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Effect of raw materials on the properties of ZrB_2-YAG-Al_2O_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_2O_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_2O_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_2O_3 ceramics is better than that of ZrB_2-YAG materials.

Key words: ZrB_2-YAG-Al_2O_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 aluminium, 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 aluminum 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@$A1_2O_3$-Y_2O_3 core-shell composite particles are successfully synthesized by co-precipitation method [12-14]. TEM of the ZrB_2@$A1_2O_3$-Y_2O_3 core-shell composite particles were shown in Fig. 1. Superfine Al_2O_3-Y_2O_3 composite powder was synthesized with aluminum nitrate, yttrium nitrate and ammonia via the co-precipitation method. Superfine Al_2O_3-Y_2O_3 composite powder was calcined at 1000 °C to obtain superfine YAG powder. YAG was

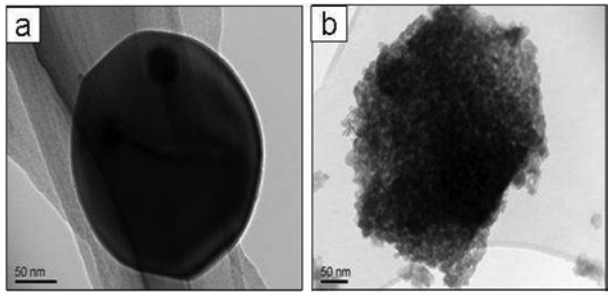

Fig. 1. TEM of the coated ZrB_2 powder with Al_2O_3-Y_2O composite powder (a-Original ZrB_2 particle and b-Coated ZrB particles after calcined at 600 °C).

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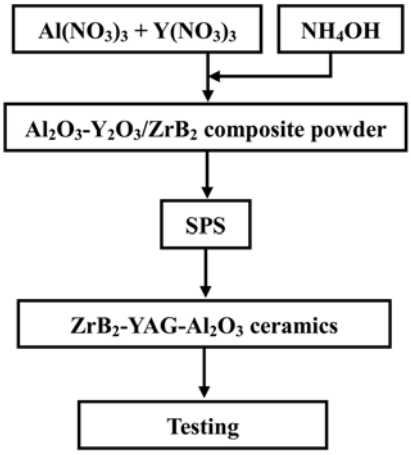

Fig. 2. The process flow diagram of preparing ZrB_2-YAG-Al_2O_3 ceramics with coated raw materials.

Table 1. Sorts of sintered ZrB_2 ceramics via the SPS.

Ceramics	YAG:$A1_2O_3$ (mol)	Phases
Z	–	ZrB_2
Z-Y	–	ZrB_2 + YAG
Z-YA	1 : 1	ZrB_2 + YAG + $A1_2O_3$
Z-Y3A	1 : 3	ZrB_2 + YAG + $A1_2O_3$
Z-Y6A	1 : 6	ZrB_2 + YAG + $A1_2O_3$

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_2O_3 ceramics were obtained (Tab. 1). The process flow diagram is shown was Fig. 2.

ZrB_2-YAG and ZrB_2-YAG-Al_2O_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_2O_3-Y_2O_3 composite powder and mixed ZrB_2 with YAG powder, respectively. The Z-axis displacement (2) shows the lesser shrink displacement below 950 ºC, the biggish shrink displacement is shown from 950 ºC to

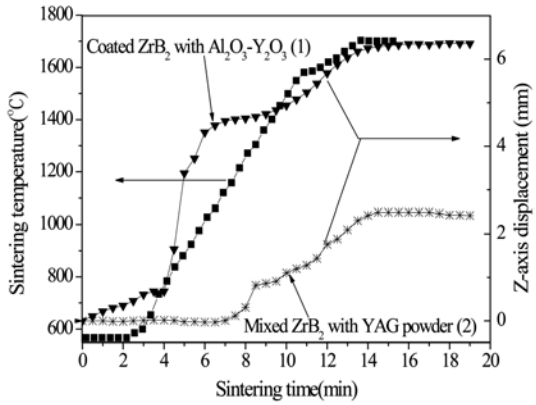

Fig. 3. Sintering shrinkage curve of YAG-ZrB_2 ceramics.

