Discussion on the Phase Diagram of Y$_2$O$_3$-Partially Stabilized Zirconia and Interpretation of the Structures

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Y$_2$O$_3$-partially stabilized zirconia shows various microstructures, for example, twinned, herring-bone, lenticular, domain, tweed, modulated, martensitic tetragonal structures, anti-phase boundaries and short range ordering. In order to interpret the formation mechanisms of these structures, the phase diagram of the ZrO$_2$-Y$_2$O$_3$ system at low Y$_2$O$_3$ contents proposed by the present authors was investigated. It was concluded that cubic-tetragonal transformation in ZrO$_2$ was para-ferroelastic second order transition and that the (cubic+tetragonal) two-phase region in the diagram was regarded as a miscibility gap. From these standpoints, the formation mechanisms of complex microstructures are also discussed.

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I. Introduction

Y$_2$O$_3$-stabilized zirconia is an interesting ceramics as high strength materials, solid electrolytes and so on(1). This ceramics shows various morphologies of microstructure(2)-(4), for example, twinned, herring-bone, lenticular, domain, tweed, modulated, martensitic tetragonal structures, anti-phase boundaries and short range ordering. In order to understand the formation processes of these structures, the phase diagram is very important. Many diagrams(5)-(15) for the ZrO$_2$-Y$_2$O$_3$ system have been reported, but great discrepancies between them can be seen. The Scott’s diagram(5)(6) is often referred, but it lacks high temperature data over 1873 K. Recently, the present authors proposed a new diagram as shown in Fig. 1(16)(17). The shape of phase boundaries is very characteristic. In this paper the phase diagram is described and then the formation mechanisms of various microstructures are discussed in terms of this diagram.

II. Previous Results

Sintered$^{(16)(17)}$ and arc-melted$^{(3)}$ specimens were used. The former was made of co-precipitation powders in which 1.5 mass% HfO$_2$ and 0.017 mass% Al$_2$O$_3$, 0.007 mass% Fe$_2$O$_3$ and TiO$_2$ were contained as impurities. The latter was made of mixed powders of pure
(99.9%) ZrO$_2$ and Y$_2$O$_3$. In Fig. 1, tetragonal (t.)-monoclinic (m.) transformation temperatures determined from sintered specimens by means of dilatometry$^{(16)}$ are shown. The equilibrium conjugated compositions of t. and cubic (c.) grains in the annealed sintered specimens were examined by XMA$^{(17)}$. The composition of the tetragonal phase was also estimated from the t.-m. transformation temperature obtained by dilatometry. These data are also plotted in Fig. 1.

Specimens for electron microscopy (EM) and electron diffraction (ED) were prepared from discs about 0.2 mm in thickness by an ion-beam thinning machine. Some typical examples of microstructures in the arc-melted specimens are shown. Figure 2$^{(3)}$ shows "lenticular", "tweed" and "herring-bone" structures in the as-cast 5 mol% Y$_2$O$_3$ (5Y) and 3Y-specimens. Figure 3$^{(3)}$ shows a modulated structure observed in the annealed 5Y- and 3Y-specimens. This structure appeared homogeneously regardless of the original microstructures (matrix, lenticular, and herring-bone structures). The modulated structure is perpendicular to $\langle 111 \rangle$, and the wave length decreased with lowering temperature. This structure change was considered to be "spinodal decomposition". When the specimen was annealed at a temperature above the spinodal line, nucleation-growth type precipitation took place. Figure 4 shows the platelet t.-phase precipitated in c.-matrix in an arc-melted 5Y-specimen annealed at 1975 K for 3.6 ks. The ED-pattern shows that this matrix is tetragonal. This means that the matrix was cubic at the annealing temperature but became rapidly tetragonal during cooling. Fine contrast of "domains" parallel with arrow marks can be seen. The habit planes of domains are $\{100\}^2$.

Similar structures could be observed in the sintered specimens. Figure 5$^{(17)}$ shows "tweed"
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and "domain" structures coexisting in a 3Y-specimen quenched from 2173 K. Figure 6 shows a modulated structure in a 3Y-specimen which was quenched from 2223 K and followed by annealing at 1723 K for 86.4 ks. The habit planes of this modulated structure was determined to be [111].

Figure 7 shows TEM and ED photographs of an as-cast 10Y-specimen, where no tetragonal structure can be seen and haloed ED patterns suggest the presence of short range ordering (SRO)(18).

III. Discussion

The characteristic shape of phase boundaries is shown in Fig. 1. But a similar diagram in shape can be found in the iron alloy systems in which magnetic transformation curves intersected miscibility gaps(19)(20).

1. c.-t. transformation in ZrO$_2$

Aldebert et al.(21) examined the temperature dependence of lattice parameters of pure ZrO$_2$ and found that the tetragonality of t.-lattice,
Aizu (22) stated that the crystal structure of t.-ZrO₂ was classified as m3mF4/m mm type, and that crystals of this type had a possibility of para-ferroelastic transition. If this is the case of ZrO₂, t.-ZrO₂ is ferroelastic and c.-ZrO₂ is paraelastic. In other words, the state of parallel orientation of c-axes of elementary t.-lattices corresponds to the t.-phase, and the randomly oriented state to the c.-phase. In the paraelastic state, the lattice is softened and the c.-axis in an elementary lattice fluctuates among 3 axes with time, accompanying displacement of 8 O²⁻ ions around a Zr⁴⁺ ion. The para-ferroelastic transition is considered to be a “displacive” type and a second order transition like para-ferromagnetic and para-ferroelectric transitions having Curie's temperatures.

