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Improving the surface hardness of zirconia toughened alumina (ZTA) composites by surface treatment with a boehmite sol

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Abstract

This paper reports a novel way of enhancing the hardness of a zirconia-toughened alumina (ZTA) composite with a zirconia content of 20 vol% by surface treatments with a boehmite sol. More specifically, a ZTA composite was first prepared by heat-treating a mixture of alumina and zirconia powders containing Cr_2O_3 and $SrAl_{11}CrO_{19}$, as a reinforcement at 1400 °C for 1 h, and then infiltrating them with the boehmite sol, followed by heat-treatment at 1650 °C for 1 h to densify them. This treatment led to a significant increase in the surface hardness of the ZTA composite, which was attributed mainly to an increase in the volume fraction of an alumina phase with greater hardness, whereas the flexural strength and fracture toughness decreased slightly. The Vickers hardness, flexural strength and fracture toughness were 17.1 ± 2.5 GPa, 738 ± 88 MPa and 4.2 ± 0.11 MPa $m^{1/2}$, respectively.

Keywords: C. Mechanical properties; E. Biomedical applications; Alumina; Zirconia-toughened alumina

1. Introduction

Alumina (Al_2O_3) with high density and purity has been used extensively for artificial hip prostheses and dental implants on account of its outstanding strength, hardness and good biocompatibility [1]. However, this material has relatively low fracture toughness, i.e. poor resistance to crack propagation, which is likely to cause catastrophic failure in service. Therefore, considerable effort has been made to improve the mechanical properties of alumina, for example, by adding metal or ceramic particles to the alumina matrix as reinforcement [2].

Zirconia-toughened alumina (ZTA), an alumina-based composite, can provide much higher fracture toughness (>12 MPa $m^{1/2}$) than pure alumina (~3 MPa $m^{1/2}$) [2–4]. The main toughening mechanisms of ZTA are stress-induced transformation toughening and microcrack toughening, which are attributed mainly to the transformation of zirconia grains from the tetragonal to monoclinic phase [3,4]. Thus far, a number of attempts have been made to optimize the mechanical properties of ZTA composites by controlling their microstructure and composition using a range of manufacturing methods [5–9]. In particular, considerable effort has been recently made to improve the wear resistance and hardness of these composites, which are much lower than those of alumina [10–12] using a range of approaches, including achieving a homogenous phase distribution [13] and the addition of hard Al_2O_3 and SiC particles [14] or soft oxides as a solid lubricant [15]. However, it is still the subject of extensive research to develop new methods that can improve the wear resistance and hardness of ZTA composites without deteriorating their outstanding strength and toughness.

Therefore, this study proposes a novel way of improving the surface hardness of a ZTA composite by surface treatment with a boehmite (AlO(OH)) sol, followed by sintering at 1650 °C for 1 h. The effect of the boehmite sol on the microstructural evolution of the composite was examined by scanning electron microscopy and energy dispersive spectroscopy. The mechanical properties of the composites, such as Vickers hardness, flexural strength and fracture toughness, were measured. The change in hardness of the composite was also measured as a function of the distance from the surface.

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2. Experimental procedure

Zirconia-toughened alumina (ZTA) composites with a zirconia content of 20 vol% were produced by conventional solid state sintering at 1650 °C for 1 h in which commercial alumina powder (Alfa Aesar/Avocado Organics, Ward Hill, MA, USA) with an average particle size of 0.3 μm and tetragonal zirconia polycrystals (TZ-3Y; Tosoh Co., Tokyo, Japan) were used as the starting materials. In addition, 5 vol% of CrO_2 (Junsei Chemical Co., Ltd., Japan) and $SrAl_{11}CrO_{19}$ powder, which was synthesized by heat-treating a mixture of $SrCO_3$ (Sigma Aldrich, St. Louis, MO, USA), Al_2O_3 (Alfa Aesar/Avocado Organics, Ward Hill, MA, USA), and Cr_2O_3 (Junsei Chemical Co., Ltd., Japan) at 1500 °C for 1 h [16] were added to improve the mechanical properties of the ZTA composite [17,18]. The mixed powders were die pressed using a mold with a 10 mm diameter, followed by cold isostatic pressing (CIP) at 200 MPa.

