Cubic-to-Tetragonal (t') Transformation in Zirconia-Containing Systems

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The coexistence of the cubic fluorite and tetragonal phases in rapidly quenched samples was studied in the ZrO$_2$-MO$_{1.5}$ systems for M = Sc, In, Y, and rare earths (R). Spontaneous transformation from metastable cubic phase was triggered at room temperature by a mechanical force. Isolated tetragonal platelets in the cubic matrix were bounded by {101} habit planes and contained anti-phase boundaries. The tetragonality decreased with stabilizer content and vanished at around 18 mol% for M = Y and R, 23 mol% for M = Sc, and 25 mol% for M = In, all at room temperature. With increasing temperature, the tetragonality initially increased because of anisotropic thermal expansion, then decreased rapidly, after reaching a maximum, as the temperature for the tetragonal-to-cubic transformation was approached. Being a first-order martensitic transformation, the cubic-to-tetragonal transformation is accompanied by a discontinuous change of tetragonality and a hysteresis loop as the temperature or composition passes through the equilibrium value. [Key words: zirconia, transformations, microstructure, phase diagrams, quenching.]

I. Introduction

A rapid phase transformation from a cubic (c) to a tetragonal symmetry in the ZrO$_2$-YO$_{1.5}$ system was first reported by Scott in 1975. This tetragonal phase was later found to be different from the regular tetragonal phase that existed in most of the zirconia systems. Notably, it had a smaller tetragonality, a higher yttrium content, many anti-phase domain boundaries (APB) never seen in the regular tetragonal phase, and a higher stability against further distortion into the monoclinic symmetry. Following Miller et al., this phase has been termed t' phase to distinguish it from the regular tetragonal t phase. Lanteri et al. later emphasized that the t' phase was not an equilibrium phase in contrast to the t phase which formed from the c phase by precipitation.

Recently this cubic-to-tetragonal transformation was observed in a number of zirconia-rare-earth oxide (RO$_{1.5}$) systems prepared by rapid melt quenching. The tetragonality in these systems followed a unique compositional dependence regardless of the trivalent stabilizing dopant oxides used. Simi-}
III. Results and Discussion

(1) Microstructure and Coexistence of c and t' Phases

Some SEM micrographs of representative microstructures of the t' phase in the ZrO$_2$-MO$_{1.5}$ (M = Sc, In, Y) are presented in Fig. 1. Their morphology is similar in all the systems studied and contains closely spaced twin platelets of certain crystallographic orientations. In most cases, more than one twin orientation, including sometimes the so-called “herring-bone” structure, are present within a single grain. Some variants apparently intersect each other, as can be seen from the SEM micrograph shown in Fig. 2. The above features are characteristic of phase transformations involving lattice distortion, both for martensitic transformations and for diffusion-controlled phase precipitations. The twins could come either from the c-to-t' transformation itself, as incorporated in the so-called “lattice invariant deformation” (LID) operation during the transformation, or from the mechanical accommodation of the product t' phase subsequent to the transformation. This distinction cannot be ascertained by mere examination of the final microstructure. Indeed, from a phenomenological, crystallographic viewpoint, it can be readily predicted that the cubic-to-tetragonal transformation will most likely entail the (011)(011) twinning systems in the microstructure to minimize the distortional energy. Such an analysis has been performed by Kato and co-workers for zirconia systems, which explains the experimental observations very well.

We have made a special effort to investigate whether the c-to-t' transformation can be triggered at room temperature and, if so, whether the microstructure can be preserved to reveal the coexistence of the c and t' phases. Some of the successful attempts are described below. In one case, a quenched specimen containing 14.0 mol% ScO$_{1.5}$ was first identified to be essentially cubic by X-ray diffraction. It was then mechanically polished in order to induce the c-to-t' transformation. In Fig. 3 we show the X-ray diffraction patterns before and after polishing. The as-quenched sample gives rise to only cubic reflections; after polishing, the coexistence of tetragonal reflections becomes prominent as readily seen from the splitting of the (113) and the (202) peaks and the broadening of the (222) peak.

