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Formation of diffusionlessly transformed tetragonal phases in rapid quenching of ZrO_2–Y_2O_3 melts

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ZrO_2 polycrystals, partially stabilized by 2 to 7 mol % Y_2O_3, were arc-melted and rapidly quenched using an arc-imaging furnace with a hammer-anvil unit. Some of the specimens were further annealed at 1700° C for 3 h in air. The phases and the microstructures of these ZrO_2–Y_2O_3 polycrystals were examined through X-ray diffraction and transmission electron microscopy. Special emphasis was placed upon the examination of the microstructure of the metastable tetragonal phase (t′ phase) which was formed by a diffusionless transformation of the high-temperature cubic phase. It was found that the t′ phase exhibits a twinned and mosaic structure made of alternating layers of twin-related variants. A comparison of the present experimental results with other related works has also been made.

1. Introduction

Y_2O_3 partially stabilized ZrO_2 polycrystals are well known as high strength and high toughness ceramics [1], and the stress-induced tetragonal to monoclinic transformation of metastable precipitates is believed to be an important influence on the toughness enhancement. It has been pointed out, however, that not all of the tetragonal phases contribute to the toughening [2]. It is the so-called t phase, which is precipitated by the decomposition of the high-temperature cubic phase (the c phase), that can cause transformation to monoclinic symmetry by external stresses. On the other hand, the t′ phase, which is the product of the diffusionless transformation of the cubic phase when the material is rapidly cooled below the equilibrium temperature between the cubic and tetragonal phase, is believed not to be transformable to the monoclinic symmetry.

With the advantage of the initially more homogeneous mixture of ZrO_2 and Y_2O_3 components, several workers have tried to obtain the t′ precipitates by cooling from melts rather than sintered products. Lanteri *et al.* [2] have reported the growth of a well twinned structure which was formed as a result of the decomposition of the t′ phase into the t and c phases when the polycrystal was annealed at 1600° C up to 100 h. Sakuma *et al.* [3] reported the occurrence of a spinodal decomposition as evidence of the existence of the modulated structure when a sample is annealed at 1500° C which is within the tetragonal-cubic two-phase region in the phase diagram of ZrO_2–Y_2O_3 system. However, these investigations do not satisfactorily explain the precipitation phenomenon of the t′ phase since they do not pay enough attention to the cooling rate from melts. As the c → t′ transformation occurs in a diffusionless manner, the cooling rate should dominate the stability and morphology of the t′ phase. Therefore, in order to suppress the occurrence of diffusion-controlled phase transformations [4], we have employed a rapid-quenching technique of melts in the present study. This technique ensures that a tetragonal phase, if any, is in fact the metastable t′ phase whose composition is the same as that of the melts. In addition, we have examined the effect of annealing the as-quenched specimens to investigate the occurrence of diffusion-controlled structural changes. The results of X-ray diffraction analysis and the transmission electron microscopic observation will be reported below.

2. Experimental procedure

Y_2O_3 (99.99%, Shin-Etsu Chemicals, Tokyo, Japan) and ZrO_2 (99.9%, Mitsuwa Pure Chemicals, Osaka, Japan) powders in various amount ratios were mixed in an agate mortar with ethyl alcohol for 3 h. After drying, pellets of the ZrO_2–Y_2O_3 mixtures with 2 to 7 mol % Y_2O_3 were formed. The pellets were melted in an arc imaging furnace schematically shown in Fig. 1 [5]. The spherical melted samples of about 3 mm in diameter were rapidly quenched by a hammer–anvil type unit made of copper. A hemispherical hollow of 2 mm in diameter was made on the surface of the hammer to capture the unmelted bottom part of the sample resulting in the improvement of the rapid quenching effect of the melt. The quenching rate was expected to be higher than 10^5 K sec^{-1} judging from other quenching techniques such as the one using a twin roller [6]. Films of the ZrO_2–Y_2O_3 polycrystals of 30 to 40 μm thick were thus obtained.

