Preparation of High-density YAG/ZrB₂ Multi-phase Ceramics by Spark Plasma Sintering

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ZrB₂ and YAG are widely applied because of some excellent properties, but ZrB₂ is difficult to prepare as a high-density ceramic, and it is easily oxidized in high temperature air, which limits the application of ZrB₂ materials. To obtain high-density multi-phase ceramics, in this paper, Al₂O₃ and Y₂O₃ are added into ZrB₂ raw material to prepare high-density YAG/ZrB₂ multi-phase ceramics by spark plasma sintering. Through the above analysis, it is proposed that 1600°C is regarded as a critical sintering temperature (Tc) to fabricate YAG/ZrB₂ multi-phase ceramics. Only if the sintering temperature is higher than Tc can a nearly full density composite be achieved. The microstructure of sintered YAG/ZrB₂ multi-phase ceramics after 4 minutes at 1600°C is a better compact, the density and relative density are 5.5865 g/cm³ and 99.40% respectively, which indicates that high-density YAG/ZrB₂ multi-phase ceramics have been fabricated successfully.

Key words: ZrB₂, YAG, Multi-phase ceramics, Densification behavior, Relative density, Spark plasma sintering.

Introduction

Due to some excellent properties, ZrB₂ is widely applied to many industries [1-5]. Although ZrB₂ has there excellent properties, it is difficult to prepare a high-density ZrB₂ ceramic, and it is easily oxidized in high temperature air, which limits the application of ZrB₂ materials [6-8]. Yttrium aluminium garnet (YAG or Al₂O₃-Y₃O₅) has attracted substantial interest, because of its extreme chemical and physical properties, especially high-temperature strength and stability, it is widely applied in some industries [9-11]. To overcome some problems with single phase ceramics, materials research has moved from single phase to multi-phase materials to prepare higher performance materials [12].

At the present time, there are a number of sintering methods for the preparation of ZrB₂ ceramics, such as, common sintering, high pressure sintering (HPS), self-propagating high-temperature synthesis (SHS), high isostatic sintering (HIP) and spark plasma sintering (SPS) [13-16]. The bulk is sintered using the stronger impulsive current through the electric mould or sintered materials in the SPS system. Accordingly SPS shows some merits, such as, fast sintering, short cycle time, high temperature, etc. [17, 18], which is used to prepare YAG/ZrB₂ multi-phase ceramics.

To obtain a high-density for better oxidation resistance ZrB₂ ceramics, in this paper, Al₂O₃ and Y₂O₃ are added into ZrB₂ raw material to prepare high-density YAG/ZrB₂ multi-phase ceramics by SPS.

Materials and Experiment

Commercially available ZrB₂ powder (99.5% in purity) was used. Synthesized superfine Al₂O₃-Y₃O₅ composite powder with aluminum nitrate, yttrium nitrate and ammonia via the co-precipitation method was used. The Al₂O₃-Y₂O₃/ZrB₂ composite powder was prepared with the Al₂O₃-Y₂O₃/ZrB₂ composite powder and ZrB₂ powder via a mechanical ball milling method. Then the Al₂O₃-Y₂O₃/ZrB₂ composite powder was loaded into in a graphite mould with an inside diameter of 20 mm. The temperature was automatically raised to 600°C, then monitored and regulated by an optical pyrometer aimed at the mould surface. A heating rate of 100 K·minute⁻¹ between 600°C and various chosen temperatures was performed, the graphite mould was removed, and YAG/ZrB₂ multi-phase ceramics were obtained. A process flow diagram is shown in Fig. 1.

Materials were sintered using the SPS method (Mode: SPS-1050, Japan), and the density was established with a precise electronic balance via the Archimedes' principle (Model: Sartorius BS210S, Germany) and compared to the YAG/ZrB₂ theoretical density. Microstructural analysis was performed by scanning electron microscopy (SEM) (Model: JSM-5610LV, Japan).

