-axis displacement (1) shows the quick shrink displacement from 700 °C to 950 °C, the biggish shrink displacement also is shown from 950 °C to 1600 °C, Z-axis displacement is not varied basically above 1600 °C. Al$_2$O$_3$-Y$_2$O$_3$ composite powder of coated ZrB$_2$ are loose (Fig. 1), Al$_2$O$_3$ react with Y$_2$O$_3$ to form YAG from 700 °C to 950 °C [15], which makes ceramic body cause the first biggish shrinkage. YAG is melted and filled the space among ZrB$_2$ particles in the SPS system above 950 °C [16-17], which brings about the second biggish shrinkage. The
relative density of prepared ZrB$_2$-YAG and ZrB$_2$-YAG-Al$_2$O$_3$ multi-phase ceramics with different raw materials is shown in Fig. 4, which indicate the raw materials adding YAG and Al$_2$O$_3$ help for the densification of ZrB$_2$ ceramics.

**Effect of raw materials on the mechanical property**

Fracture toughness of sintered ceramics with different raw materials are shown in Fig. 5, which indicates that fracture toughness of sintered ceramics with coated raw materials is higher than that of sintered ceramics with mixed raw materials under the same phase and phase content conditions. Because YAG or YAG-Al$_2$O$_3$ phase is gathered in the space among the ZrB$_2$ particles after sintered with mixed raw materials by SPS (Fig. 6-a and b), however, YAG or YAG-Al$_2$O$_3$ phase is gathered on the crystal boundary among the ZrB$_2$ particles after sintered with coated raw materials (Fig. 6-c and d), YAG and YAG-Al$_2$O$_3$ as the reinforced phase are homogeneously dispersed, which makes the reinforced effect be better. From Fig. 6, the ZrB$_2$ grain size is shown, the ZrB$_2$ grain size of sintered ceramics with coated raw materials is more homogeneous and finer than that of sintered ceramics with mixed raw materials. Because reinforced phase may arrest the growth of the ZrB$_2$ grain during the sintering process [18]. The fine grain size helps to increase the mechanical property of ceramics. The mechanical property of YAG-Al$_2$O$_3$ composite materials is higher than that of YAG single-phase materials [19], which makes ZrB$_2$-YAG-Al$_2$O$_3$ multi-phase ceramics pose the higher Fracture toughness.

**Effect of raw materials on the oxidation resistance**

Oxidation layer thickness of sintered ZrB$_2$ ceramics with different raw materials after oxidized in the air at 1600 °C for 1 hour is shown in Fig. 7, which indicates that oxidation layer thickness of sintered ceramics with coated raw materials is thinner than that of sintered ceramics with mixed raw materials under same phase and phase content conditions. Because ZrB$_2$ particles are coated with YAG or YAG-Al$_2$O$_3$ phase in the sintered ceramics with coated raw materials (Fig. 6-c and d), which makes ZrB$_2$ particles be isolated with YAG or YAG-Al$_2$O$_3$ phase. The coated ZrB$_2$ particles are prevented oxidation to reach the aim of oxidation resistance of ZrB$_2$ ceramics, which indicates sintered...
ceramics with coated raw materials help to increase the oxidation resistance of ZrB$_2$ ceramics. SEM of oxidation layer thickness of sintered ZrB$_2$ ceramics with different raw materials after oxidized in the air at 1600 °C for 1 hour is shown in Fig. 8, which indicates oxidation layer of sintered ceramics with coated raw materials is denser than that of sintered ceramics with mixed raw materials. In other words, oxidation resistance of sintered ceramics with coated raw materials is better than that of sintered ceramics with mixed raw materials. From Fig. 7 and 8, which indicate the oxidation resistance of ZrB$_2$ ceramics adding the Al$_2$O$_3$ is better. Because the diffusion coefficient of oxygen in the Al$_2$O$_3$ is lower than that of oxygen in the YAG, and the Al$_{18}$B$_4$O$_{33}$ is produced through reacting with Al$_2$O$_3$ and B$_2$O$_3$ at high temperature to coat the surface of ZrB$_2$ ceramics [20].

Conclusions

ZrB$_2$-YAG and ZrB$_2$-YAG-Al$_2$O$_3$ multi-phase ceramics with different raw materials are prepared with SPS, which indicate the raw materials adding YAG and Al$_2$O$_3$ help for the densification of ZrB$_2$ ceramics. Fracture toughness of sintered ceramics with coated raw materials is higher than that of sintered ceramics with mixed raw materials under the same phase and phase content conditions. The mechanical property of ZrB$_2$-YAG-Al$_2$O$_3$ materials is higher than that of ZrB$_2$-YAG materials. Oxidation layer thickness of sintered ceramics with coated raw materials is thinner than that of sintered ceramics with mixed raw materials. The results indicate sintered coated structure ceramics with coated raw materials help to increase the mechanical property and oxidation resistance of ZrB$_2$-YAG ceramics. The oxidation resistance of ZrB$_2$-YAG-Al$_2$O$_3$ ceramics is better than that of ZrB$_2$-YAG materials.

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