

The effect of a reinforcement phase on the oxidation mechanism of ZrB₂-YAG-Al₂O₃ ceramics

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ZrB₂ and YAG are widely applied because of some excellent properties, but ZrB₂ is easily oxidized in high-temperature air. To make ZrB₂ ceramics have a better oxidation resistance, high-density ZrB₂-YAG-Al₂O₃ ceramics were prepared. The effect of a reinforcement phase on the oxidation mechanism of ZrB₂-YAG-Al₂O₃ ceramics is investigated at different high temperature ranges. The results show that the overall tendency of the weight gain of ZrB₂-YAG ceramics and ZrB₂ ceramics are similar, but the weight gain of ZrB₂-YAG ceramics is less than that of ZrB₂ ceramics. The weight gain tendency of three types of ceramics are similar below 1000, the weight gain of ZrB₂-YAG and ZrB₂-YAG-Al₂O₃ ceramics have a mild tendency between 1000 and 1300, the weight gain tendency of ZrB₂-YAG ceramics and ZrB₂ ceramics are similar at 1300, however, the weight gain tendency of ZrB₂-YAG-Al₂O₃ ceramics became mild at 1300 due to the Al₁₈B₄O₃₃ coating on the ceramic surface. The weight gain rapidly increased for 1h, then the weight gain tendency became mild after 1 h. The weight gain tendency of ZrB₂-YAG-Al₂O₃ ceramics is similar by contrast with ZrB₂-YAG ceramics and ZrB₂ ceramics for 1 h, the weight gain tendency of ZrB₂-YAG-Al₂O₃ ceramics is extremely mild at a higher oxidation temperature after 1 h.

Key words: ZrB₂, Ceramics, Reinforcement phase, Oxidation mechanism

Introduction

Zirconium diboride (ZrB₂) has attracted substantial interest because of its extreme chemical and physical properties, such as, a high melting point, superior hardness and low electrical resistance. ZrB₂ has several applications such as for Hall-Heroult cell cathodes for electrochemical processing of aluminum, evaporation boats, crucibles for handling molten metals, thermowell tubes for steel refining, thermocouple sleeves for high-temperature use, nozzles, plasma electrodes, or as a dispersoid in metal and ceramic-matrix composites for heaters and igniters [1-4]. However, ZrB₂ is easily oxidized in high-temperature air to impact on its high-temperature strength, which restricts its applied range [5-6]. Some excellent oxidation-resistance materials are considered as an assistant phase for ZrB₂ materials to prepare ZrB₂ ceramics to improve the high-temperature performance of ZrB₂ materials, such as Al₂O₃-ZrB₂, SiC-ZrB₂, LaB₂-ZrB₂, and ZrO₂-ZrB₂ [7-9].

Yttrium aluminium garnet (YAG or Y₃Al₅O₁₂) adopts the cubic garnet structure, it is of great interest as a high-temperature engineering material, due to its high-temperature strength coupled with low creep rates [10-14], which indicates that YAG ought to be a suitable

matrix and reinforcing material [15-16].

To make ZrB₂ ceramics have a better oxidation resistance, high-density ZrB₂-YAG-Al₂O₃ ceramics were prepared using Al₂O₃-Y₂O₃/ZrB₂ composite powders with spark plasma sintering. In this paper, the effect of the reinforcement phase on the oxidation mechanism of ZrB₂-YAG-Al₂O₃ ceramics is discussed.

Materials and Experiment

Analytical grades of aluminum nitrate, yttrium nitrate, ammonia and commercially-available ZrB₂ powder (99.5% in purity) were used. ZrB₂ particles were coated with Al₂O₃-Y₂O₃ composite particles via a co-precipitation method [17]. Different types of ZrB₂-YAG-Al₂O₃ ceramics were prepared using Al₂O₃-Y₂O₃/ZrB₂ shell-core composite particles with spark plasma sintering (SPS). ZrB₂-YAG-Al₂O₃ ceramics were oxidized in air by a furnace, the weight and microstructure of ZrB₂-YAG-Al₂O₃ ceramics were tested after oxidation. The process flow diagram is shown in Fig. 1.