The prepared green sample was heat-treated at 1400 °C for 1 h and machined into bar shape ~3.75 mm × 5 mm × 50 mm in size and then ground using an 800 grit diamond wheel. Subsequently, the samples were infiltrated with a boehmite (AlO(OH)) sol prepared using a similar method to that reported in the literature [19], followed by heat-treatment at 1650 °C for 1 h for densification. For comparison, a ZTA sample without a surface treatment with a boehmite sol was sintered directly at 1650 °C for 1 h.

The microstructural evolution of the ZTA composites was examined by scanning electron microscopy (SEM, JSM-6330F, JEOL Techniques, Tokyo, Japan). The density of the samples was measured using Archimedes's method. The crystalline phases and chemical compositions of the sample were characterized by X-ray diffraction (XRD, M18XHF-SRA, Mac Science Co., Yokohama, Japan) and energy dispersive spectroscopy (EDS) attached to the SEM, respectively. The size of alumina grains was measured using the linear intercept method.

For mechanical testing, the tensile surface of the sample ~3 mm × 4 mm × 40 mm in size was polished to 1 μm using diamond slurries and chamfered to minimize machining flaws. The 4-point flexural strength was measured using a screw-driven load frame (Instron 5565, Instron Corp., Canton, MA, USA) at a constant crosshead speed of 1 mm/min with an inner and outer span of 10 and 30 mm, respectively. The fracture toughness was measured using the indentation method with an applied load of 98 N according to a method reported in the literature [20]. Vickers hardness tests were carried out using a standard diamond indenter with an indentation load of 9.8 N. More than five samples were tested to obtain the mean value and standard deviation.

3. Results and discussion

Fig. 1 shows a typical XRD pattern of a ZTA composite produced with surface treatment using a boehmite sol, followed by sintering at 1650 °C for 1 h. The sample showed strong peaks associated with crystalline α-alumina and tetragonal zirconia phases. A trace amount of a crystalline $SrAl_{11}CrO_{19}$ phase (JCPDS card # 26-0976), which was added as a reinforcement was also detected. However, no noticeable secondary phases were observed. This suggests that the boehmite sol could be converted completely to an α-alumina phase during heat-treatment [21].

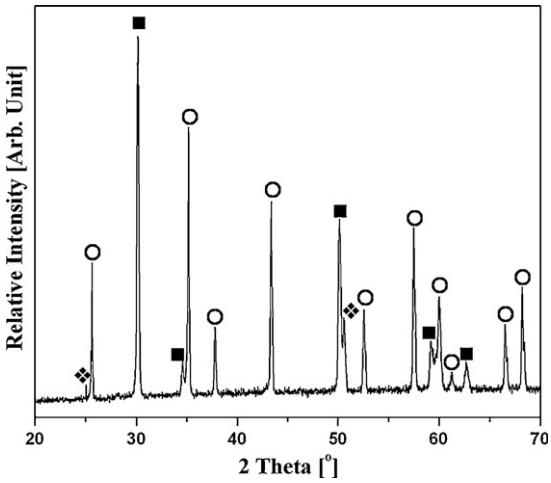

Fig. 1. XRD pattern of the ZTA composite produced with a surface treatment with a boehmite sol, and sintered at 1650 °C for 1 h. (■) TZP, (○) Al_2O_3 and (❖) $SrAl_{11}CrO_{19}$.

Fig. 2 shows typical SEM images of the ZTA composites without and with a surface treatment with the boehmite sol, respectively. Both samples were well densified. In addition, $SrAl_{11}CrO_{19}$ platelets, indicated by an arrow, were observed in the sample produced without the surface treatment (Fig. 2(A)), which would be expected to be quite beneficial to the mechanical properties of the ZTA composites [22]. However, the sample produced with the surface treatment showed much larger grain size with a higher proportion of alumina grains (Fig. 2(B)) due to the conversion of the boehmite sol to an alumina phase during heat-treatment [21].

Table 1 lists the mechanical properties of the composites produced with and without the surface treatment with the boehmite sol, such as the Vickers hardness, flexural strength and fracture toughness. The composite produced with the surface treatment showed a higher hardness than that produced without the surface treatment. This improvement was attributed mainly to the increase in the volume fraction of the alumina phase with higher hardness. On the other hand, the flexural strength and toughness were decreased slightly by the surface treatment, presumably due to an increase in the volume fraction of the alumina phase that has relatively low strength and toughness compared to those of the TZP material [1]. However, it should be noted that these values are comparable to those of conventional ZTA composites [23]. This suggests that the surface hardness of the ZTA composites can be improved considerably by a surface treatment with the boehmite sol.