Some of the rapidly quenched products were

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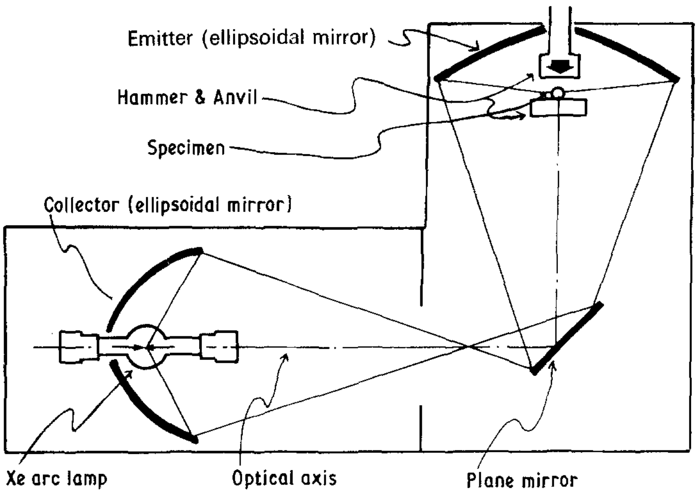

Figure 1 Schematic illustration of a rapid quenching system combined with an arc imaging furnace.

subsequently annealed at 1700° C in air for 3 h in an ordinary furnace and then quenched into water.

An X-ray diffraction analysis of films was conducted to identify the existing phases and the lattice parameters of each phase. The rapidly quenched (and annealed) samples were thinned by an ion bombardment technique and then the microstructure was examined on a Hitachi H-700 transmission electron microscope (TEM) under the acceleration voltage of 200 kV.

3. Results and discussion

The existing phases in the as-quenched and annealed samples identified by X-ray diffraction, are summarized in Table I. In the present ZrO_2–Y_2O_3 system with 2 to 7 mol % of Y_2O_3, three solid phases with monoclinic, tetragonal and cubic structure can exist depending on the composition and the heat treatment of the polycrystals. Therefore, for the phase identification, the intensities of the $(1\,1\,\bar{1})$ (monoclinic), (004) (tetragonal) and (400) (cubic) reflections were examined. For convenience, the tetragonal phase was indexed on the basis of the face-centred lattice. As shown in Table I, the monoclinic phase cannot be found regardless of the composition and heat treatment. In the range of the composition quoted in Table I, the phase diagram of the ZrO_2–Y_2O_3 system [7] indicates that all the samples should have been passed through the tetragonal-cubic two-phase region upon quenching. The fact that most of the phases present in as-quenched samples are tetragonal (most probably the t′ phase) suggests that the equilibrium temperature between the c and t phases lies above room temperature even for a composition higher than 7.0 mol % Y_2O_3. The cubic phase in the as-quenched sample is considered to be the one retained at room temperature in a supercooled condition. In other words, the diffusionless c → t′ transformation was not complete upon quenching to room temperature and in order to have been entirely of the t′ phase, further cooling below room temperature is necessary. After annealing at 1700° C for 3 h, the c phase markedly precipitates out of the t′ phase for the compositions higher than 3.5 mol % Y_2O_3. Therefore, the c phase observed in the annealed samples is made of the previously retained one upon quenching and the precipitated one during the annealing. Although we can conceive that these two different types of the c phase have different compositions and, thus, lattice parameters, the X-ray diffraction pattern was not clear enough to establish that such a difference

TABLE I Existing phases identified after X-ray diffraction

		Y_2O_3 (mol %)							
		2.0	2.5	3.0	3.5	4.0	4.5	6.0	7.0
As-quenched	M	–	–	–	–	–	–	–	–
	T	S	S	S	S	S	S	S	m
	C	w	w	w	w	w	w	w	m
Annealed 1700° C 3 h	M	–	–	–	–	–	–	–	–
	T	S	S	S	S	m	m	m	m
	C	w	w	w	w	m	m	m	S

M Monoclinic, T Tetragonal, C Cubic, S strong, m medium, w weak, – none.

