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Grain growth in nanograined aluminum oxide by high-pressure torsion: Phase transformation and plastic strain effects

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A B S T R A C T

Application of severe plastic deformation (SPD) to different materials usually leads to significant grain refinement and accelerated phase transformations. This study reports the occurrence of grain growth in nanocrystalline Al_2O_3 by SPD processing via high-pressure torsion (HPT) due to a phase transformation from γ with the cubic structure to α with the rhombohedral structure. This transformation was significantly enhanced by pressure and plastic strain and occurred at ~650 K below the $\gamma \rightarrow \alpha$ transition temperature. The γ phase after HPT processing could be detected only in nanograins or in the nano-sized laths with the $(1\bar{3}1)\gamma//(01\bar{4})\alpha$ and $[001]\gamma//[100]\alpha$ coherent orientation relationship.

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Al_2O_3 is thermodynamically stable in the form of α (corundum) phase with the rhombohedral crystal structure [1]. Al_2O_3 has several metastable phases (transition aluminas) such as γ and η with the cubic structure, δ with the tetragonal structure, θ with the monoclinic structure, κ with the orthorhombic structure and χ with the hexagonal structure [1]. Among these metastable phases, the γ phase has received significant attention due to its industrial application as a high-temperature catalyst or catalyst support [2].

The thermal stability of γ phase, which is usually present in the nanocrystalline form with large surface area [3,4], has been investigated under different conditions of temperature and pressure [5,6]. The γ phase transforms to the α phase with increasing the temperatures to 1273–1473 K under atmospheric pressure [1–6], although the δ and θ phases may form from the γ phase at lower temperatures [1,7]. A few studies showed that the transition temperature is reduced under high hydrostatic pressure [5,6]. For example, the $\gamma \rightarrow \alpha$ transition was reported to occur at 1023 K [5] or 1073 K [6] under 1 GPa.

Despite systematic studies on the effect of temperature and pressure on the $\gamma \rightarrow \alpha$ transition [3–7], the influence of plastic strain on this transition and resultant microstructural evolutions is not well understood yet. The main drawback for such studies is the technical limitations in the introduction of plastic strain on hard and brittle oxides. A few studies reported that high-energy ball milling could enhance the $\gamma \rightarrow \alpha$ transition [8,9]. However, due to complexity of phenomena during ball milling, these studies attributed the enhanced transformation to local pressure/temperature increase during ball milling [8,9].

High-pressure torsion (HPT), a severe plastic deformation (SPD) method in which the material experiences measurable plastic strain under pressure between two rotating anvils [10,11], is an ideal method to investigate the effect of plastic strain on the $\gamma \rightarrow \alpha$ transition and microstructural changes. The HPT method is widely used for grain refinement in metallic materials [12,13], although grain coarsening by HPT processing was also reported in nanograined Ni [14], Cu [15] and Ni-Fe [16]. Several publications showed that the HPT method has high potential to control the phase transformations and achieve grain refinement not only in metals but also in various non-metallic materials [17,18] including minerals [19] and oxides (ZrO_2 [20], $BaTiO_3$ [21], TiO_2 [22], Y_2O_3 [23] and ZnO [24]).

In this study, and for the first time, nanocrystalline γ-Al_2O_3 powders are severely strained by HPT and the effect of plastic strain on phase transformations and microstructural evolutions is investigated under different pressures and temperatures. In contrary to the reported grain refinement in severely strained α-Al_2O_3 [25], a low-temperature $\gamma \rightarrow \alpha$ transformation and grain coarsening occur in γ-Al_2O_3 by HPT processing.