A set of SEM micrographs of this sample, before and after polishing, are presented in Fig. 4. They illustrate a substantial increase of the platelike t' variants due to polishing and provide direct evidence that the transformation is a martensitic one. The coexistence of the cubic and the t' phases was further verified by TEM using thin foil samples of the same compositions subject to a similar quenching heat treatment. The electron diffraction pattern shown in Fig. 5(a) reveals both the cubic and the tetragonal reflections of one variant. This tetragonal variant forms iso-
Fig. 2. A 6.0 mol% Y₂O₃ arc-melted sample containing several orientations of t' phase.

lated platelets in Fig. 5(b) under bright field and Fig. 5(c) under dark field. From a trace analysis, the habit plane of the t' phase was found to lie along the [101] planes which are expected for the cubic-to-tetragonal transformation.⁹,¹⁰

In addition to the above example, the coexistence of the cubic and the t' phases was also observed in a 14.0 mol% YO₁₅ sample, as shown in Fig. 6. A TEM study with imaging through (112) reflections with a [111] zone axis in another 14.4 mol% YO₁₅ sample has also been conducted. As described in the Appendix, the latter result unequivocally confirms that the cubic phase can coexist with tetragonal variants at room temperature.

The dark-field image in Fig. 5(c), taken using the characteristic tetragonal diffraction spot {112}, shows within the t' plates features which are reminiscent of the APB described by other workers for YO₁₅-containing zirconia transforming at higher temperatures. Their presence in the room-temperature-transformed specimens strongly suggests that the mechanically induced c-to-t' transformation at room temperature is probably of the same nature as those occurring at higher temperatures or during cooling, as extensively reported by other investigators.²-¹² Specifically, we believe that in all cases, the c-to-t' transformation proceeds martensitically, beginning with one variant, followed by other variants, and twins necessitated by strain-accommodation considerations, especially if motivated by an increasing driving force as during subsequent cooling.

Finally, the existence of single-variant tetragonal platelets within a cubic matrix implies some incomplete strain energy relief during martensitic transformation. Anti-phase domains are theoretically of the same crystallographic orientation and not capable of self-accommodation commonly ascribed to other LID such as twins. This situation is not unusual, however, for zirconia transformation. Indeed, both for the nucleation of the tetragonal-to-monoclinic transformation,¹³ and for the growth of the orthorhombic-to-monoclinic transformation⁰ coherent, single-variant habit relationships between the parent and product phases have already been established in this ceramic.

(2) Compositional Dependence of Tetragonal Distortion

Lattice parameters at room temperature in various ZrO₂-MO₁₅ systems are presented in Fig. 7. The unit-cell volumes of the cubic and the tetragonal phases are plotted in Fig. 8. By comparison, the results of the ZrO₂-YO₁₅ and ZrO₂-YbO₁₅
Fig. 5. TEM micrographs of a 14.0 mol% ScO\(_{1.5}\) sample containing cubic and t' phases: (a) selected area diffraction pattern showing c and t' reflections; (b) tetragonal variant (bright field) showing \{101\} habit planes; (c) same variant (dark field from \{112\}) showing anti-phase boundaries inside t'.
shown in Fig. 11, with the feature of the tetragonality maximum highlighted in the inset for one composition. Also included are the data for pure ZrO$_2$ between 1100$^\circ$ and 2400$^\circ$C, reported by Aldebert et al., which are complemented by the tetragonality of pure ZrO$_2$ at room temperature, placed at 1.020, taken from Fig. 9 (see symbol "*"). It is clear that as the yttria content increases, the tetragonality decreases and the maximum on the tetragonality curve shifts to a lower temperature. As before, these data can be normalized using a* and replotted in Fig. 12 as a function of YO$_{1.5}$ composition. At higher temperatures, the onset of tetragonality is higher at a small stabilizer content but it also decreases faster as the stabilizer content increases. Indeed, as already seen in Fig. 11, the pure zirconia which undergoes the c-to-t transition at 2300$^\circ$C has a maximum tetragonality of around 1.025 at about 1700$^\circ$C. This is the highest tetragonality (the largest normalized a and the smallest normalized c) of any zirconia system and is indicated in Fig. 12 by a set of arrows.