Results and Discussion

Densification behavior during the SPS process

Figure 2 shows the shrinkage curves of samples.
sintered at 1500, 1700, 1800°C. Owing to uniaxial pressure and high temperature sintering, the samples shrunk rapidly to accelerate densification. With further heating and a holding state, the shrinkage behavior retards and finally stops. From Fig. 2, it is discernible that the rate of shrinkage at different sintering temperatures is obviously different. The sample sintered at 1500°C continuously shrunk during heating and the holding state, and its shrinkage rate was more sluggish than those sintered at 1700 and 1800°C. It can be also seen from Fig. 2(b and c) that, when temperature is raised to 1600°C (dashed line), the samples stop shrinking, which indicates the samples are achieving nearly full density. The result of measured density supports the above explanation. The composites sintered at 1700 and 1800°C possess 99.36% and 99.40% of theoretical density, respectively, but the composites sintered at 1500°C only achieved 96.37% of theoretical density, as listed in Table 1.

During the SPS process, the action of the locally high temperature created by the plasma as well as the Joule heating from the pulse current results in producing YAG (Fig. 3) and melting YAG to promote shrinkage [19, 20]. When the sintering temperature was raised to 1600°C, the amount of molten YAG increased and liquid phase sintering took place to lead the sample finally to stop shrinking and realize the sample densification. Thus, in the present study, it is proposed that 1600°C is regarded as a critical sintering temperature (Tc) to fabricate YAG/ZrB₂ multi-phase ceramics. Only if sintering temperature is higher than Tc, can a nearly full density composite be achieved.

**Microstructure of YAG/ZrB₂ multi-phase ceramics**

Microstructures sintered at different temperatures are shown in Fig. 4. It is clear that the amount of pores in

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**Table 1.** Effect of temperature and holding time sintering parameters under 20 MPa pressure on the density of YAG/ZrB₂ multi-phase ceramics

<table>
<thead>
<tr>
<th>Samples</th>
<th>T (°C)</th>
<th>Holding time (minute)</th>
<th>Experimental density (g/cm³)</th>
<th>Relative density (%) (YAG/ZrB₂ theor.=5.62 g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1500</td>
<td>2</td>
<td>5.42</td>
<td>96.37</td>
</tr>
<tr>
<td>2</td>
<td>1600</td>
<td>2</td>
<td>5.57</td>
<td>99.16</td>
</tr>
<tr>
<td>3</td>
<td>1700</td>
<td>2</td>
<td>5.58</td>
<td>99.36</td>
</tr>
<tr>
<td>4</td>
<td>1800</td>
<td>2</td>
<td>5.59</td>
<td>99.40</td>
</tr>
<tr>
<td>5</td>
<td>1600</td>
<td>4</td>
<td>5.59</td>
<td>99.40</td>
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<tr>
<td>6</td>
<td>1600</td>
<td>6</td>
<td>5.59</td>
<td>99.40</td>
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</tbody>
</table>

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**Fig. 1.** A process flow diagram for preparing YAG/ZrB₂ multi-phase ceramic materials.

**Fig. 2.** Effect of sintering temperature on shrinkage characteristic of YAG/ZrB₂ multi-phase ceramics (a) 1500°C, (b) 1700°C, (c) 1800°C.

**Fig. 3.** XRD of materials (a) ZrB₂ raw materials, (b) Synthesized Al₂O₃-Y₂O₃ composite powder, (c) YAG/ZrB₂ multi-phase ceramic.

**Fig. 4.** Microstructures of YAG/ZrB₂ multi-phase ceramics sintered at different temperatures.
the samples sintered at 1500°C is more than for those sintered at 1700°C and 1800°C, which is corresponding with the results of the measured density. With increasing sintering temperature, YAG melts to fill in the pores, which leads to the pores disappearing. With prolonging holding time, the pores are filled sufficiently by the melted YAG, which leads to increase the density, as listed in Table 1. High-density YAG/ZrB₂ multi-phase ceramics were successfully fabricated, the sample is shown in Fig. 5.

**Conclusions**

Through the above analysis, it is proposed that 1600°C is regarded as a critical sintering temperature (Tc) to fabricate YAG/ZrB₂ multi-phase ceramics. Only if the sintering temperature is higher than Tc, can a nearly full density composite be achieved. The microstructure of a YAG/ZrB₂ multi-phase ceramic sintered at 1600°C for 4 minutes is a better compact, the density and relative density is 5.59 g/cm³ and 99.4% respectively, which indicates that high-density YAG/ZrB₂ multi-phase ceramics were successfully fabricated.

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**References**