研 究

Fabrication of Fine-Grained 3Y-TZP/ β -Al₂O₃ Composites

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SYNOPSIS

Fine-grained 3Y-TZP/ β -Al₂O₃ ($\sim$ NaAl₁₁O₁₇) composites have been prepared by pressureless sintering of planetary-ball-milled 3Y-TZP and β -Al₂O₃ powders. In the composites, β -Al₂O₃ particles with about 0.2 – 3 μ m in size were homogeneously dispersed in the TZP matrix with the grain size of $\sim$ 200 nm. The β -Al₂O₃ addition slightly improved Vickers hardness and fracture strength. Fracture toughness of the composite, however, was almost the same as that of the pure TZP and neither crack bridging nor crack deflection was observed for the composites. This result indicates that rather strong bonding may exist between 3Y-ZrO₂ matrix and fine β -Al₂O₃ particles.

KEY WORDS

tetragonal zirconia polycrystals, beta alumina, pressureless sintering, microstructure, mechanical properties

1 Introduction

Tetragonal zirconia polycrystalline (TZP) ceramics and TZP-matrix composites have been widely studied because they exhibit attractive mechanical properties¹⁻³. In particular, TZP/ α -Al₂O₃ composites have been widely investigated due to their very high fracture strength¹ and the superplastic deformability⁴. The zirconia addition to the β -Al₂O₃ (i.e. β -Al₂O₃/ZrO₂ composites) has also attracted much attentions (viz., for the ion-conducting electrolyte applications⁵⁻⁹).

Ceramic particles with β -Al₂O₃ or related magnetoplumbite crystal structure generally possess hexagonal platelike or needlelike shapes. They can act as second-phase reinforcement materials in ZrO₂ ceramics. Ce-TZP/Al₂O₃/CeMnAl₁₁O₁₉¹⁰, Ce-TZP/La(Fe,Al)₁₂O₁₉¹¹, and Y-TZP/BaFe₁₂O₁₉^{12,13} are counted among the ZrO₂/magnetoplumbite systems. However, there have been only limited studies on the β -Al₂O₃-added ZrO₂-matrix (i.e. ZrO₂/ β -Al₂O₃) composites. Troczynski and Nicholson¹⁴ reported that a partially stabilized zirconia (PSZ)/20 vol% β -Al₂O₃ composite exhibited extensive nonelastic deformation during fracture. The nonelastic deformation behavior in Ref.14 was analyzed using a theoretical model by Lambrieger¹⁵⁻¹⁷. Although the composite had fairly high fracture energy ($\sim$ 500 J/m²) compared with that of a pure PSZ ($\sim$ 50 J/m²), the fracture strength of the composite, 127 MPa, may be insufficient for some structural

applications; in their study, a PSZ (8 wt% Y₂O₃¹⁴, corresponding to $\sim$ 4.5 mol% Y₂O₃) and large-grained β -Al₂O₃ (120 μ m) were used. Thus, in the ZrO₂-Y₂O₃- β -Al₂O₃ system, higher fracture strength seems to be obtained by using high-strength TZP and fine-grained β -Al₂O₃.

This paper reports the fabrication of fine-grained 3 mol%-Y₂O₃-doped ZrO₂ (3Y-TZP)/20 vol% β -Al₂O₃ composites. Microstructure and some mechanical properties of the composites will be discussed.

2 Experimental Procedure

2.1 Sample preparation

Experimental procedures are schematically summarized in Fig.1. Commercially available 3Y-TZP (TZ-3Y, 0.3 μ m, Tosoh Co., Ltd., Japan) and Na- β -Al₂O₃ ($\sim$ NaAl₁₁O₁₇, < 150 μ m, Kojundo Chemical Laboratory Co., Ltd., Japan) powders were used as the starting materials. First, the β -Al₂O₃ powder was planetary ball-milled under the acceleration of 4 G in ethanol for 12 h using zirconia balls in a zirconia pot. The first-milling effect was evaluated by using a transmission electron microscope (TEM, Model 4000FX, JEOL Tokyo, Japan). Fig.2(a) shows a TEM image of the β -Al₂O₃ powder after planetary-ball milling (4 G, 12 h). The powder was well-refined by the planetary ball-milling. An electron diffraction image of a milled particle is given in Fig.2(b). The β -Al₂O₃ crystal structure was kept after the high-energy milling process. Second,

the 3Y-TZP powder and a proper amount of ethanol were added to the β -Al₂O₃ slurry, satisfying the composition of 3Y-TZP: β -Al₂O₃ = 80:20 in vol%. It was further planetary ball-milled in the same condition as the first milling. The mixed slurry was dried, subsequently dry-ball-milled for 24 h, and then, sieved through a 100 mesh screen, producing the 3Y-ZrO₂/20 vol% (~12 wt%) β -Al₂O₃ mixed powder. The mixed powder was cold isostatically pressed at 200 MPa after mold-pressing. The green compacts were sintered in air at 1300–1550°C for 2 h. The composites sintered at 1400°C will be mainly discussed.

