Research Article

Effect of TiO$_2$ Addition on the Properties of Al$_2$O$_3$-ZrO$_2$ Composites Prepared by Spark Plasma Sintering

I. Akin, E. Yılmaz, O. Ormanci, F. Sahin, O. Yucel, and G. Goller

Department of Metallurgical and Materials Engineering, Istanbul Technical University, Istanbul 34469, Turkey
Address correspondence to G. Goller, goller@itu.edu.tr

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Abstract In this study, monolithic Al$_2$O$_3$ and Al$_2$O$_3$/3Y-TZP (90–10 vol%) and Al$_2$O$_3$/3Y-TZP with 5 wt% TiO$_2$ composites were prepared by spark plasma sintering (SPS) at temperatures of 1350, 1460 °C and 1300 °C for 300 s under a pressure of 40 MPa, respectively. Shrinkage of the specimens during SPS process was continuously monitored. Densities of the composites were determined by the Archimedes’ method. Vickers hardness ($H_V$) was measured under loads of 9.8 N. Fully dense Al$_2$O$_3$ and Al$_2$O$_3$/3Y-TZP composites containing 0 and 5 wt% TiO$_2$ with a relative density of 99% were obtained. Vickers hardness of the composites decreased with increasing TiO$_2$ content from 19.8 ± 0.4 GPa to 17.3 ± 0.3 GPa.

Keywords spark plasma; sintering; alumina; zirconia; titania

1 Introduction

Monolithic alumina and zirconia ceramics are widely used for orthopedic implants such as total hip and knee replacement prostheses due to their excellent mechanical properties, high wear resistance, and biocompatibility. It is well known that yttria stabilized tetragonal zirconia (3Y-TZP) has higher strength and fracture toughness than alumina, because of transformation toughening mechanism. A new generation ceramic for joint prostheses, zirconia toughened alumina, possesses higher fracture strength and toughness compared to monolithic alumina [2,4,5].

The effects of additives for alumina ceramics have been aimed to decrease the sintering temperature, improve microstructure and properties. The effect of TiO$_2$ addition has been reported to promote the sintering behavior and grain growth phenomena in several studies [5]. TiO$_2$ addition enhanced diffusivity due to the Al$^{3+}$ vacancies, as generated by Ti$^{4+}$ substituting for Al$^{3+}$ [1,3,5].

The purpose of this study is to investigate the sintering behavior, densification and hardness of the Al$_2$O$_3$, Al$_2$O$_3$/3Y-TZP (90–10 vol%) and Al$_2$O$_3$/3Y-TZP (90–10 vol%) with 5 wt% TiO$_2$ composites prepared by spark plasma sintering (SPS) method. The phase analysis and microstructures of the specimens were also investigated.

2 Materials and methods

Al$_2$O$_3$ (Baikowski Grade SM8, France, an average particle size of 0.6 μm), 3Y-TZP (Tosoh Grade TZ-3Y, Japan, an average particle size of 0.05–0.1 μm) and TiO$_2$ (Anatase, Merck, product code 1.00808, Germany) powders were used as starting materials (Table 1). The raw materials were weighed in appropriate quantities, ball milled in ethanol for 24 h and then dried. A graphite die 50 mm in inner diameter was filled with the mixture, followed by sintering using an SPS apparatus (SPS-7.40 MK-VII, SPS Syntex Inc.). Pure Al$_2$O$_3$ was sintered at 1350 °C, Al$_2$O$_3$/3Y-TZP composites with and without TiO$_2$ were sintered at 1300 and 1460 °C with a heating rate of 1.7 °C/s in vacuum. A uniaxial pressure of 40 MPa and pulsed direct current (12 ms/On, 2 ms/Off) were applied during the entire process. The current was controlled manually during monitoring the displacement behavior of the samples. The crystalline phases were identified by X-ray diffractometry (XRD; Rigaku MiniFlex) in the 2θ range of 10–80° with Cu Kα radiation. The densities of the specimen were determined by Archimedes’ method and converted to relative density using theoretical densities of Al$_2$O$_3$, yttria stabilized ZrO$_2$ and TiO$_2$. The fracture surface of the samples were coated with a thin film platinum and subjected to microscopic investigation by a field emission scanning electron microscope (FE-SEM; JEOL JSM-7000F). Microhardness tests were applied to the polished samples under a constant load of 9.8 N with 12 s indentation time.

