Tetragonal Phase in $\text{ZrO}_2\text{-Y}_2\text{O}_3$ Ceramic System

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$\text{ZrO}_2\text{-Y}_2\text{O}_3$ セラミックス系に出現する正方晶

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The phase stability of the cubic and tetragonal phase in $\text{ZrO}_2\text{-}2\text{-}6\text{ mol}\% \text{Y}_2\text{O}_3$ is studied by X-ray diffraction method and transmission electron microscopy. Two kinds of tetragonal phase, t and t' , and a cubic (t'') phase, are identified consistently. The t -phase is the equilibrium tetragonal phase, which transforms martensitically to the monoclinic phase on further cooling. The t' -phase has a thin plate or lamellar structure, and is formed in the decomposed structure of the cubic (t'') phase. The high resolution electron microscopy reveals that the fine domains (t' -phase) due to displacement of oxygen atoms appear dispersedly in the initial stage of decomposition, resulting in the tweed contrast.

[Received February 18, 1986]

Key words : Zirconia, Ytria partially stabilized zirconia, Phase transformation, Phase decomposition, Martensitic transformation, X-ray diffraction, (High resolution) Transmission electron microscopy

1. Introduction

The phase transformation in the conventional partially stabilized zirconia (PSZ) such as yttria-PSZ, magnesia-PSZ and calcia-PSZ has been extensively studied in conjunction with the enhancement of toughness and strength in ceramics¹⁾⁻³⁾. The high temperature phase having a fluorite cubic structure makes decomposition, on annealing, into meta-stable phase of a tetragonal and cubic structure, which is further transformed martensitically to a monoclinic one on cooling. The martensitic transformation is utilized to increase the toughness of the ceramics by absorbing the strain energy concentrated at the propagating crack tip in the ceramics^{4),5)}.

The toughening mechanism is concerned with the morphology of the metastable tetragonal precipitates. Recently, Claussen⁶⁾ has made discussion on the microstructural change of PSZ ceramics, and the distribution of the tetragonal phase. In comparison with magnesia-PSZ and calcia-PSZ, yttria-PSZ exhibits more complicated transformation behavior. There have been reported several contradictory results on the metastable tetragonal phase in the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ system. For example, three kinds of equilibrium phase diagrams are reported so far, as shown altogether in Fig. 1⁷⁾. The quantitative extent of the two phase region of the cubic and tetragonal

phase is slightly different each other. They appear to be caused partly by the distribution of oxygen vacancies and partly by the difficulty of getting a homogeneous or equilibrium phase.

It is suggested that a displacive transformation from a cubic to tetragonal phase could occur in cooled $\text{ZrO}_2\text{-}2\text{-}7\text{ mol}\% \text{Y}_2\text{O}_3$ system^{8),9)}. The tetragonal phase formed by the displacive transformation is stable and not transformed to monoclinic

Fig. 1. Equilibrium phase diagram in $\text{ZrO}_2\text{-Y}_2\text{O}_3$ system.

phase by the subsequent cooling. Heuer et al.¹⁰⁾ studied the instability of a cubic phase and manifested two kinds of tetragonal solid solutions, t -ZrO₂ and t' -ZrO₂ formed in a single crystal containing 8 wt% Y₂O₃ grown by skull melting. The nature of t - and t' -ZrO₂ phase determined by Heuer, however, is considerably different from the t -phase reported so far. The t' -ZrO₂ phase is quite stable in that no transformation takes place by crushing the specimens. Recently, they have reported on more detailed results in the conventional sintered ceramics¹¹⁾. They showed several unusual microstructural features such as 90° tetragonal twins containing antiphase domain boundaries.

Hannink¹²⁾ studied the morphology of the tetragonal phase precipitated in ZrO₂-5 mol% Y₂O₃, where the tweed contrast with spacing of about 55 nm was observed. The specimens were prepared by sintering of powders at 1300°C and solution-treated in the fluorite phase field at 1800°C using a gas fired furnace. The tweed contrast was interpreted by the precipitation of small tetragonal particles. Large rectangular plate-like agglomerates were observed on aging for 100 h at 1300°C.