ZrB₂-YAG-Al₂O₃ ceramics were prepared with the SPS method (Mode: SPS-1050, Japan). Oxidation were treated in a furnace (Mode: Nabertherm LHT04, Germany). Phase analysis was identified by X-ray powder diffraction (XRD) (Model: D/Max-RB, Japan). Microstructural analysis was performed by scanning electron microscopy (SEM) (Model: JSM-5610LV, Japan). Oxidation layer thickness analysis was performed with electron probe microanalysis (EPMA)

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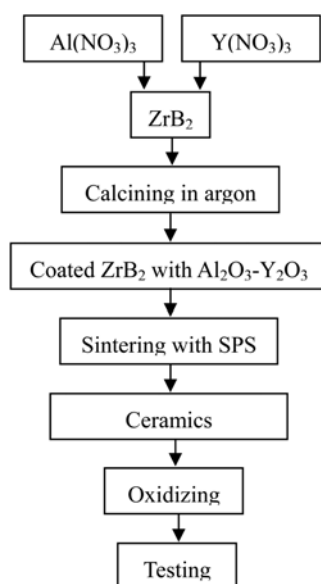


Fig. 1. The process flow diagram

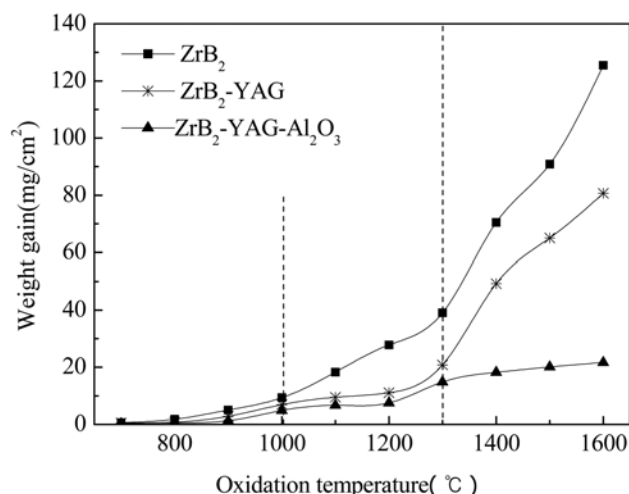


Fig. 2. Effect of oxidation temperature on weight gain of ceramics

(Model: JXA-880R, Japan).

Results and Discussion

Effect of the reinforcement phase on the oxidation mechanism of $\text{ZrB}_2\text{-YAG-Al}_2\text{O}_3$ ceramics at different oxidation temperatures

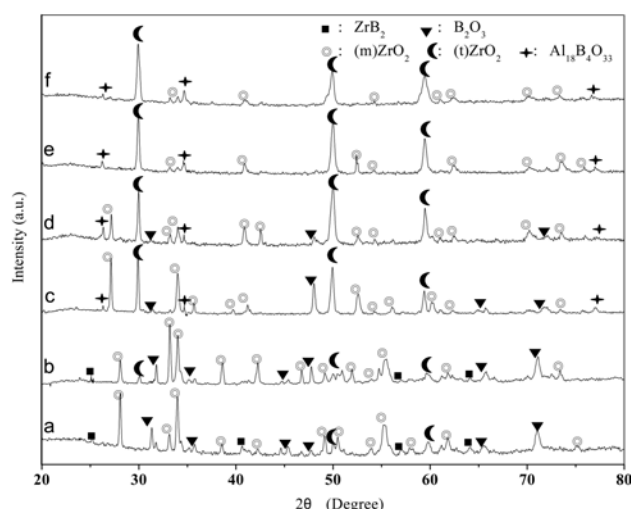


Fig. 4. Effect of oxidation temperature on the surface phase of $\text{ZrB}_2\text{-YAG-Al}_2\text{O}_3$ ceramics (a-1100 °C, b-1200 °C, c-1300 °C, d-1400 °C, e-1500 °C and f-1600 °C)

