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*Research Article*

# Effect of $TiO_2$ Addition on the Properties of $Al_2O_3$-$ZrO_2$ Composites Prepared by Spark Plasma Sintering

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**Abstract** In this study, monolithic $Al_2O_3$ and $Al_2O_3$/3Y-TZP (90–10 vol%) and $Al_2O_3$/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 $Al_2O_3$ and $Al_2O_3$/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 $19.8 \pm 0.4$ GPa to $17.3 \pm 0.3$ 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 composites, 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 $Al_2O_3$, $Al_2O_3$/3Y-TZP (90–10 vol%) and $Al_2O_3$/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.

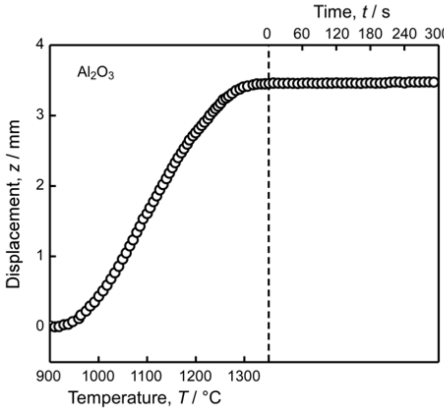
## 2 Materials and methods

$Al_2O_3$ (Baikowski Grade SM8, France, an average particle size of 0.6 $\mu$m), 3Y-TZP (Tosoh Grade TZ-3Y, Japan, an average particle size of 0.05–0.1 $\mu$m) 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 $Al_2O_3$ was sintered at 1350 °C, $Al_2O_3$/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 $2\theta$ range of 10–80° with Cu K$\alpha$ radiation. The densities of the specimen were determined by Archimedes' method and converted to relative density using theoretical densities of $Al_2O_3$, 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.

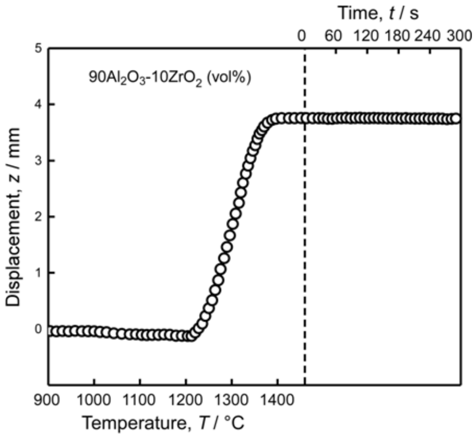
| Material grade | Supplier | $Y_2O_3$ (mol%) | $Al_2O_3$ (wt%) | Grain size[a] (nm) |
|---|---|---|---|---|
| TZ-3Y | Tosoh | 3 | 0.1 | 27 |

[a] According to the supplier datasheets.

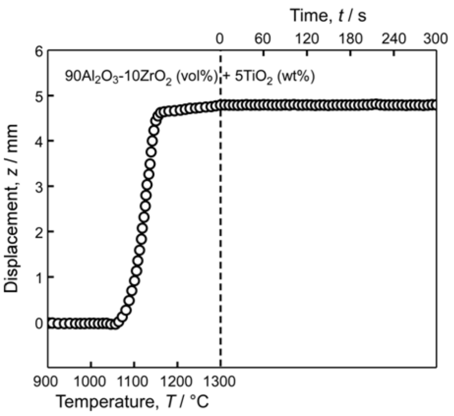
**Table 1:** $ZrO_2$ starting powders.




(a)




(b)




(c)

**Figure 1:** Displacements of the composites, and the time dependence of isothermal displacement at sintering temperatures.

## 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 $Al_2O_3$ and $Al_2O_3$/3YTZP composites without $TiO_2$ and with 5 wt% $TiO_2$, and isothermal shrinkage at sintering temperatures.

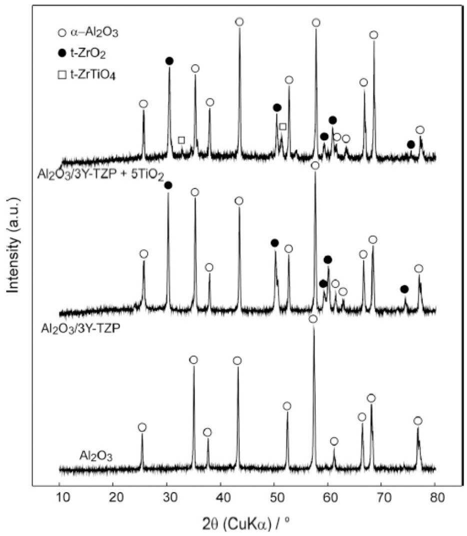



**Figure 2:** XRD patterns of $Al_2O_3$ and $Al_2O_3$/3Y-TZP composites.

The shrinkage of $Al_2O_3$ started at 950 °C and completed at 1310 °C. The starting temperature of shrinkage (1060 °C) for the $Al_2O_3$/3Y-TZP composites containing 5 wt% $TiO_2$ was significantly lower than that of $Al_2O_3$/3Y-TZP (1200 °C). Thus, the presence of 5 wt% $TiO_2$ promoted the densification of $Al_2O_3$/3Y-TZP and decreased the sintering temperature of $Al_2O_3$/3Y-TZP composites from 1460 to 1300 °C.

