Microstructural Evolution in Rapidly Quenched ZrO₂-3 mol% Y₂O₃ by Annealing

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ZrO₂-3 mol% Y₂O₃ 超急冷体の時効処理によるミクロ構造変化

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ZrO₂-3 mol % Y₂O₃ was rapidly quenched from melts, and annealed at 1700°C for 48 h in air. X-ray diffraction analysis and TEM observation revealed that the tetragonal phase in as-quenched samples was nontransformable and the phase in annealed samples was transformable under external stresses. The tetragonal phase in as-quenched samples was formed by diffusionless transformation of the cubic phase. Upon annealing, the microstructures did not change discontinuously, but the tetragonal twins coarsened.

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1. Introduction

Tetragonal zirconia polycrystal (TZP) is well known for its high strength and high fracture toughness. One of the proposed toughening mechanisms is the stress induced martensitic transformation of tetragonal phase into monoclinic symmetry. However, there are two kinds of tetragonal phases to be considered; one is transformable and the other is nontransformable¹⁾. The former is a decomposed phase (t phase) from high temperature cubic phase within the cubic-tetragonal phase region of the ZrO₂-Y₂O₃ system. The latter is a diffusionlessly transformed phase (this phase was called t' phase by Lanteri et al.¹⁾) from the cubic phase when the material is rapidly cooled below the equilibrium temperature between the tetragonal and cubic phases. As the formation of the t' phase is determined by the cooling rate, the microstructure, stability, and mechanical properties of TZP can be controlled by the cooling process during the annealing and/or sintering program.

To examine the microstructure and the stability of the tetragonal phases, specimens fabricated from melts, instead of sintered products, have

been utilized by many investigators because of their homogeneity in composition¹⁾⁻³⁾. The object of the present work is to study the microstructure and stability of the tetragonal phases, especially the t' phase, before and after annealing at a high temperature. After annealing, the t' phase is expected to decompose into t and c (cubic) phases. To maximize the formation of the t' phase upon sample fabrication, rapid quenching from melts was performed. The rapid-quenching technique minimizes the possibility of the occurrence of a diffusion controlled c→t transformation. In the present paper we call the tetragonal phase in the as-quenched sample as t' phase. However, there seems to be some effects of an external load during rapid quenching on the formation of tetragonal phases⁴⁾. That is, the c→t' transformation during the rapid quenching might be a stress induced diffusionless transformation⁵⁾. This will be discussed in another paper⁶⁾.

2. Experimental

ZrO₂ powder (99.9%, Mitsuwa Pure Chemicals) and Y₂O₃ powder (99.99%, Shin-Etsu Chemicals) were used for preparing ZrO₂-

3 mol% Y_2O_3 . The powders were mixed in an agate mortar and pressed into a pellet of 5 mm diameter and 3 mm thick. The pellet was melted using an arc imaging furnace⁷⁾ and then rapidly quenched by a copper-made hammer-anvil apparatus. Films of 30 to 40 μm thick were obtained, where the quenching rate was expected to be higher than 10^5 K/s ⁴⁾. Some of the as-quenched films were further annealed at 1700°C for 48 h in air. The specimens were rapidly air-cooled by removing from the furnace after the annealing. To examine the effect of external stress on the stability of the tetragonal phases, some of the as-quenched and annealed specimens were crushed and ground into powder in a B_4C mortar for several times. The existing phases were studied by X-ray diffraction (Rigaku, RU-200, $\text{Cu K}\alpha$, 40 kV-80 mA), and the microstructure of the foils prepared by ion beam thinning was examined by a transmission electron microscope (Hitachi, H-700, 200 kV).

3. Results and discussion

X-ray diffraction profiles are shown in Fig. 1. Before crushing, the tetragonal phase was the only phase to be identified in both as-quenched and annealed specimens. After crushing and grinding for 1 min, monoclinic phase was seen only in the annealed samples. The volume fraction of the monoclinic phase was calculated by the calibration method by Toraya et al.⁸⁾, and the values were 26, 42, 63 and 79% after each sequence of 1 min crushing and grinding. The value would approach nearly 100%, if the crushing and grinding were further conducted.