The weight gain of different ceramics after oxidized at different oxidation temperatures for 1 hour is shown in Fig. 2. The weight gain of ZrB_2 ceramics below 1300 is slower than that of ZrB_2 ceramics at 1300, because the ZrB_2 is oxidized to produce B_2O_3 and ZrO_2 [18], the reaction speed is faster at 1300, and the evaporation rate of B_2O_3 is faster, which make the ceramics materials show bigger pores (Fig. 3-a). The large numbers of channels for the diffusion of O_2 are retained at higher oxidation temperatures [19]. The overall tendency of the weight gain of $\text{ZrB}_2\text{-YAG}$ ceramics and ZrB_2 ceramics are similar, but the weight gain of $\text{ZrB}_2\text{-YAG}$ ceramics is less than that of ZrB_2 ceramics, because the oxidation layer microstructure of $\text{ZrB}_2\text{-YAG}$ ceramics is more compact than that of ZrB_2 ceramics (Fig. 3-b). The weight gain tendency of ceramics are similar below 1000, the weight gain tendency of $\text{ZrB}_2\text{-YAG}$ and $\text{ZrB}_2\text{-YAG-Al}_2\text{O}_3$ ceramics becomes mild between 1000 and 1300, the weight gain tendency of $\text{ZrB}_2\text{-YAG}$ ceramics and ZrB_2 ceramics are similar at 1300, however, the weight gain tendency of $\text{ZrB}_2\text{-YAG-Al}_2\text{O}_3$ ceramics becomes mild at 1300. Because the oxidation layer of $\text{ZrB}_2\text{-YAG-Al}_2\text{O}_3$ ceramics show the most compact microstructure (Fig. 3-c), the number of channels for the diffusion of O_2 are

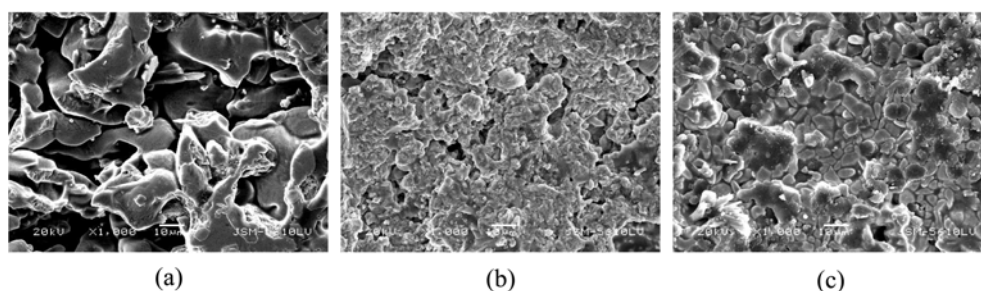


Fig. 3. The oxidation layer microstructure of ceramics oxidized at 1600 for 1 h (a- ZrB_2 , b- $\text{ZrB}_2\text{-YAG}$, c- $\text{ZrB}_2\text{-YAG-Al}_2\text{O}_3$)

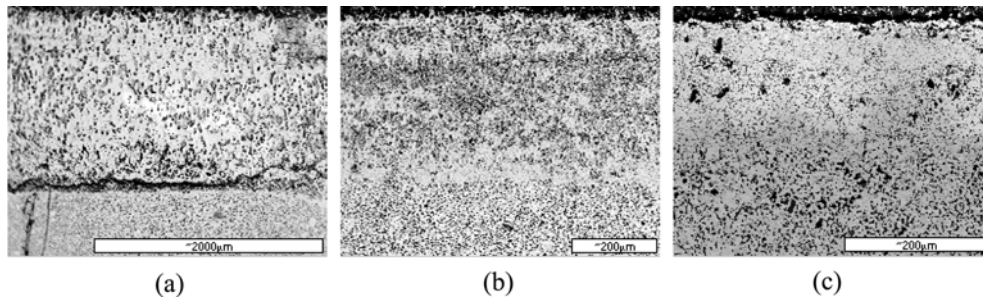


Fig. 5. The oxidation layer thickness of ceramics oxidized at 1600 for 1 h (ZrB_2 , b- ZrB_2 -YAG, c- ZrB_2 -YAG- Al_2O_3)