The XRD patterns of the $Al_2O_3$ and $Al_2O_3$/3Y-TZP composites sintered at different temperatures for 300 s are shown in Figure 2. X-ray analysis indicated that $\alpha$-$Al_2O_3$ 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 $Al_2O_3$ and $Al_2O_3$/3Y-TZP composites at load of 9.8 N. $Al_2O_3$/3Y-TZP (90–10 vol%) composite had higher hardness than

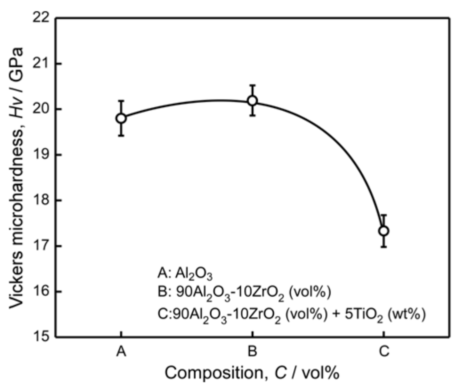



**Figure 3:** Vickers hardness of $Al_2O_3$ and $Al_2O_3$/3Y-TZP composites.

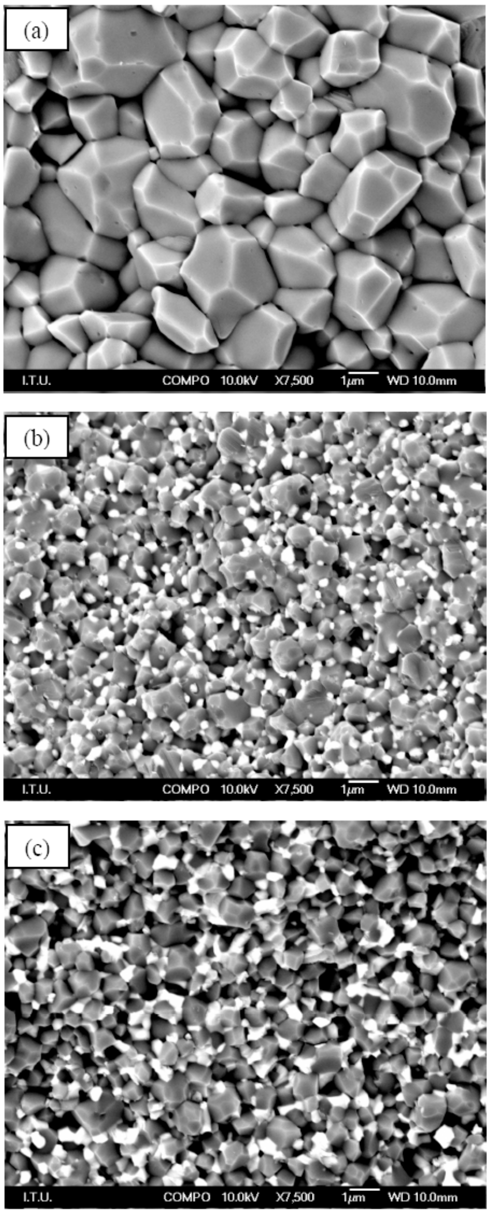



**Figure 4:** Fracture surface micrographs of (a) monolithic $Al_2O_3$ sintered at 1350 °C, (b) $Al_2O_3$-3Y-TZP sintered at 1460 °C, and (c) $Al_2O_3$-3Y-TZP + $5TiO_2$ sintered at 1300 °C for 300 s.

the monolithic $Al_2O_3$. The hardness of $Al_2O_3$ slightly increased with the addition of 10 vol% yttria stabilized (3 mol%) $ZrO_2$ (3Y-TZP) from 19.8 to 20.2 GPa. The addition of 5 wt% $TiO_2$ decreased the Vickers hardness of $Al_2O_3$/3Y-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 $Al_2O_3$ and $Al_2O_3$/3Y-TZP composites are shown in Figure 4. In Figure 4(a), $Al_2O_3$ 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 $Al_2O_3$-3Y-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 $Al_2O_3$/3Y-TZP composites containing 5 wt% $TiO_2$. The grain size of alumina was not significantly changed by the addition of $TiO_2$.

## 4 Conclusions

$Al_2O_3$ and $Al_2O_3$/3Y-TZP composites were prepared by SPS at temperatures of 1300–1460 °C for 300 s under 40 MPa. The addition of 5 wt% $TiO_2$ improved densification of $Al_2O_3$/3Y-TZP and decreased the sintering temperature of $Al_2O_3$/3Y-TZP composites from 1460 to 1300 °C. The presence of 10 vol% 3Y/TZP slightly increased the hardness of $Al_2O_3$ and suppressed the grain growth of alumina.

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