The effect of a surface treatment with the boehmite sol on the microstructural evolution of the ZTA composite was examined according to the distance from the surface. Fig. 3(A)–(C) shows typical SEM images taken from regions at various distances (25–50 μm, 75–100 μm, 100–125 μm) from the

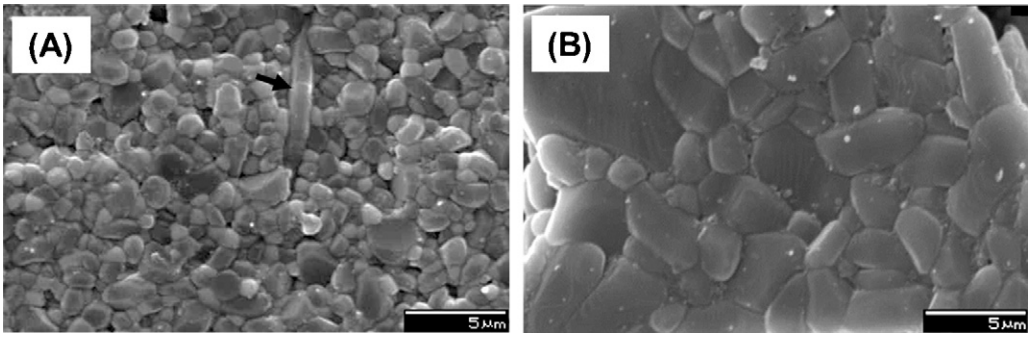

Fig. 2. EM images of ZTA composites produced (A) without and (B) with a surface treatment with a boehmite sol, and sintered at 1650 °C for 1 h.

Table 1
Vickers hardness, flexural strength, and fracture toughness of the ZTA samples prepared (A) without and (B) with a surface treatment with a boehmite sol and sintered at 1650 °C for 1 h.

	Vickers hardness (GPa)	Flexural strength (MPa)	Fracture toughness (MPa $m^{1/2}$)
Without surface treatment	15.2 ± 1.3	838 ± 141	4.7 ± 0.13
With surface treatment	17.1 ± 2.5	738 ± 88	4.2 ± 0.11

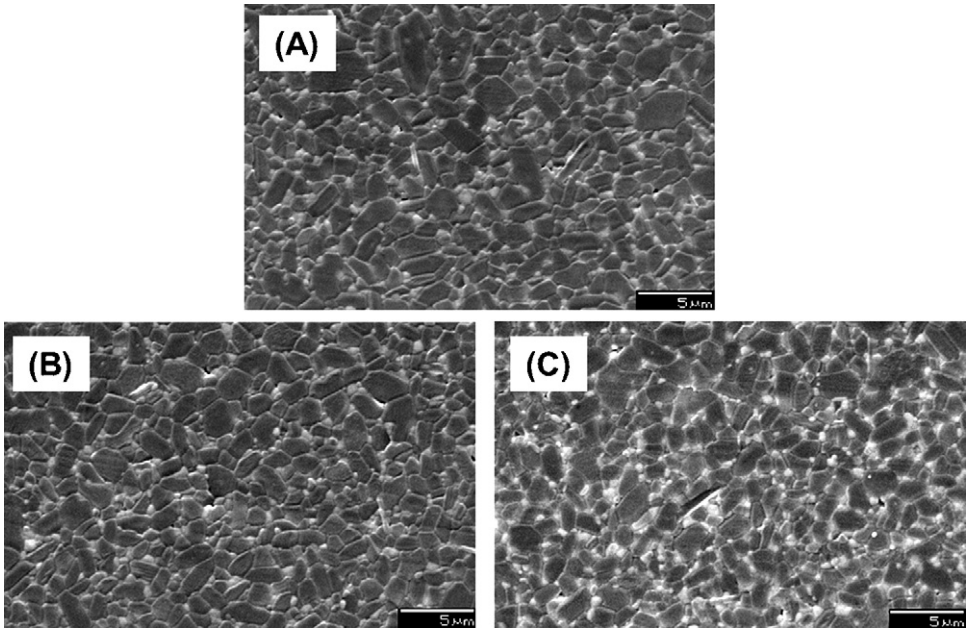

Fig. 3. SEM images of the ZTA composite produced with a surface treatment with a boehmite sol, showing the microstructures developed in the regions at various distances of (A) 25–50 μm, (B) 75–100 μm, and (C) 100–125 μm from the surface.

surface. The fraction of alumina grains that appeared in dark contrast decreased with increasing distance from the surface, which was also confirmed by EDS.