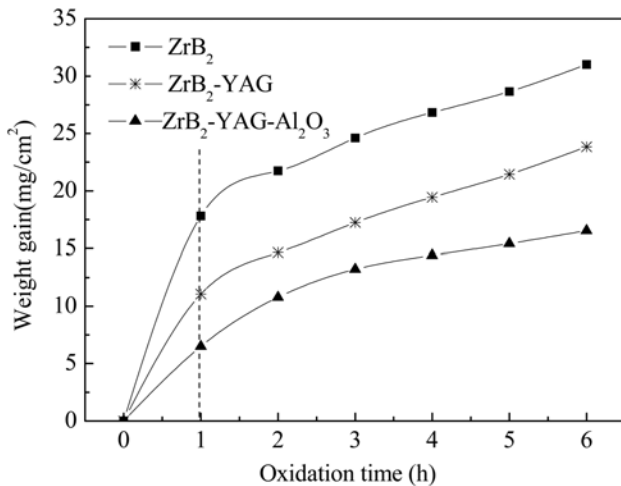


Fig. 6. Effect of oxidation time on weight gain of ceramics at 1200

least. The surface phase analysis of oxidized ZrB_2 -YAG- Al_2O_3 ceramics shows aluminum borate ($\text{Al}_{18}\text{B}_4\text{O}_{33}$) through the reaction of Al_2O_3 and B_2O_3 at 1300 (Fig. 4), which has melted and coated the surface of ZrB_2 -YAG- Al_2O_3 ceramics to form a compact oxidation-resistance layer [20]. The oxidation layer thickness of ZrB_2 -YAG- Al_2O_3 ceramics is the thinnest among the three types of ceramics (Fig. 5).

Effect of the reinforcement phase on the oxidation mechanism of ZrB_2 -YAG- Al_2O_3 ceramics during different oxidation times

The effect of oxidation time on the weight gain of ceramics at 1200 is shown in Fig. 6, which indicates an overall tendency of the weight gain of the three types of ceramics are similar, the weight gain rapidly increased in 1 h and the weight gain tendency become

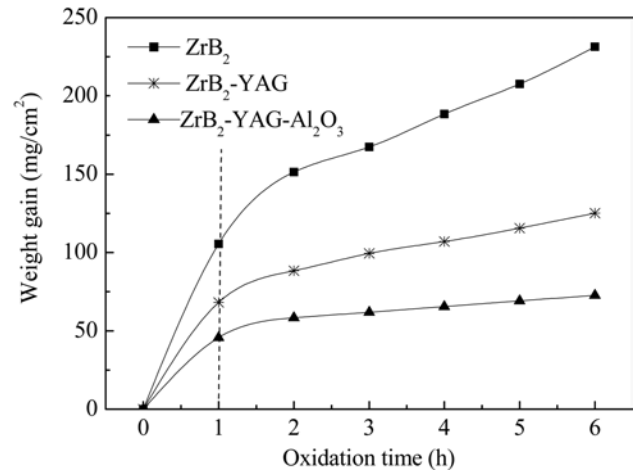


Fig. 8. Effect of oxidation time on the weight gain of ceramics at 1600

mild after 1 h. Because the oxidation mechanism of ceramics is similar, the only difference is the density of the oxidation layer (Fig. 7), which is the physical oxidation resistance. The weight gain is increased by prolonging the oxidation time, the oxidation layer thickness is increased, the diffusion distance of O_2 becomes longer from the surface to the inside, the weight gain gradually becomes slower. The weight gain of ZrB_2 -YAG- Al_2O_3 ceramics is least, the mechanism is not only from the compact oxidation layer microstructure but the inferior diffusivity of O_2 in the Al_2O_3 .