Since the annealing at 1700°C for 48 h is conceived to cause the diffusion controlled decomposition of t' phase into t and c phases, if we admit the phase diagram of the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ system⁹⁾, the lattice parameters of tetragonal phase in as-quenched and annealed specimens should be different. However, X-ray diffraction suggested that there was no significant change in the lattice parameter. Moreover, no c phase was identified in the annealed samples. Since the fraction of Y_2O_3 in the present work (3 mol%) is very close to the solubility limit of Y_2O_3 in tetragonal ZrO_2 ⁹⁾, it appears that the decomposition, if any, could not be detected by these X-ray diffraction studies. It should be noted, however, that the tetragonal phase in the as-quenched samples, the t' phase, is apparently nontransformable, and the phase in the annealed samples, the t phase, is transformable by the application of external stresses.

Typical appearance of the tetragonal precipitates is shown in Fig. 2. In an as-quenched sample, tetragonal precipitates of 100 to 300 nm width are finely twinned and put together like a mosaic as shown in Fig. 2 (a, b). This microstructure consist of equal amounts of three tetragonal variants as shown by the selected area diffraction pattern and the dark field image. After annealing, as shown in Fig. 2 (c, d), the tetragonal precipitates are no longer mosaic like but transgranularly grown, but they still remains the twin relationships with each together, where the microstructure can also be explained by the consistence of the three variants. However no cubic phase could be identified in these grains. The

Fig. 1. X-ray diffraction profile of as-quenched and annealed $\text{ZrO}_2\text{-3 mol \% Y}_2\text{O}_3$. Note that the tetragonal phase was transformed into monoclinic symmetry by crushing and grinding only in annealed samples.

Fig. 2. Tetragonal precipitates observed by TEM.
 (a) Bright field image of as-quenched material, Zone axis (111).
 (b) Dark field image of (a). $(11\bar{2})$ reflection.
 (c) Bright field image of annealed material, Zone axis (111).
 (d) Dark field image of (c). $(11\bar{2})$ reflection.

above results suggest that the annealing at 1700°C caused the coarsening of tetragonal twins, without any evident crystallographic evolution.

The interaction between a propagating crack and the tetragonal precipitates are demonstrated in Fig. 3. As shown in Fig. 3 (a), tetragonal precipitates in the as-quenched samples showed no transformation by a stress field of a propagating crack: there was no change in the microstructure of finely twinned tetragonal precipitates, and the crack was shielded at the thicker part of the specimen. On the other hand, as shown in Fig. 3 (b), tetragonal precipitates in the annealed sample transformed into monoclinic symmetry when a crack encountered. These behaviors of the tetragonal phases are consistent with the results by X-ray diffraction mentioned previously. It should be noted that in Fig. 3 (b), the tetragonal to monoclinic martensitic transformation did not occur throughout the tetragonal grain (5 to $10\text{ }\mu\text{m}$ in size) but occurred only in the vicinity of crack (about $1\text{ }\mu\text{m}$ in width).

The monoclinic twins seem to be formed by a shear stress perpendicular to the direction of crack propagation. However we could not define the accurate orientation of these monoclinic precipitates.

The reason why the tetragonal phase becomes transformable by annealing can not be sufficiently described by the present work. However, if we admit that the composition and the crystallographic morphology of t and t' phases are very similar, as observed in the present study, the coarseness of the tetragonal twins may be one of the criterion to determine the transformability. Chen reported that the transformability of tetragonal precipitates can be controlled by their size, shape and interaction with the matrix¹⁰⁾. It seems that a similar effect should be considered in the present problem. Another possibility lies in the difference in dislocation density. Since the rapidly quenched product of the t' phase is conceived to contain much more dislocations compared with the annealed t phase, due to cubic to tetragonal

Fig. 3. TEM photographs demonstrating the interaction between a propagating crack and the tetragonal precipitates. (a) as-quenched and (b) annealed. In the annealed specimen, tetragonal precipitates were transformed into monoclinic symmetry in the vicinity of the crack.

diffusionless transformation, the dislocations may prevent the tetragonal to monoclinic transformation effectively. In fact, it is known in metallurgical systems that the dislocations internal stresses sometimes act as barriers against the transformation¹¹⁾. In any case, further study is necessary to discuss the transformability of the

tetragonal phase in more detail.

4. Concluding remarks

A diffusionlessly transformed tetragonal phase, t' phase, was fabricated by rapid quenching of melts. They were subsequently annealed at 1700°C for 48 h in air to convert into t phase. The t' phase was nontransformable and the t phase was transformable under external stresses. Transmission electron microscope observation suggested that the microstructures of the t and t' phases are essentially the same except for the coarsening of the tetragonal twins.

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