2. (c.+t.) miscibility gap in the ZrO₂-Y₂O₃ system

It is well known as a packing rule that the ratio of cation and anion radii, r_c/r_a, controls the coordination number, N in typical ionic crystals. According to this rule, for example, N is 8 when 1>r_c/r_a>0.73. A Zr⁴⁺ ion in c.-ZrO₂ lattice is surrounded with 8 O²⁻ ions;
nevertheless the value of \( r_{zz}/r_0 \) is only 0.66. Therefore, the fluorite structure becomes unstable in a low temperature range\(^7\). On the other hand, t.- and m.-ZrO\(_2\) are more or less stable, because the nearest distances between Zr\(^{4+}\) and O\(^{2-}\) ions are shortened by the decrease in crystal symmetry as shown in Fig. 8. The O\(^{2-}\) ions in paraelectric lattice, without these stabilization mechanisms probably vibrate in a special mode at high temperatures. Similar but weaker behavior is also expected in t.-lattice because it is not so stable yet. These speculations are supported by the evidence that the molal specific heat of c.-ZrO\(_2\) (and t.-\(\text{ZrO}_2\)?) exceeds 9R (R is a gas constant) which is the value expected from the Neumann-Kopp’s law, as shown in Fig. 9.

The above considerations led us to the conclusion that the c.-t. transformation in ZrO\(_2\) was a second order transition between paraelectric states.

Figure 10\(^5\) shows the lattice parameters of as-cast zirconia containing Y\(_2\)O\(_3\) at room temperature. The tetragonality, \(c_t/a_t\), decreases with Y\(_2\)O\(_3\) content down to 1.00 (c.-lattice) at 8 mol\% Y\(_2\)O\(_3\), and it seems that the lattice

\[\text{Fig. 9 Specific heat of pure ZrO}_2:\text{ Reference data for other compounds are inserted.}\]
changes continuously from t. to c. with Y$_2$O$_3$ content as in a single solid solution phase, and the (c. + t.) two-phase region in Fig. 1 seems to be a miscibility gap in a solid solution system.

### 3. Thermodynamical consideration

As mentioned already, Nishizawa(19)(20) discussed the shape of miscibility gap when it was intersected a para-ferro magnetic transformation curve.

Figure 11 shows a schematic representation of the free energy (G) vs Y$_2$O$_3$ concentration (X) curves at several temperatures. Two concaves appear at lower temperatures with decreasing free energy, $\Delta G$'s by the formation of ferroelastic state and SRO.

### 4. Formation mechanisms of various microstructures

The formation mechanisms of various microstructures will be discussed in the light of these free energy-concentration (G-X) curves. As mentioned above, twinned, lenticular, herring-bone and domain t.-structures were formed in the quenched specimens by diffusionless transformation. Figure 12 shows dark field EM and ED photographs of an as-cast 6Y-specimen, in which twinned the t.-structure and curvilinear APB's can be seen. APB's can be revealed with a diffraction beam having an odd-even mixed index in the ED-pattern taken at $\{111\}$ incidence.

During cooling from the c.-stable region, c.-t. transition proceeds rapidly by displacement of O$^{2-}$ ions, and APB's are introduced. At the temperatures just below the Curie's point, the tetragonality is small, and a local accommodation structure, "domain", is formed. With lowering temperature, the tetragonality increases, and large scale accommodation, "twinning" takes place. "Lenticular" and "herring-bone" structures are also formed by twinning ($90^\circ$ twin$^{(9)(20)}$).

When the as-cast and quenched sintered specimens having 3 to 7 mol% Y$_2$O$_3$ are annealed, spinodal decomposition or normal precipitation takes place depending on the annealing temperature and concentration as expected from the G-X curves. The critical condition is given by inflection points, r. and s. on the G-X curve as shown in Fig. 11. Spinodal decomposition is a diffusion-type phase change, but the diffusion species is important. Because in ZrO$_2$ containing c.-stabilizer (Y$^{3+}$, Ca$^{2+}$ etc.), the diffusion constant of O$^{2-}$ is $10^5$ to $10^7$ times as large as those of cations, the decomposition accompanying the diffusion of O$^{2-}$ ions alone can proceed easily even in the process of quenching. The habit planes of typical modulated structure formed by high temperature annealing were restricted to be $\{111\}$ which is normal to the elastically softest directions. This $\{111\}$ type accommodation structure is more effective in releasing the transformation stress than the $\{100\}$ type "domain" structure. Figure 13 shows the microstructure of an arc-melted specimen annealed at 1973 K for 0.6 ks, in which straightened (flattened) APB's are laying in parallel to the modulated structure having $\{111\}$ habit planes.
Fig. 12 Dark field TEM photographs of the same field in an as-cast 6Y-specimen with twinned t.-phase and APB’s.

Fig. 13 Dark field TEM photograph of 3Y-specimen annealed at 1973 K for 0.6 ks, showing APB’s and modulated structure.
IV. Conclusions

The shape of phase boundaries in the phase diagram of the ZrO$_2$-Y$_2$O$_3$ system proposed by the present authors has a characteristic feature. This is discussed on the basis of the c.-t. transformation behavior, specific heat, ion size ratio of Zr$^{4+}$ and O$^{2-}$ and lattice parameter change with Y$_2$O$_3$ concentration. It is concluded that the c.-t. transformation in ZrO$_2$ is a para-ferroelastic second order transition, and the (c.+t.) two-phase region in the diagram is a miscibility gap in a single solid solution system. From these standpoints, the formation mechanisms of the various microstructures such as twinned, lenticular, herring-bone, tweed, domain, spinodal decomposition and APB’s structures which have been observed in the quenched and tempered PSZ, can be interpreted.

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