The effect of oxidation time on the weight gain of ceramics at 1600 is shown in Fig. 8, which indicates that the overall tendency of the weight gain of ZrB_2 -YAG ceramics and ZrB_2 ceramics are similar. However, the weight gain of ZrB_2 -YAG ceramics is

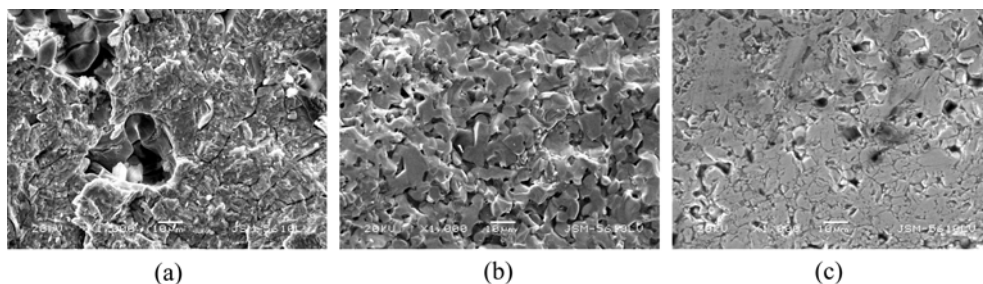


Fig. 7. Effect of oxidation time on the oxidation layer microstructure of ceramics at 1200 (a- ZrB_2 , b- ZrB_2 -YAG, c- ZrB_2 -YAG- Al_2O_3)

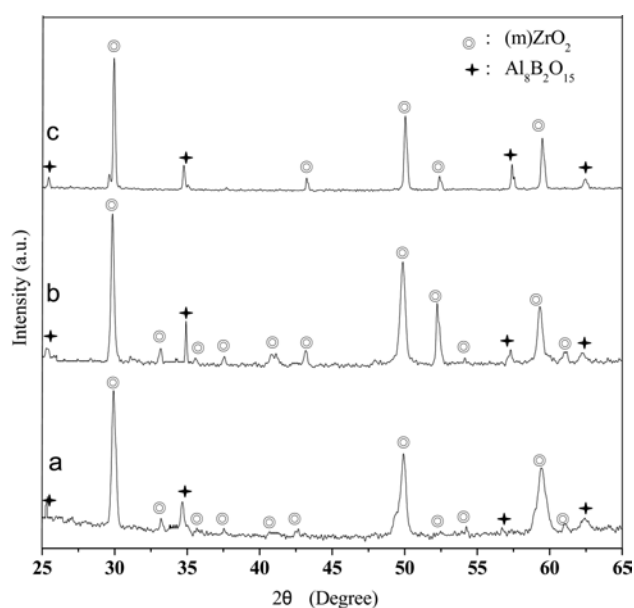


Fig. 9. Effect of oxidation time on the phases of ceramics at 1600 (a-1 h, b-3 h, c-6 h)

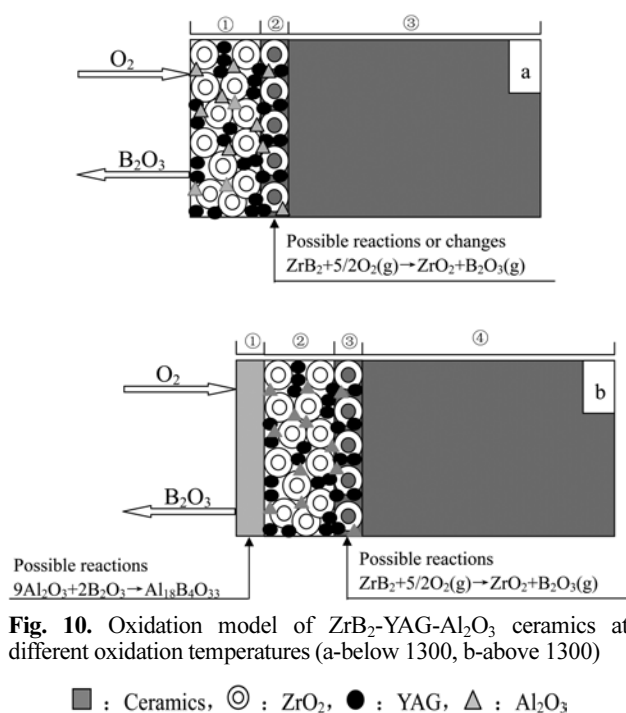


Fig. 10. Oxidation model of $\text{ZrB}_2\text{-YAG-Al}_2\text{O}_3$ ceramics at different oxidation temperatures (a-below 1300, b-above 1300)