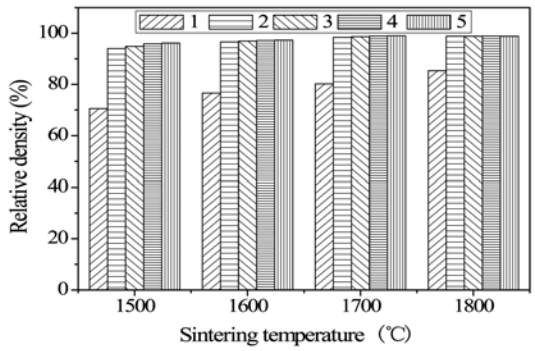

Fig. 4. Effect of sintering temperature on relative density of ceramics (1-Z ceramics, 2-Z-30 wt%Y ceramics, 3-Z-30 wt%YA ceramics, 4-Z-30 wt%Y3A ceramics and 5-Z-30 wt%Y6A ceramics).

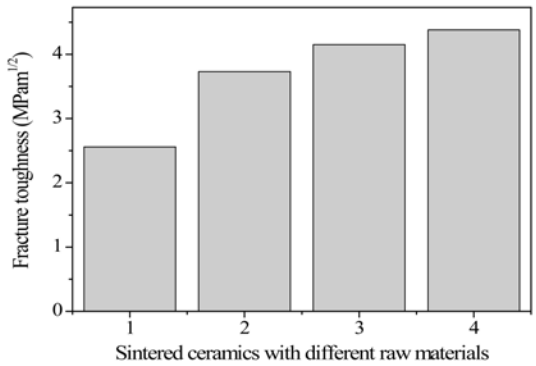

Fig. 5. Effect of raw materials on fracture toughness of ceramics (1-Mixing 30 wt%Y, 2-Mixing 30 wt%Y6A, 3-Coating 30 wt%Y and 4-Coating 30 wt%Y6A).

1600 ºC, Z-axis displacement is not varied basically above 1700 ºC. However, the Z-axis displacement (1) shows the quick shrink displacement from 700 ºC to 950 ºC, the biggish shrink displacement also is shown from 950 ºC to 1600 ºC, Z-axis displacement is not varied basically above 1600 ºC. Al_2O_3-Y_2O_3 composite powder of coated ZrB_2 are loose (Fig. 1), Al_2O_3 react with Y_2O_3 to form YAG from 700 ºC to 950 ºC [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 ºC [16-17], which brings about the second biggish shrinkage. The

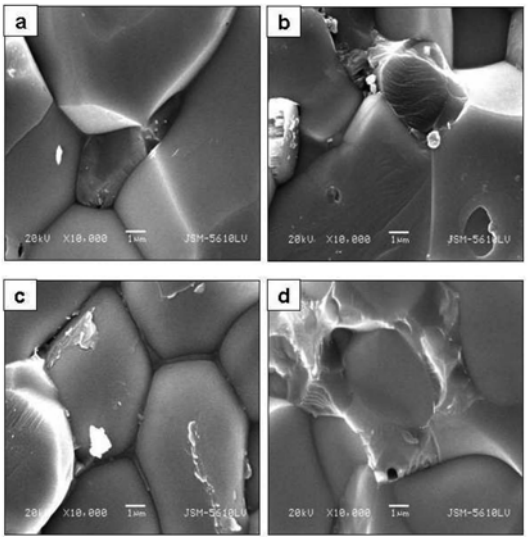

Fig. 6. Effect of raw materials on microstructure of ceramics (a-Mixing 30 wt%Y, b-Mixing 30 wt%Y6A, c-Coating 30 wt%Y and d-Coating 30 wt%Y6A).