Recently, Sakuma et al. studied the microstructure observed in ZrO₂-5.2 mol% Y₂O₃ system. The modulated phase coexisting with the thin plate is observed in the specimen annealed in the two phase region of cubic and tetragonal phase. Due to the similar microstructure to the spinodally decomposed phase in metal alloys, they indicated the spinodal decomposition mechanism for the modulated phase¹³⁾.

As mentioned above, there are several different reports concerned with the tetragonal phase in yttria-PSZ. Therefore, the present work is focused on the phase transformation from the cubic to tetragonal structure in ZrO₂-2-6 mol% Y₂O₃ systems.

2. Experimental procedure

Three kinds of fine powder produced by alcoxide sol-gel method were used for sintering. The chemical analysis of the powders indicates the compositions of 2.3, 5.0 and 5.8 mol% Y₂O₃, respectively. The green body formed by using CIP method at 7 t/cm² was sintered at 1400°C for 2 h in atmospheric condition. Densities of materials were measured by Archimedes method to be about 95% of the ideal

density of the material. Each material used in the present work was subjected to annealing at 1300°, 1500° and 1700°C for 5 h in the atmosphere to study the phase stability of the ZrO₂-Y₂O₃ system. The identification of the crystal structure was made by X-ray and electron diffraction analysis, and the study of the microstructure was performed by means of the transmission electron microscopy, in which Hitachi H-800 high resolutional analytical electron microscope was used in Application Laboratory of Naka Factory of Hitachi, Ltd..

3. Experimental results

3.1 Morphology of tetragonal phases

Figure 2 shows the X-ray diffraction profiles of the $\{400\}$ reflections in ZrO₂-2.3 mol% Y₂O₃ material (3 Y) taken at room temperature. The specimens were annealed for 5 h at 1300°, 1500° and 1700°C, respectively. The diffraction traces recorded can be indexed by assuming a face-centered tetragonal structure and face-centered cubic one, as shown in Fig. 2. The splitting of peaks observed in the figures is caused by the $K\alpha_1$ and $K\alpha_2$ component of Cu $K\alpha$ radiation. The specimen annealed at 1300°C is identified as a single phase of tetragonal structure with the axial ratio (c/a) of 1.016. The specimens

Fig. 2. X-ray diffraction profiles of $\{400\}$ reflections in a ZrO₂-2.3 mol% Y₂O₃ (3 Y) annealed for 5 h at 1700°, 1500° and 1300°C, respectively.

Fig. 3. X-ray diffraction profiles of $\{400\}$ reflections in ZrO_2 -5.0, and 5.8 mol% Y_2O_3 (5 Y, 6 Y) annealed for 5 h at 1700° , 1500° and 1300°C , respectively.

annealed at 1500° or 1700°C consist of two phase mixture of a cubic and tetragonal phase, as expected from the equilibrium phase diagram shown in Fig. 1. In most of specimens the tetragonal phase was stable at room temperature, and made martensitic transformation from the tetragonal to monoclinic structure on a subsequent cooling. The electron microscope observation was used to identify the microstructures of the tetragonal phase. The 3 Y material annealed at 1300°C exhibited the ordinary grains of tetragonal phase (t-phase) without any particular features. Their average grain size was about $0.6\ \mu\text{m}$. The monoclinic martensite phase with $(100)_m$ internal twins were sometimes observed in the 3 Y material annealed at 1700°C , in which the average grain size became large, about $1.5\ \mu\text{m}$. There were also some tetragonal grains where the martensitic transformation from the tetragonal to monoclinic phase occurred under the observation.