lower than that of ZrB_2 ceramics. The weight gain tendency of $\text{ZrB}_2\text{-YAG-Al}_2\text{O}_3$ ceramics is similar by contrast with $\text{ZrB}_2\text{-YAG}$ ceramics and ZrB_2 ceramics at 1 h. The weight gain tendency of $\text{ZrB}_2\text{-YAG-Al}_2\text{O}_3$ ceramics is extremely mild after 1 h. Because the oxidation time is longer, the amount of the aluminum borate phase is higher, the aluminum borate content is more on the surface through the XRD of ceramic surfaces (Fig. 9), the oxidation layer is more compact and the oxidation resistance of $\text{ZrB}_2\text{-YAG-Al}_2\text{O}_3$ ceramics is increased.

A model of the oxidation resistance mechanism of $\text{ZrB}_2\text{-YAG-Al}_2\text{O}_3$ ceramics

Through the above analysis and results, an oxidation model of $\text{ZrB}_2\text{-YAG-Al}_2\text{O}_3$ ceramics at high temperature is constructed, which helps to understand the oxidation mechanism of $\text{ZrB}_2\text{-YAG-Al}_2\text{O}_3$ ceramics. A sketch of the oxidation model of $\text{ZrB}_2\text{-YAG-Al}_2\text{O}_3$ ceramics is shown in Fig. 10.

Below 1300, the relative density of the oxidation layer (Fig. 10-a district) is higher due to the existing YAG and Al_2O_3 phases, which give a few channels for O_2 diffusion to react with ZrB_2 (Fig. 10-a district) in the ceramics and the ceramics (Fig. 10-a district) are protected to achieve the aim of oxidation resistance. Above 1300, ZrB_2 reacts with O_2 to form B_2O_3 (Fig. 10-b district), B_2O_3 reacts with Al_2O_3 to form $\text{Al}_{18}\text{B}_4\text{O}_{33}$ (Fig. 9). $\text{Al}_{18}\text{B}_4\text{O}_{33}$ melts and is coated on the surface of the ceramics to form protective layer for the oxidation resistance of ceramics at a high temperature (Fig. 10-b district).

Conclusions

The results are shown through above a series of analysis and discussion, the overall tendency of the weight gain of $\text{ZrB}_2\text{-YAG}$ ceramics and ZrB_2 ceramics are similar, but the weight gain of $\text{ZrB}_2\text{-YAG}$ ceramics is less than that of ZrB_2 ceramics. The weight gain tendency of three types of ceramics are similar below 1000, the weight gain of $\text{ZrB}_2\text{-YAG}$ and $\text{ZrB}_2\text{-YAG-Al}_2\text{O}_3$ ceramics show a mild tendency between 1000 and 1300, the weight gain tendency of $\text{ZrB}_2\text{-YAG}$ ceramics and ZrB_2 ceramics are similar at 1300. However, the weight gain tendency of $\text{ZrB}_2\text{-YAG-Al}_2\text{O}_3$ ceramics becomes mild at 1300 due to the $\text{Al}_{18}\text{B}_4\text{O}_{33}$ coating on the ceramic surface. The weight gain is rapidly increased in 1 h, the weight gain tendency becomes mild after 1 h. The weight gain tendency of $\text{ZrB}_2\text{-YAG-Al}_2\text{O}_3$ ceramics is similar by contrast with $\text{ZrB}_2\text{-YAG}$ ceramics and ZrB_2 ceramics at 1h. The weight gain tendency of $\text{ZrB}_2\text{-YAG-Al}_2\text{O}_3$ ceramics is extremely mild at a higher oxidation temperature after 1 h.

Acknowledgments

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