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Transparent nanocrystalline bulk alumina obtained at 7.7 GPa and 800 °C

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Transparent nanocrystalline bulk alumina was obtained at 7.7 GPa and 800 °C. The alumina has an average grain size of ~150 nm and an in-line transmission of 71% for a wavelength of 640 nm and a thickness of 0.8 mm. The values of microhardness and fracture toughness were found to be 25.5 ± 0.3 GPa and 2.9 ± 0.3 MPa m^{1/2}, respectively. The hardness value is consistent with the previously determined Hall–Petch relation and fracture toughness is independent of grain size.

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Alumina is the most widely used oxide in industry. Recently, production of fine-grained transparent alumina has been widely studied because of the simultaneous improvement in mechanical and optical properties. Hot isostatic pressing (HIP) has traditionally been employed to fabricate transparent alumina materials. Krell et al. [1] and Apetz and van Bruggen [2] employed very similar experimental techniques: both groups utilized HIP at temperatures of 1200–1400 °C and pressure as high as 200 MPa after presintering in air. Apetz and van Bruggen [2] reported the sintering of highly transparent alumina with an in-line transmission of 71% at a wavelength of 645 nm and an average grain size of about 300 nm. Krell et al. [1] also obtained transparent alumina whose in-line transmission exceeds 50%.

Recently, spark plasma sintering (SPS) has been employed to obtain highly transparent alumina. Kim et al. [3] successfully fabricated transparent alumina with an in-line transmission of 50% at a wavelength of 640 nm and an average grain size of 270 nm. The sintering temperature was 1150 °C under uniaxial pressure of 80 MPa. Grasso et al. [4] improved the SPS technique to increase uniaxial pressure to 500 MPa and obtained highly transparent alumina with an in-line transmission of 64% at a wavelength of 645 nm. The sintering temperatures were 950 and 1000 °C. They demonstrated that the sintering temperature of transparent alumina is lowered by 200 °C by increasing the uniaxial pressure of the SPS process. Anselmi-Tamburini et al. [5] also showed that a pressure increase in the SPS process up to 1 GPa enables sintering of nanocrystalline oxides at temperatures below 950 °C. They demonstrated that the temperature required for obtaining dense ceramics (relative density of 95%) decreases with pressure and that the temperature decrease produces a marked decrease in grain growth [5].

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There have been several studies using high-pressure apparatus with a solid pressure medium generating pressure above 1 GPa to obtain the bulk form of alumina [6–8]. Unfortunately, there has been no report on fabrication of transparent alumina with simultaneously enhanced mechanical properties under elevated pressures. Here we report that highly transparent nanocrystalline bulk alumina with an in-line transmission of 71% and microhardness of 25.5 GPa was obtained at 7.7 GPa and 800 °C using a belt-type apparatus [9]. To our knowledge, this is the lowest temperature at which highly transparent alumina has been obtained.

We carried out a series of experiments at temperatures between 400 and 1400 °C at a fixed pressure of 7.7 GPa. The starting material was commercially available α -Al₂O₃ powder (TM-DAR, Taimei Chemicals Co. Ltd., Tokyo, Japan) with a purity of 99.99% and a particle size of 100 nm (measured by the company). Attention was paid to minimize the moisture adsorption on surfaces of alumina grains by adhering to the following sampling procedure. The as-received powder was heated in a vacuum (0.1 Pa) at 450 °C for 2 h using a furnace connected directly to a dry glove box where oxygen and humidity were controlled to less than 1 ppm in a nitrogen atmosphere. After cooling, the powder was enclosed in a sample capsule made of a tantalum sleeve, tantalum disks and graphite lids in the glove box so that the entire sample preparation process was carried out in a dry atmosphere. Without this sampling procedure, transparent alumina has never been obtained under the pressure in the present study.