relative density of prepared ZrB_2-YAG and ZrB_2-YAG-Al_2O_3 multi-phase ceramics with different raw materials is shown in Fig. 4, which indicate the raw materials adding YAG and Al_2O_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_2O_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_2O_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_2O_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_2O_3 composite materials is higher than that of YAG single-phase materials [19], which makes ZrB_2-YAG-Al_2O_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_2O_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_2O_3 phase. The coated ZrB_2 particles are prevented oxidation to reach the aim of oxidation resistance of ZrB_2 ceramics, which indicates sintered

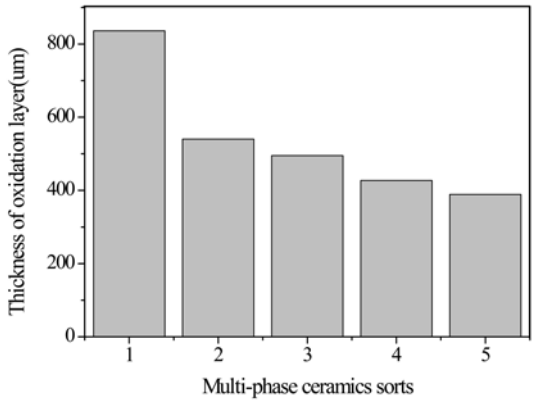

Fig. 7. Thickness of oxidation layer of ceramics after oxidized for 1 h at 1600 °C (1-Z ceramics, 2-Z-40 wt%Y ceramics, 3-Z-40 wt%YA ceramics, 4-Z-40 wt%Y3A ceramics, 5-Z-40wt%Y6A ceramics).

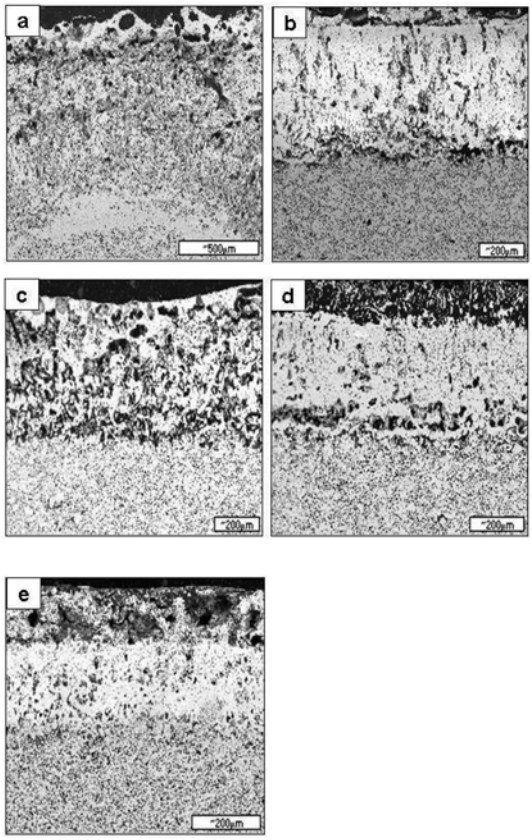

Fig. 8. Oxidation layer of different ceramics after oxidized for 1 h at 1600 °C (a-Z ceramics, b-Z-40 wt%Y ceramics, c-Z-40 wt%YA ceramics, d-Z-40 wt%Y3A ceramics, e-Z-40 wt%Y6A ceramics).

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_2O_3 is better. Because the diffusion coefficient of oxygen in the Al_2O_3 is lower than that of oxygen in the YAG, and the $Al_{18}B_4O_{33}$ is produced through reacting with Al_2O_3 and B_2O_3 at high temperature to coat the surface of ZrB_2 ceramics [20].

Conclusions

ZrB_2-YAG and ZrB_2-YAG-Al_2O_3 multi-phase ceramics with different raw materials is prepared with SPS, which indicate the raw materials adding YAG and Al_2O_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_2O_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_2O_3 ceramics is better than that of ZrB_2-YAG materials.

Acknowledgments

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