Table 1: ZrO$_2$ starting powders.

<table>
<thead>
<tr>
<th>Material grade</th>
<th>Supplier</th>
<th>Y$_2$O$_3$ (mol%)</th>
<th>Al$_2$O$_3$ (wt%)</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TZ-3Y</td>
<td>Tosoh</td>
<td>3</td>
<td>0.1</td>
<td>27</td>
</tr>
</tbody>
</table>

$^a$ According to the supplier datasheets.
3 Results and discussion

The densification of the specimens during SPS process was evaluated by the displacement of punch rods due to the shrinkage of the samples. Figure 1 shows the displacements of Al$_2$O$_3$ and Al$_2$O$_3$/3Y-TZP composites without TiO$_2$ and with 5 wt% TiO$_2$, and isothermal shrinkage at sintering temperatures.

The shrinkage of Al$_2$O$_3$ started at 950 °C and completed at 1310 °C. The starting temperature of shrinkage (1060 °C) for the Al$_2$O$_3$/3Y-TZP composites containing 5 wt% TiO$_2$ was significantly lower than that of Al$_2$O$_3$/3Y-TZP (1200 °C). Thus, the presence of 5 wt% TiO$_2$ promoted the densification of Al$_2$O$_3$/3Y-TZP and decreased the sintering temperature of Al$_2$O$_3$/3Y-TZP composites from 1460 to 1300 °C.

The XRD patterns of the Al$_2$O$_3$ and Al$_2$O$_3$/3Y-TZP composites sintered at different temperatures for 300 s are shown in Figure 2. X-ray analysis indicated that α-Al$_2$O$_3$ and tetragonal ZrO$_2$ became fully crystalline and monoclinic ZrO$_2$ peaks did not appear at the end of the sintering process.

Figure 3 shows the Vickers hardness of Al$_2$O$_3$ and Al$_2$O$_3$/3Y-TZP composites at load of 9.8 N. Al$_2$O$_3$/3Y-TZP (90–10 vol%) composite had higher hardness than
the monolithic \( \text{Al}_2\text{O}_3 \). The hardness of \( \text{Al}_2\text{O}_3 \) slightly increased with the addition of 10 vol\% yttria stabilized (3 mol\%) \( \text{ZrO}_2 \) (3Y-TZP) from 19.8 to 20.2 GPa. The addition of 5 wt\% \( \text{TiO}_2 \) decreased the Vickers hardness of \( \text{Al}_2\text{O}_3/3\text{Y-TZP} \) composite from 20.2 to 17.3 GPa. This relatively low hardness could be mostly due to the 2 wt\% porosity.

Microstructures of fracture surfaces of \( \text{Al}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3/3\text{Y-TZP} \) composites are shown in Figure 4. In Figure 4(a), \( \text{Al}_2\text{O}_3 \) consisted of both large and small equiaxed grains 0.5–3 \( \mu \)m in size and straight grain boundaries. Figure 4(b) demonstrates the SEM image of fracture surface of \( \text{Al}_2\text{O}_3/3\text{Y-TZP} \). In this figure, alumina grains (grey) in size of 0.6–1.5 \( \mu \)m and 3Y-TZP grains (white) in size of 0.05–0.1 \( \mu \)m are shown. Figure 4(c) is the SEM micrograph of \( \text{Al}_2\text{O}_3/3\text{Y-TZP} \) composites containing 5 wt\% \( \text{TiO}_2 \). The grain size of alumina was not significantly changed by the addition of \( \text{TiO}_2 \).

4 Conclusions

\( \text{Al}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3/3\text{Y-TZP} \) composites were prepared by SPS at temperatures of 1300–1460 °C for 300 s under 40 MPa. The addition of 5 wt\% \( \text{TiO}_2 \) improved densification of \( \text{Al}_2\text{O}_3/3\text{Y-TZP} \) and decreased the sintering temperature of \( \text{Al}_2\text{O}_3/3\text{Y-TZP} \) composites from 1460 to 1300 °C. The presence of 10 vol\% 3Y/TZP slightly increased the hardness of \( \text{Al}_2\text{O}_3 \) and suppressed the grain growth of alumina.

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References