Powders of nanocrystalline γ-Al_2O_3 with a purity level of 99.99% and particle sizes of 2–3 μm were used as the starting materials in this study. Almost 500 mg of the powders were placed between two HPT anvils (made of WC - 11 wt% Co having holes with 10 mm diameter and 0.25 mm depth on the surface), and processed at $T = 77$ K (in liquid

nitrogen), 300 K (room temperature), 573 K and 723 K (maximum achievable temperature in the authors' HPT facility) under nominal pressures of $P = 2$ GPa, 4 GPa and 6 GPa. The shear strain ($\gamma = 2\pi r N / h$; γ: shear strain; r: distance from disc center, N: number of turns, h: thickness of disc [11]) was introduced by rotating the lower HPT anvil with respect to the upper one for either 1/16, 1/4, 1 and 4 turns with a rotation speed of 1 rpm.

Following the HPT process, the phase transformation in samples, which were in the form of squeezed discs with ~0.8 mm thickness, was examined by X-ray diffraction (XRD) analysis using Cu Kα radiation. The fraction of α phase in wt% was estimated from the integrated XRD peak intensities of $(113)_{\alpha}$ and $(400)_{\gamma}$ located at 43.35° and 45.86°, respectively as $I_{(113)\alpha}/(I_{(113)\alpha} + I_{(400)\gamma} / 1.12)$ [6]. The microstructure of samples was examined by Cs-corrected transmission electron microscopy (TEM) in the bright-field imaging mode, selected-area electron diffraction (SAED) mode, high-resolution imaging mode and corresponding fast Fourier transform (FFT) analysis. Thin foils for TEM observations were prepared by crushing the edge part of discs and spreading them onto carbon grids.

To evaluate the phase transformations, all samples were examined by XRD analysis. Fig. 1 shows the XRD profiles of the samples after processing by HPT for (a) 1 turn under 6 GPa at various temperatures, (b) 1 turn at 573 K under various pressures and (c) different turns under 6 GPa at 723 K. Note that the profile referred as $P = 0$ GPa in Fig. 1 (b) achieved for a reference sample after annealing at 723 K for 1 h without application of pressure. Examination of Fig. 1 indicates several points.

First, no $\gamma \rightarrow \alpha$ phase transformation occurs by annealing the sample at 723 K, which is quite reasonable because the reported temperature for this transition is 1273–1473 K [1–6].

Second, no phase transformation is detected under 6 GPa by increasing the temperature from 77 K to 573 K, but a $\gamma \rightarrow \alpha$ transition occurs at 723 K under 4 and 6 GPa (i.e. at ~650 K below the $\gamma \rightarrow \alpha$ transformation). The formation of γ phase under higher pressures should be due to the compact crystal structure of α phase when compared to the γ phase [1,7].

Third, the peaks for the γ phase are so broad, indicating the presence of a high density of structural defects and/or nanocrystals with large surface area [3,4]. But the peaks for the α phase are much sharper than those for the γ phase, indicating that the crystallite size of α phase is large and that crystals contain a small defect density. In contrary to the current peak contraction, an earlier study showed that the application of HPT at room temperature to micro-powder of α-Al$_2$O$_3$ leads to peak broadening without any phase transformation [25].

Fourth, a comparison between the broad peaks of α phase and the sharp peaks of α phase after different number of HPT turns in Fig. 1 (c) indicates that the fraction of α phase increases with increasing the plastic strain, as shown more clearly in Fig. 2. It is apparent that the fraction of α phase increases with increasing the strain, but reaches a steady-state-like level of 66 wt% at large strains. This presence of the steady state at large strains is similar to the reported saturation of microstructure [12,13], mechanical properties [10,26] and phase transformations [20–23] to the steady states at large strains.