The X-ray diffraction profiles of ZrO_2 -5.0 and 5.8 mol% Y_2O_3 materials which are subjected to the same heat treatment as above are indicated in Fig. 3 (A) and (B), respectively. The diffraction trace taken, for example from the specimen annealed at 1500°C , exhibits clearly extra peaks other than the cubic and tetragonal peaks shown

Fig. 4. Electron micrographs showing thin plates in a ZrO_2 -5.8 mol% Y_2O_3 (6 Y) annealed at 1500°C for 5 h. (A) is a bright field image, (B) is the selected area diffraction pattern, and (C) is the dark field image taken with 112 fluorite-forbidden reflection. APB's are observed in matrix.

in Fig. 2. In order to make clear the complicated features of X-ray diffraction traces, the transmission electron microscope observation was made for the specimens annealed at each temperature. Figure 4 (A) indicates thin plates (t') observed in a ZrO_2 -5.8 mol% Y_2O_3 (6 Y) material annealed at 1500°C for 5 h. These thin plates are always observed in the materials where the complicated features of X-ray profiles are shown. Therefore, it can be concluded that the extra peaks in Fig. 3 correspond to the thin plates observed in Fig. 4 (A). The composition of yttrium and zirconium atoms in the t' -phase and the matrix is analyzed by energy dispersive spectral analysis of X-rays (EDX) and is found to be the same between them within the limits of experimental error. By the tilting experiment of a specimen under the electron microscope, the traces of the interface of the thin plates are determined to be parallel to $\{101\}$ planes of the matrix phase. The morphology of these thin plates are similar to plates reported by Gupta et al.⁹⁾ and Heuer et al.¹⁰⁾.

As shown in the selected area diffraction pattern of Fig. 4 (B), the 112 forbidden reflections for the fluorite structure appear under the $(02\bar{1})$ zone axis illumination condition (Fig. 4 (A)). The dark field image taken with the 112 reflection reveals the presence of the contrast such as antiphase domain boundaries (APB's) in the matrix, as indicated in Fig. 4 (C). Naturally, the contrast of APB's disappears on the dark field image taken by 224 fundamental reflection. It is well known that these APB's are caused by the phase difference between the ordered phase which is attributed to the "up-down" displacements of oxygen atoms off the related fluorite positions¹⁰⁾.

3.2. Tweed contrast

In many grains of 6 Y material annealed at 1500°C for 5 h, the tweed contrast coexisting with thin plates has been observed within a grain, as seen in Fig. 5. The lamellae appear along with the striations of tweed contrast. The tweed contrast in the matrix has been studied in ZrO_2 -5.8 mol% Y_2O_3 (6 Y) material annealed at 1700°C for 5 h, where it appears in the whole grain and no lamellar structures are formed. Corresponding to this microstructure, X-ray diffraction trace shows weak superlattice peaks and a broad shoulder around the $\{400\}$ cubic peaks. In the selected area diffraction pattern of electron microscopy, the fluorite-forbidden reflections are always

Fig. 5. Bright field image demonstrating thin plates coexisting with tweed phase in a ZrO_2 -5.8 mol% Y_2O_3 (6 Y) annealed at 1500°C for 5 h.

Fig. 6. Dark field electron micrograph taken with 112 fluorite-forbidden reflection in (110) diffraction pattern in a ZrO_2 -5.8 mol% Y_2O_3 (6 Y) annealed at 1500°C for 5 h.

observed. Very weak streaks are also observed in the direction perpendicular to the trace of striations of tweed contrast. It is to be noted, however, that no tetragonal reflections have been observed either in the X-ray diffraction trace or in the electron diffraction pattern. Therefore, the cubic or the distorted tetragonal phase exhibiting the superlattice spots may tentatively be called t'' -phase. The dark field image taken with the 112 extra reflection reveals that the fine domains are arranged along the macroscopical striations of tweed contrast, as shown in Fig. 6. The dark portions in the figure might correspond either to the other two variants of the t'' -phase or the fluorite cubic phase.