The initial increase of the tetragonality is a consequence of thermal expansion which is higher along the c axis than along the a axis. This result can be intuitively understood as due to the different bond strengths in the c and a axes, with the longer axis having a weaker bond. Despite the thermal expansion anisotropy, the tetragonality eventually decreases as the...
t'-to-c transformation temperature, which decreases with increasing stabilizer contents, approaches.

Finally, as mentioned previously, the c-to-t' transformation involves only pure shear and no dilatation. This was also verified for the reverse t'-to-c transformation. Specifically, dilatometry curves were obtained for a 13.5 mol% YO1.5 sample heated to 1000°C; no discontinuous dimensional change was detected.

IV. Implications

The observation of the spontaneous, shear-dominant c-to-t' transformation at room temperature, induced by a mechanical force, unambiguously identifies the transformation as a martensitic one. It proceeds with a characteristic (101) habit plane which is generally expected for the cubic-to-tetragonal transformation. At equilibrium, the order parameter under- goes a discontinuous change for a first-order transformation. For the same reason, as the temperature increases, the tetragonality must experience a discontinuous change for a first-order transformation. In this regard, the extension of the cubic phase somewhere into the tetragonal "wedge" of Figs. 7 and 9 is unavoidable—otherwise it would be a second-order phase transformation. For the same reason, as the temperature increases, the tetragonality must experience a discontinuous drop to unity at a certain temperature, even though the high-temperature data of Figs. 10 and 11 are not sufficiently refined to manifest this discontinuity more clearly.

To elucidate the above point further, the relationships between the free energy diagram, phase diagram, and the tetragonality or order parameter, with their composition and temperature dependence are schematically illustrated in Figs. 13 and 14 for the zirconia alloys. Here, we will use two separate free energy curves for the tetragonal and the cubic phases, respectively, which is appropriate for the first-order phase transformation. In Fig. 13(a), the free energy diagram is represented as a function of composition. The composition where the two branches meet is denoted by X0, and the two equilibrium compositions determined by the common tangent are denoted by X1 and X2. As pointed out by Heuer et al.,5,10,12 a displacive c-to-t' transformation can occur in any supercooled composition less than X0. Alternatively, if an arbitrary tetragonal distortion, such as the one recently discussed by Negita,29 is introduced to the cubic phase of a fixed composition, the free energy may be traced schematically as a function of order parameter by adopting a phenomenological Ginzburg–Landau type of description.27,28 This is illustrated in Fig. 13(b) for a first-order transformation. The locus along the local

Fig. 10. Tetragonality as a function of temperature in a 14.8 mol% ScO1.5 sample.

Fig. 11. Tetragonality vs temperature in ZrO2-YO1.5 system. Arrows indicate locations of tetragonality maxima, one of them highlighted in the inset. Data of pure zirconia at high temperatures taken from Ref. 23.

Fig. 12. Normalized lattice parameters at three temperatures of ZrO2-(Y,Yb)O1.5 systems. Full symbols for tetragonal and open symbols for cubic. Arrows indicate lattice parameters of pure zirconia at its peak tetragonality near 1700°C.
Fig. 13. Free energy as a function of (a) composition and (b) order parameter and temperature. Also shown in (c) is a ZrO$_2$-RO$_{1.5}$ phase diagram.

Fig. 14. Order parameter as a function of (a) composition, (b) temperature, and (c, d) both.

One additional observation of our study is of interest from a crystal chemistry viewpoint. For YO$_{1.5}$ and RO$_{1.5}$-containing zirconia, the composition when $\eta$ extrapolates to zero can be placed at around 19 mol% at 0 K. Ho has used a simple model based on the consideration of coordination number to arrive at an estimation of 20 mol% as that required for stabilizing the cubic phase. The data for YO$_{1.5}$ and RO$_{1.5}$ are consistent with his model. However, ScO$_{1.5}$ and InO$_{1.5}$ apparently are not as effective for stabilization as YO$_{1.5}$ and RO$_{1.5}$, and their required composition to reduce $\eta$ to zero (by extrapolation) is definitely above 20 mol%. This difference might be due to their smaller ionic radii and/or different types of bonding as compared to those of YO$_{1.5}$ and RO$_{1.5}$ in zirconia. We should...
note, however, that the thermodynamic equilibrium usually does not coincide with \( \gamma = 0 \) in first-order transformations. This feature is already illustrated in Figs. 14(a) to (d).