Figure 1 shows a photograph of the recovered samples. The sample obtained at 400 °C is opaque (Fig. 1a). It was more fragile than other samples obtained at higher temperatures. The recovered sample has an irregular shape because the sample was broken during recovery. The samples obtained at 600, 700 and 800 °C are transparent (Fig. 1b–d). The sample obtained at 800 °C with a holding time of 30 min exhibits the highest transparency (Fig. 1d). We obtained two samples, one transparent and one translucent, from a single experiment performed at 700 °C (Fig. 1c). Since the two sample capsules were loaded in a single high-pressure cell assembly, these samples were sintered at almost identical pressure and temperature conditions. The presence of a small amount of water in the sample, which can be caused by not sealing the sample capsule perfectly, might affect the transparency of the sintered materials. At temperatures above 1000 °C, the recovered samples are translucent (Fig. 1e). We performed X-ray

Figure 1. A photograph of polycrystalline bulk alumina obtained at a fixed pressure of 7.7 GPa and temperatures between 400 and 1400 °C using a belt-type apparatus. (a) 400 °C with a holding time of 180 min. (b) 600 °C, 60 min. (c) 700 °C, 60 min. These two samples were obtained from a single experiment. (d) 800 °C, 30 min (S5654). (e) 1000 °C, 10 min.

diffraction measurements for all the recovered samples and confirmed that all the samples are composed of a single phase of corundum (α -Al₂O₃). The peak widths of the transparent samples (600–800 °C) are wider than those of the translucent samples obtained at >1000 °C, and appear to increase with increasing 2θ angle. These results indicate that the grain sizes of the transparent samples are smaller than those of the translucent samples (>1000 °C) and that elastic strains are accumulated in grains of the transparent samples.

We measured in-line transmissions of two samples obtained at 800 °C (run numbers are S5649 and S5654) using a double-beam spectrophotometer. The S5649 sample has a thickness of 1.499 mm and the S5654 sample has a thickness of 1.313 mm. Using the raw data, we calculated in-line transmission (T_2) at a sample thickness of 0.8 mm (t_2) using the following equation: $T_2 = (1 - R)[T_1/(1 - R)]^{(t_2/t_1)}$, where R is the reflection loss for two alumina surfaces ($= 0.14$) and T_1 is the measured in-line transmission for the original sample thickness of t_1 [1]. The calculated results are shown in Figure 2. Previous results for pure alumina [1–4,10] are also shown in the figure for comparison. The in-line transmissions for the two samples are almost identical. The in-line transmission of the S5649 sample is 70% for a wavelength of 640 nm and that of the S5654 sample reaches 71% for the same wavelength. Our samples are as transparent as those obtained by Apetz and van Bruggen [2] and Krell et al. [10]. We can see a general tendency for the relation between the fabrication temperature of transparent alumina (T_{ta}) and the sintering pressure: T_{ta} decreases with pressure. T_{ta} is 1200 °C for HIP at 200 MPa [1,2,10], 950 °C for SPS at 500 MPa [4] and 800 °C for high-pressure sintering at 7.7 GPa using the belt-type apparatus shown in the present study. Recently, Kim et al. [11] clearly showed that T_{ta} decreases with pressure for MgO-doped alumina using the SPS technique. Pressure may help to close pores, which are one of the most important origins of light scattering.

Figure 2. In-line transmission of transparent alumina at a sample thickness of 0.8 mm. The samples (S5649 and S5654) were obtained at 7.7 GPa and 800 °C, with a holding time of 30 min. Results from previous studies for pure alumina are also shown for comparison.

We observed the microstructure of a transparent sample obtained at 800 °C (S5654). Figure 3a shows a secondary electron image from a fracture surface observed by means of a field emission scanning electron microscope (FESEM). The average grain size is about 150 nm. This fracture surface clearly shows that intergranular fracture is dominant in this sample. We also performed transmission electron microscopy observations for this sample. A large view of a foil fabricated by the focused ion beam technique shows that this sample is composed of randomly oriented nanosized grains (Fig. 3b). Many interference fringes were observed in grains (Fig. 3c). Some of them appear to be typical moiré patterns composed of parallel straight lines, as indicated by the blue arrows in Figure 3d. Others are broader and curved, and sometimes intersect with each other, as indicated by the red arrows in Figure 3c. Careful observations at different tilting angles revealed that these broad and curved fringes are also likely to be moirés, which are created by more complex interference and convolution of diffracted and transmitted beams, such as superposition of more than three lattices and/or of grains that are elastically deformed at the grain boundaries.