The microstructure of the phase mentioned above is examined by high resolution electron microscopy, which is one of the useful technique to study the meta-stable state. The mixed state of the variants of the t'' -phase or the fluorite cubic (c) and t'' -phase is revealed by the observation

Fig. 7. High resolution transmission electron micrograph showing distribution of cubic and t'' -phase in tweed contrast in a ZrO_2 -5.8 mol% Y_2O_3 (6 Y) annealed at 1700°C for 5 h.

under the $\langle 110 \rangle$ pole axis illumination condition. The reflections used were 002, $1\bar{1}1$ and $2\bar{2}0$ ones. The (001) lattice fringes with the spacing of 0.51 nm were observed dispersedly in the matrix, in addition to the fundamental (002), ($1\bar{1}1$) and ($2\bar{2}0$) lattice fringes. As indicated by t'' notations in the photograph, the size of the region where the (001) lattice fringes are observed is comparable to that of small domains shown in Fig. 7. It is be noted, however, that the region C does not always indicate a fluorite cubic structure, because the possibility of variants of the t'' -phase is left for the region C. The crossed lattice fringes in the photograph are those of ($1\bar{1}1$) and ($1\bar{1}\bar{1}$) plane whose lattice spacing is 0.30 nm.

4. Discussion

It is manifested in the above that there are two kinds of tetragonal phase t , t' and one cubic or distorted tetragonal t'' -phase which are different in morphology. Accordingly, the X-ray diffraction patterns show their own characteristics. For example, the 6 Y material annealed at 1700°C exhibits the characteristic profile for the t'' -phase. The 5 Y and 6 Y material exhibit large peaks of t'' -phase when it is annealed at 1700° and 1500°C , respectively. Assuming that the a -axis of the t' -phase has almost the same length with the cubic phase, its axial ratio is determined to be 1.006. It is significant, as indicated in the previous section, that the thin plate (t' -phase) appears from the tweed contrast and no thin plate is formed in a cubic phase with no tweed contrast phase.

A big controversy has been evoked on whether the transformation from cubic to tetragonal is

martensitic one, or not. The thin plate has the habit plane of $\{101\}$ type, as shown in Fig. 4. The detectable compositional difference between the thin plate and the matrix is not obtained. Hence, these results strongly support the interpretation that the formation mechanism of the thin plate is martensitic transformation, though no internal twins as the lattice invariant shear appear in the thin plate.

The high resolution electron microscope observation shows the coherent decomposition in a cubic phase. The periodic fringes ascribed to the t'' -regions in the decomposed matrix are exhibited in some dispersed area. The dark field image as shown in Fig. 6 also reveals the appearance of fine t'' domains. Because the sample has been annealed in the two-phase coexisting region of the equilibrium phase diagram, the occurrence of the decomposition is expected to be a mixture of a cubic and tetragonal phase. Therefore, it is still a possibility of a tetragonal structure for the t'' -phase, though no tetragonality has been proved in the diffraction pattern. Consequently, if it has a tetragonal structure, the distortion should be considerably small in the present case. Taking account of the configurational strain energy involved in the decomposed phase, one of the authors indicates the possibility of the decomposition into a mixture of cubic and tetragonal phase¹⁰.

When the structure factor is considered, the fluorite-forbidden reflections are evoked from the displacement of oxygen atoms along the c -axis. That is, they can be observed in the diffraction pattern as the result of the ordering of oxygen atoms, even though the compositional fluctuation does not give rise to the tetragonal distortion.

5. Conclusion

The morphology of the two kinds of tetragonal phase (t and t') and cubic or distorted tetragonal phase (t'') observed in the conventional sintered ZrO_2 -2-6 mol% Y_2O_3 has been studied using X-ray diffractometry and transmission electron microscopy. The high resolution electron microscopy reveals the fine coherently decomposed cubic or distorted tetragonal t'' -phase in the tweed structure. The tetragonal t' -phase having a thin plate structure has the tetragonality of 1.006 and is reasonably inferred to be formed by martensitic transformation from the

tweed structure.

Acknowledgement Authors would like to express their thanks to Mr. Tsuruta and Mr. Kitahara in Application Laboratory of Naka Factory of Hitachi, Ltd. for their help in carrying out the high resolution electron microscopy.

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