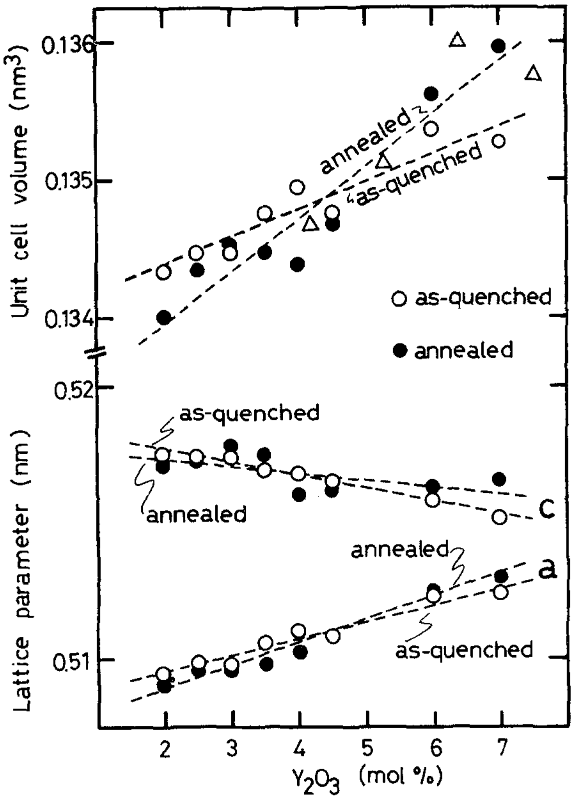

Figure 2 Lattice parameter and unit cell volume of the tetragonal phase as a function of composition. The triangle symbols denote the data obtained by Saiki *et al.* [8] of zone melt grown samples subsequently annealed at 1700° C for 24 h in air.

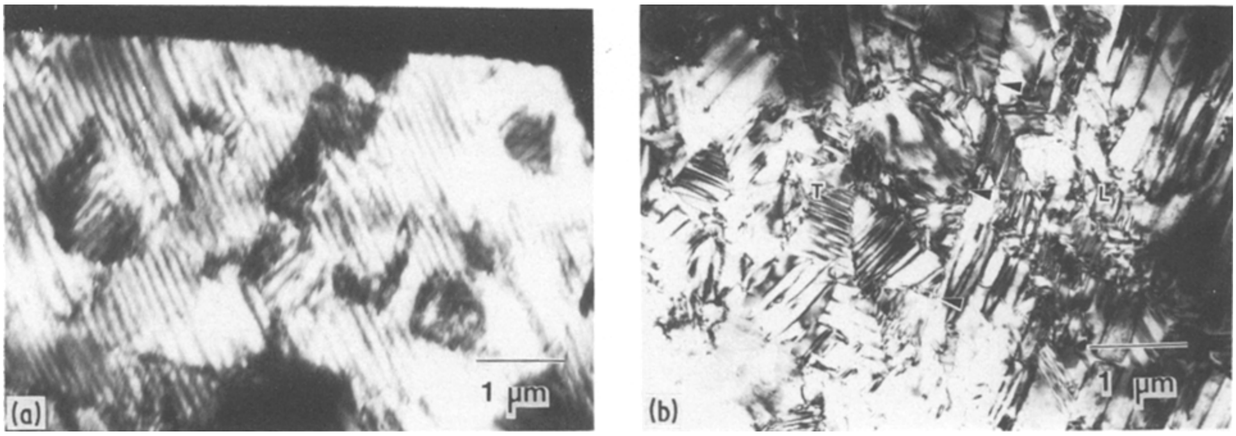

Figure 3 Bright field images of ZrO_2–Y_2O_3 polycrystals (as-quenched, 4.0 mol % Y_2O_3); (a) the "twinned structure", and (b) the "twinned/mosaic structure (T)" made of t′ phase, and lenticular t′ precipitates in a cubic matrix (L). Arrows denote grain boundary.

was due to the insufficient intensity and the broadening of the Bragg peak.

The variation in the lattice parameter of tetragonal phase on the composition of the polycrystals is shown in Fig. 2; the broken lines are drawn by a least squares method. Decreasing tetragonality (the c/a ratio) with the Y_2O_3 contents appears to be characteristic of the t′ phase derived from the cubic phase. On the other hand, the unit cell volume of the tetragonal phase appears to be an increasing function of the Y_2O_3 content. Upon annealing, the unit cell volume slightly decreases except for the specimens with 6 to 7 mol % Y_2O_3. If the metastable t′ phase had decomposed to t and c phases during annealing, the unit cell volume of the tetragonal phase should decrease after the annealing since the Y_2O_3 content in the t phase is less than that in the t phase. However, for 6 and 7 mol % composition it was increased. Saiki *et al.* [8] also showed almost similar unit cell volumes for the samples annealed at 1700° C for 24 h after growing by zone melting. Thus, the reason for the increase in the unit cell volume for the 6 and 7 mol % composition after annealing cannot be understood in a straightforward manner. However, it may be possible that the decomposition of the t′ phase into t and c phases has not been completed during the employed annealing condition and further investigation is necessary to clarify the cause of this abnormal experimental result. This will be discussed elsewhere [9]. In fact, Saiki *et al.* also observed the similar unit cell volumes for the samples annealed at 1700° C for 24 h after growing them by zone melting [8] as shown in Fig. 2.