We carried out Vickers indentation tests to measure the microhardness (H_V) and to evaluate fracture toughness (K_{IC}). The tests were performed for five samples: two samples obtained at 700 °C (Fig. 1c), two samples

obtained at 800 °C (S5649 and S5454) and a transparent sample fabricated by SPS. The average grain sizes of the samples obtained at 700 and 800 °C were about 150 nm, as determined by fracture surface observations using the FESEM. For the SPSed sample, we followed the sintering procedure proposed by Kim et al. [3]. We obtained a transparent alumina with an average grain size of about 300 nm, which is also consistent with the result by Kim et al. [3]. The applied load for the indentation tests was 3.92–19.6 N, with a holding time of 15 s. H_V was calculated using the following equation: $H_V = 1854.4 P/d^2$, where P is the applied load (N) and d is the arithmetic mean of the two diagonals (μm) of a Vickers indentation trace. K_{IC} was calculated from the crack length, c , using the following equation: $K_{IC} = \xi (E/H_V)^{1/2} (P/c^{3/2})$, where E is the Young's modulus (GPa) and ξ is a calibration constant of 0.016 [12]. For highly transparent samples, we optically observed cracks formed inside the samples through the surfaces. They appear to be median/radial types of cracks at least at an applied load of 19.6 N. In order to determine Young's modulus, we measured the bulk density and sound velocities (compressional and shear wave velocities) for samples obtained at 800 °C (S5649 and S5654) using the Archimedes technique and the ultrasonic pulse–echo method [13], respectively. These samples are fully dense within errors: the density of sample S5649 was $3.96 \pm 0.04 \text{ g cm}^{-3}$ and sample S5654 had a density of $3.99 \pm 0.04 \text{ g cm}^{-3}$ (theoretical density: 3.986 g cm^{-3}). The obtained Young's modulus was 403 GPa, which is consistent with that calculated from single-crystal elastic constants [14] within mutual experimental errors.

The H_V of sample S5654 was $25.5 \pm 0.3 \text{ GPa}$ at an applied load of 3.92 N, while that of the SPSed sample was $23.1 \pm 0.2 \text{ GPa}$ at the same applied load. Figure 4a shows the comparison between present and previous data [6,15,16]. The present data are consistent with the Hall–Petch relation determined by Mishra et al. [6]. They determined this relation at an applied load of 3.92 N. To our knowledge, the present hardness value is one of the highest for polycrystalline bulk alumina because of the very small grain size of about 150 nm.

Figure 3. Scanning and transmission electron micrographs of transparent nanocrystalline bulk alumina obtained at 7.7 GPa and 800 °C, with holding time of 30 min (S5654). (a) An example of secondary electron images of a fracture surface. (b) A large view of a foil fabricated by the focused ion beam technique. The inset is an example of the electron diffraction patterns suggesting that this sample is composed of randomly oriented grains. (c) An example of transmission electron micrographs. (d) An enlarged view of the area indicated by the white square in (c). In (c) and (d), many interference fringes were observed in grains. Some of them were typical moiré patterns, indicated by blue arrows in (d). Other broader and curved fringes, indicated by red arrows in (c), are also likely to be moiré patterns created by more complex interference and convolution of diffracted and transmitted electron beams (see text).

Fig. 4. Mechanical properties of polycrystalline bulk alumina. (a) Grain size dependence of microhardness. The present data are consistent with the Hall–Petch relation determined by Mishra et al. [6]. (b) Grain size dependence of fracture toughness. The upper and lower bars represent the maximum and minimum values of each measurement. Fracture toughness is independent of grain size. The inset is an example of photographs of the Vickers indentation trace with cracks at an applied load of 19.6 N for a transparent alumina sample obtained at 7.7 GPa and 700 °C.

K_{IC} was evaluated at applied loads between 3.92 and 19.6 N. The K_{IC} of sample S5654 was $2.9 \pm 0.3 \text{ MPa m}^{1/2}$. Yao et al. [17] carefully determined the grain size dependence of fracture toughness for polycrystalline bulk alumina with a grain size varying from $\sim 290 \text{ nm}$ to $\sim 3.3 \mu\text{m}$. They demonstrated that the fracture toughness is independent of grain size. Although we evaluated fracture toughness by using the indentation fracture method, the present data at grain sizes of $\sim 150 \text{ nm}$ and $\sim 300 \text{ nm}$ show consistency with the data of Yao et al. [17] (Fig. 4b). The values of K_{IC} stay constant at $\sim 3 \text{ MPa m}^{1/2}$ down to a grain size of $\sim 150 \text{ nm}$. Fracture toughness of polycrystalline bulk alumina cannot be improved by reducing the grain size.

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