Lastly, although the \( t' \) phase is usually very resistant to the tetragonal-to-monoclinic transformation, we did occasionally evidence such transformation after mechanical polishing in our study. Similar marginally transformable \( t' \) phases were also found in a 4.6 mol% CaO stabilized ZrO\(_2\) and a 6.0 mol% MgO stabilized ZrO\(_2\).\(^{33}\) Recent results of Virkar and co-workers further discovered that, as the twin boundaries were removed by mechanical poling, the \( t' \) phase could undergo spontaneous tetragonal-to-monoclinic transformation.\(^{34}\) Since it is well-known in the martensite literature that substructures can impede martensitic growth, it is plausible that twin boundaries are the growth obstacles that render the \( t' \) phase seemingly untransformable. Together, these observations reinforce our impression that the \( t' \) phase and \( t \) phase differ only in their range of composition, and that they are fundamentally the same tetragonal phase in the zirconia solid solution.

V. Conclusions

The coexistence of the cubic fluorite and tetragonal phases in rapidly quenched samples has been explored in the ZrO\(_2\)-MO\(_{1.5}\) systems for \( M = \) Sc, In, Y, and rare earths (R). The following conclusions are reached.

1. Spontaneous transformation from metastable cubic phase to tetragonal phase can be triggered at room temperature by a mechanical force and the phase interface is sharp. Thus, the transformation is a martensitic one and is likely to be triggered by heterogeneous nucleation.

2. Isolated tetragonal platelets in the cubic matrix are bounded by \{101\} habit planes. They also contain anti-phase boundaries. Mechanical twinning may follow the transformation to give rise to a multiply-twinned microstructure commonly associated with the so-called c-to-t' transformation reported in the literature.

3. The tetragonality decreases with stabilizer content and vanishes around 18 mol% for \( M = \) Y and R, 23 mol% for \( M = \) Sc, and 25 mol% for \( M = \) In, all at room temperature. Thus, ScO\(_2\) and InO\(_2\) apparently have a different stabilizing effect from that of rare-earth oxides or yttria in the zirconia solid solutions.

4. With increasing temperature, the tetragonality initially increases because of anisotropic thermal expansion, reaching a maximum before it decreases again as the equilibrium temperature for the tetragonal-to-cubic transformation is approached. As discontinuous change of tetragonality and a hysteresis loop accompany the transformation as the temperature or composition passes through the equilibrium value.

5. The \( t' \) and \( t \) phases are fundamentally the same tetragonal polymorph in the zirconia solid solutions.
Further TEM Verification of the Coexistence of c and t' Phases

The coexistence of c and t' phases was also found in a sample containing 14.4 mol% YO1.5. The TEM micrograph in Fig. A1 shows the t' plates emanating from the grain boundary and terminating inside the grain. Grains containing more than one variant of the t' phase, while still maintaining a cubic matrix, were also found as shown in the TEM micrograph of Figs. A2(a), which is a dark-field image using (112) reflection along the [113] zone axis. The diffraction patterns in Fig. A2(b) reveal two variants, both visible in Fig. A2(a) along with their characteristic ABP. To further verify that there are no other tetragonal variants, we followed a procedure used by Heuer and co-workers. 5,12 Noting that all three variants in the t' phase could be imaged through (112) reflections with [111] zone axis, we tilted the sample to this zone axis and took selected area diffraction patterns from region A (which contains two variants) and region B (which contains one variant) of Fig. A2(a). In region A, shown in Fig. A2(c), we found only two sets of (112) reflections, one being weaker than the other. This indicates that there are two variants of the t' phase in region A, and one is dominant. In region B, shown in Fig. A2(d), we found essentially only one set of (112) reflections, with the other two nearly invisible. This indicates that one variant exists in region B. These observations are in obvious agreement with the dark-field image of Fig. A2(a), and leave no doubt that the matrix is not tetragonal. In other words, the t' variant is embedded in a cubic matrix.

References