Some typical TEM micrographs are shown in Fig. 3. For as-quenched materials, most of the microstructures are classified as a "twinned structure" or a "mosaic structure", made of the tetragonal precipitates, as representatively shown in Fig. 3. In the "twinned structure", the two twin related variants are in contact along the $\{1\,0\,1\}$ planes, and this structure is essentially the same as the well twinned structure reported by Lanteri *et al.* for annealed samples after solidification of melts [2]. Electron diffraction analysis suggests that the "mosaic structure" is essentially equivalent to the "twinned structure" except for the coarseness of the twins. In addition to these microstructures, lenticular tetragonal precipitated embedded in the cubic matrix, as marked "L" in Fig. 3, were frequently observed adjacent to the "twinned mosaic" structure for specimens with relatively higher Y_2O_3 contents. This cubic phase was identified by comparing the electron diffraction patterns from the zone axis of [1 1 1]. The cubic phase seen in this structure seems to be a quenched and retained product of the high temperature cubic phase and the frequency of observation of the cubic phase in TEM is consistent with the results from X-ray diffraction, that is, as the Y_2O_3 content increased, the cubic phase increased. The "twinned structure" is seen in the as-quenched materials and it represents the microstructure of the t′ phase. It should be pointed out that the dominant microstructure formed was still the "twinned/mosaic" structure even after annealing, although the twin width became wider. According to the works by Lanteri *et al.* [2], on the other hand, the "colony structure" did not appear without annealing at 1600° C, that is, they regard the well twinned structure as a characteristic morphology of the t phase. The present work, however, suggests that the morphology of the t′ phase is quite similar to that of the t phase.

4. Concluding remarks

ZrO_2–Y_2O_3 polycrystals mainly consist of the tetragonal t′ phase which is transformed in a diffusionless manner from the cubic phase, were fabricated by rapid quenching of melts. TEM observation revealed that the characteristic microstructure was made of twinned t′ precipitates. In the as-quenched materials, a small amount of the cubic phase was also found to exist. This cubic phase is most probably the retained high temperature cubic phase with the same composition as the t′ phase, and the indication of the occurrence of the decomposition of the t′ phase into t and c phases was found from the X-ray diffraction. These preliminary results suggest that the cooling rate is a critical factor in determining the existing phases and morphologies of the ZrO_2–Y_2O_3 system, and the rapid quenching technique could provide important insights into the role of the phase stability of ZrO_2 containing materials.

References

1. N. CLAUSSEN, "Advances in Ceramics", Vol. 12, edited by N. Claussen, M. Ruhle and A. H. Heuer (American Ceramic Society, Columbus, 1984) p. 325.
2. V. LANTERI, A. H. HEUER and T. E. MITCHELL, *ibid.* pp. 118-30.
3. T. SAKUMA, Y. YOSHIZAWA and H. SUTO, *J. Mater. Sci.* **20** (1985) 1085.
4. S. SŌMIYA and M. YOSHIMURA, in "Zirconia Ceramics", Vol. 2, edited by S. Sōmiya and M. Yoshimura (Uchida Rokakuho, Tokyo, 1984) p. 149.
5. M. YOSHIMURA and S. SŌMIYA, in "Proceedings of International Conference on Rapidly Quenched Metals, Sendai, Japan, 1981", edited by T. Masumoto and K. Suzuki (Japan Institute of Metals, Sendai, 1982) p. 23.
6. R. OTA, H. KOZUKA and N. SOGA, *Yogyo-Kyokai-Shi* **92** (1984) 10.
7. H. G. SCOTT, *J. Mater. Sci.* **10** (1975) 1527.
8. J. SAIKI, T. YAMAKAWA, N. ISHIZAWA, K. UEMATSU, N. MIZUTANI and M. KATO, unpublished but presented at Annual Meeting of Ceramic Society of Japan, Tokyo, Japan, 1984.
9. T. NOMA, M. YOSHIMURA, M. KATO, M. SHIBATA, H. SETO and S. SŌMIYA, "Advances in Ceramics", Vol. 24 (American Ceramic Society, Columbus, 1984).

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