Fifth, the transition pressure and temperature for the $\gamma \rightarrow \alpha$ phase transformation in this study are lower than those reported earlier under static compression [5,6]. Fig. 2(b) summarizes the data reported in Ref. [6] for static compression and compare them with the data achieved in this study using the HPT process. It is apparent that the transition temperature under a given pressure shifts to lower temperatures by straining via the HPT process. The shift in transition pressure and temperature of Al$_2$O$_3$ by shearing under high pressure is basically similar to those reported in a few metallic materials [27,28] ceramics [17,29] and oxides (TiO$_2$ [22], Y$_2$O$_3$ [23] and ZnO [24]). One main reason for facilitation of phase transformations by HPT processing is due to strain-induced enhancement of kinetics, as shown by Bridgman decades ago [18,19]. Another reason is due to the formation of lattice defects and
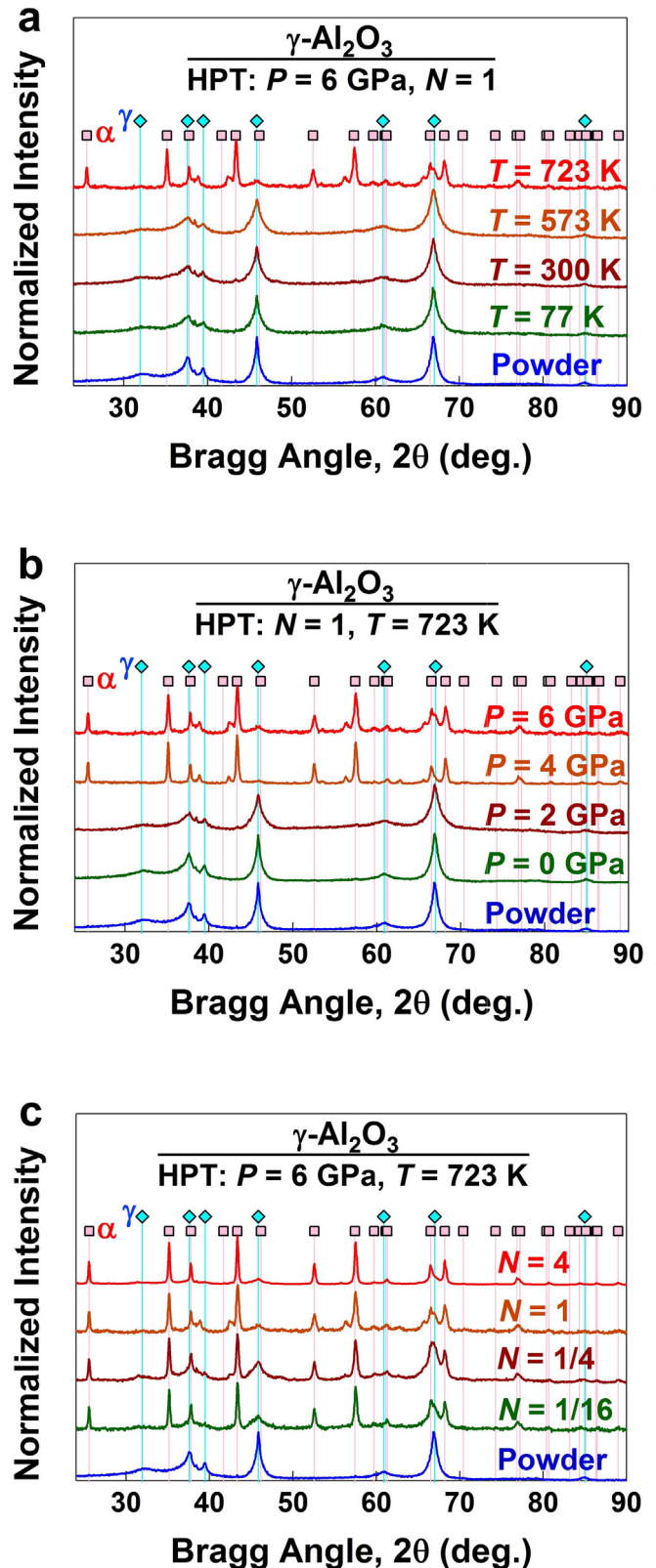

Fig. 1. XRD profiles of samples processed by HPT for (a) 1 turn under 6 GPa at different temperatures, (b) 1 turn under different pressures at 723 K and (c) different turns under 6 GPa at 723 K.

their thermodynamic effects on local temperature and pressure at the nanoscale [28,30]. A third reason can be due to the activation of shearing nucleation mechanism [31,32], as will be discussed below using the TEM observations.