2.2 Evaluation

Constituent phases of the composite were analyzed by an X-ray rotating anode diffractometer (Model Rotaflex, RIGAKU, Tokyo, Japan) operated at 40 kV and 100 mA. The microstructure was characterized by a scanning electron microscope (SEM, Model 6330F, JEOL, Tokyo, Japan). Bulk density was measured by the Archimedes method in toluene. Hardness was evaluated by the Vickers indentation method under conditions of 196 N load with loading duration of 15 s. Fracture strength at room-temperature was determined by the three-point bending test (4 mm width $\times$ 3 mm height $\times$ 40 mm length, span: 30 mm, crosshead

speed: 0.5 mm/min). Fracture toughness was evaluated by the indentation fracture method¹⁸⁾, with the indentation load of 196 N. Toughness was also determined by the SEVNB method¹⁹⁾ in full size specimens (3 mm width $\times$ 4 mm height $\times$ 40 mm length, span: 30 mm) for some pure TZP and composites.

3 Results and Discussion

Fig.3 shows an X-ray diffraction pattern of the 3Y-ZrO₂/20 wt% β -Al₂O₃ composite sintered at 1400°C for 2 h. The composite consisted of only tetragonal ZrO₂ (t-ZrO₂) and β -Al₂O₃, indicating good phase compatibility of these two phases.

SEM photographs of the monolithic 3Y-ZrO₂ and the 3Y-ZrO₂/20 vol% β -Al₂O₃ composite are given in Fig.4(a) and (b), respectively. Both materials were sufficiently dense and consisted of fine grains. The grain size of the TZP was ca. 200 nm for both materials. The β -Al₂O₃ particles were fairly small, ca. 0.2–3 μ m, compared to the previous

Fig.1 Schematic illustration of the experimental procedure.

Fig.2 TEM photographs of (a) the β -Al₂O₃ powder after first planetary-ball milling (4 G, 12 h), and (b) an electron diffraction pattern of a milled β -Al₂O₃ particle; zone axis was [001].

Fig.3 X-ray diffraction pattern of the 3Y-ZrO₂/20 vol% β -Al₂O₃ composite sintered at 1400°C for 2 h.

study¹⁴⁾. It is obvious that long-term planetary ball-milling was effective to produce the fine-grained microstructure.

The variation of relative density with sintering temperature is given in Fig.5. The relative density of both the monolithic TZP and the composites was > 99% at the sintering temperatures higher than 1400°C. At 1300°C, the monolithic TZP had higher density than the composite, suggesting that sintering process was inhibited by second-phase β -Al₂O₃ particles. However, at high temperatures, the composite showed a little higher density than the monolithic TZP. This result may be explained by (1) the transitional liquid-phase formation due to the Na ion and impurities, and (2) the compositional fluctuation during mixing and sintering processes. Further experiments are required to understand the variation of density.

Relationship between Vickers hardness and sintering temperature is plotted in Fig.6. Although the hardness decreased at higher temperatures due to the grain growth, the dependence of the hardness was similar to that of the relative density. At more than 1400°C, the composite showed higher hardness than the monolith.

Fig.4 SEM photographs of (a) the monolithic 3Y-ZrO₂ and (b) the 3Y-ZrO₂/20 vol% β -Al₂O₃ composite; both materials were sintered at 1400°C for 2 h.

Fig.5 Variation of relative density with sintering temperature.

Fig.6 Variation of Vickers hardness with sintering temperature.

Fig.7 Variation of fracture strength with sintering temperature.

Sintering temperature dependence of fracture strength is shown in Fig.7. The dependence of the monolithic ZrO₂ and that of the composites did not obviously differ from each other. However, the strength deviation at 1300°C was suppressed by the β -Al₂O₃ dispersion. The maximum fracture strength in this work, 888 MPa, was obtained for the 3Y-ZrO₂/20 vol% β -Al₂O₃ composite sintered at 1450°C.

Fig.8 shows the variation of fracture toughness with sintering temperature. According to the IF tests, all specimens had almost the same toughness value, ~ 6.0 MPa·m^{1/2}. Meanwhile, the preliminary SEVNB test showed that the toughness increased with increasing sintering temperature, probably because the transformation from tetragonal to monoclinic ZrO₂ can easily occur with increasing grain size^{20,21}. In any event, fracture toughness of the composite was almost the same as that of the pure TZP. This may be because neither crack bridging nor crack deflection takes place around β -Al₂O₃ particles (see Figs.9(a) and 9(b)). This result indicates that rather strong bonding may exist between 3Y-ZrO₂ matrix and fine β -Al₂O₃ particles.

At relatively low temperatures, $< 400^\circ\text{C}$, it was reported that TZP ceramics have good ionic conductivity, although they have less Y₂O₃ content than partially or fully stabilized zirconia²². β -Al₂O₃ (including another ion-conducting species) may modify the ionic conductivity of the TZP. Such experiments will be reported elsewhere²³.

4 Conclusions

The present work focused on producing fine-grained 3Y-TZP/ β -Al₂O₃ composites and evaluating the effects of the fine β -Al₂O₃ addition on the microstructure and mechanical

Fig.8 Variation of fracture toughness with sintering temperature.

properties.

- (1) Dense and fine-grained 3Y-TZP/ β -Al₂O₃ composites have been successfully fabricated by pressureless sintering of planetary-ball-milled 3Y-TZP and β -Al₂O₃ powders.
- (2) There was no dramatic change in mechanical properties by the addition of fine β -Al₂O₃, but a certain improvement was observed for the hardness and strength. Fracture toughness of the composite was almost the same as that of the pure TZP, indicating that rather strong bonding may exist between 3Y-ZrO₂ matrix and fine β -Al₂O₃ particles.

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Fig.9 Vickers-crack propagation in (a) the monolithic 3Y-ZrO₂ and (b) the 3Y-ZrO₂/20 vol% β -Al₂O₃ composite; both materials were sintered at 1400°C for 2 h.

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