The average grain size of the alumina grains decreased significantly from 3.97 ± 0.29 to 2.5 ± 0.04 μm with increasing the distance from the surface from 25 to 200 μm and then remained unchanged, as shown in Fig. 4. This suggests that the concentration of boehmite sol infiltrated into the composite decreased with increasing distance from the surface and was limited to a certain extent, which would result in a gradient in the microstructure, i.e. the volume fraction and size of alumina phase.

The hardness of the ZTA composite prepared with a surface treatment with the boehmite sol was measured as a function of the distance from the surface, as shown in Fig. 5. The hardness decreased from 17.1 ± 2.5 GPa to 14.9 ± 1.7 GPa with increasing distance from the surface from 25 to 225 μm. Beyond this point, the hardness did not change considerably, due to the negligible infiltration of the boehmite sol into the sample. This corresponded well to a change in the microstructure observed in Fig. 3(A)–(C). This suggests that the hardness of the ZTA composite could be improved remarkably by a surface treatment with the boehmite sol without changing its internal microstructure.

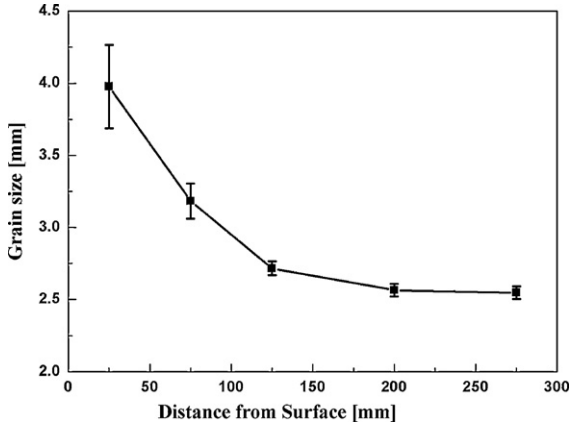

Fig. 4. Average grain size of the alumina grains as a function of the distance from the surface.

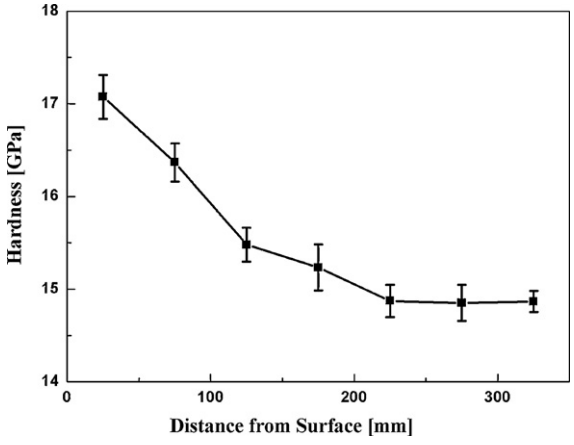

Fig. 5. Vickers hardness of the ZTA composite as a function of the distance from the surface.

4. Conclusions

The hardness of a zirconia-toughened alumina (ZTA) composite was enhanced by infiltrating it with a boehmite sol, followed by sintering at 1600 °C for 1 h. This process increased the alumina fraction due to the conversion of the boehmite sol to an alumina phase. This simple surface treatment improved the hardness of the ZTA composites significantly with little decrease in flexural strength and fracture toughness (Vickers hardness = 17.1 ± 2.5 GPa, flexural strength = 738 ± 88 MPa, and fracture toughness = 4.2 ± 0.11 MPa $m^{1/2}$). In addition, the hardness decreased with increasing distance from the surface, suggesting that the present method is very useful for improving the surface hardness of the ZTA composites without seriously deteriorating their flexural strength and fracture toughness.

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