

Phase Relationships in the $\text{ZrO}_2\text{--Sc}_2\text{O}_3$ and $\text{ZrO}_2\text{--In}_2\text{O}_3$ Systems

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Zirconia-rich subsolidus phase relationships in the $\text{ZrO}_2\text{--Sc}_2\text{O}_3$ and $\text{ZrO}_2\text{--In}_2\text{O}_3$ systems were investigated. Phase inconsistencies in the $\text{ZrO}_2\text{--Sc}_2\text{O}_3$ system resulted from a diffusionless cubic-to-tetragonal (t') phase transformation not being recognized in the past. Through three different measuring techniques, along with microstructural observations, the solubility limits of the tetragonal and cubic phases were determined.

I. Introduction

PHASE relationships in zirconia-containing systems were studied extensively in the 1960s because the cubic fluorite phase (c) in these systems has fast oxygen-ion-conducting properties.¹ Recently, the emergence of the toughening effect by the martensitic transformation of the tetragonal phase (t) to the monoclinic phase (m) has drawn considerable attention to the zirconia-rich phase region. In zirconia–trivalent metal oxide systems, the small trivalent cations Sc^{3+} and In^{3+} have been reported to have excellent oxygen ionic conductivities and different stabilization effects for zirconia solid solutions.^{1–7} However, phase relationships in the zirconia-rich region are not well-defined in the $\text{ZrO}_2\text{--Sc}_2\text{O}_3$ and $\text{ZrO}_2\text{--In}_2\text{O}_3$ systems. Four representative $\text{ZrO}_2\text{--Sc}_2\text{O}_3$ phase diagrams reported in the 1960s and 1970s indicate several inconsistencies of phase relationships as seen in Fig. 1.^{8–11} Yet, these inconsistencies have not been clearly explained. As to the $\text{ZrO}_2\text{--In}_2\text{O}_3$ system, its phase relationships were reported by Morozova in 1986.¹² In Morozova's phase diagram, the tetragonal phase region was very limited. However, a recent study reported the existence of tetragonal zirconia polycrystals (TZP) up to a composition of ~9 mol% In_2O_3 at 1200°C .⁵ These inconsistencies suggest that the phase relationships in the $\text{ZrO}_2\text{--Sc}_2\text{O}_3$ and $\text{ZrO}_2\text{--In}_2\text{O}_3$ systems should be reexamined.

Through the recent developments of phase transformation in zirconia-containing systems,^{2,3} we believe that high-temperature solid solutions being “stabilized” at an ambient temperature may have caused the controversies of phase relationships in the past. In this study, three different methods are chosen to reinvestigate the zirconia-rich phase relationships in the $\text{ZrO}_2\text{--Sc}_2\text{O}_3$ system: the X-ray diffraction method, the thermal expansion method, and the EDX composition analysis method. The X-ray diffraction method is a conventional method which has been persistently used for determining phase relationships of ceramic materials. For this X-ray diffraction method, equilibrium phases are determined either *in situ* at high temperatures or from quenched samples at room temperature. Because of several technical difficulties, the *in situ* technique has not been exclusively used. Instead, the quenching technique has been

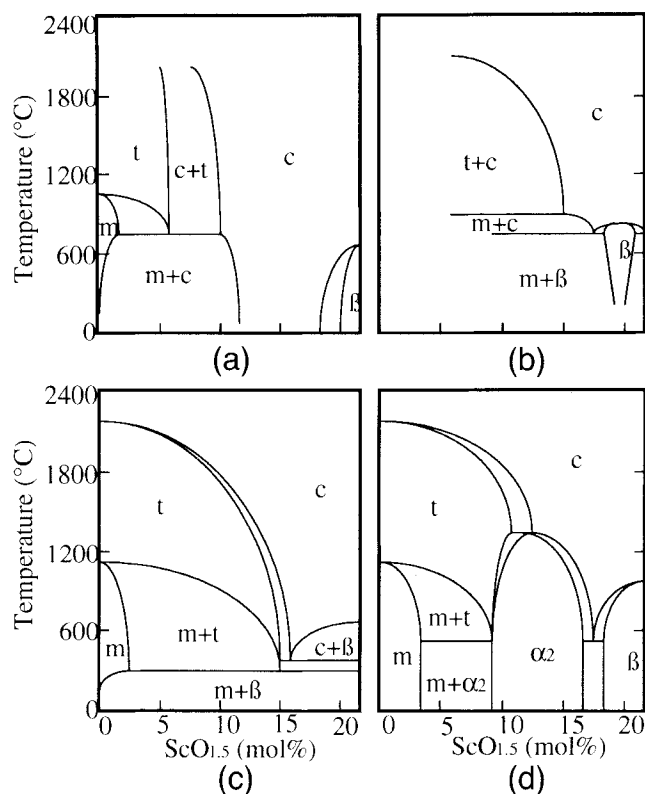


Fig. 1. Four $\text{ZrO}_2\text{--Sc}_2\text{O}_3$ phase diagrams reported from 1963 to 1977: (a) after Stricker,⁸ (b) after Spiridonov,⁹ (c) after Thornber,¹⁰ (d) after Ruh;¹¹ Symbols: c, cubic; t, tetragonal; m, monoclinic; α_2 , Ruh's tetragonal phase; β , $\text{Sc}_2\text{Zr}_7\text{O}_{17}$.

frequently used to determine most of the ceramic phase diagrams. However, this quenching technique is limited by whether the high-temperature phases are “quenched” or “stabilized” at room temperature. If the high-temperature phases are not quenched, it will cause much difficulty when using this technique. Even though zirconia solid solutions are not quenched in certain composition ranges, the phase relationships still can be defined by using the following implications: the monoclinic phase and the t' phase retained at ambient temperature should be defined as the tetragonal phase (t) and the cubic phase at high temperatures, respectively.^{2,3,13,14} The t' phase and the t phase are the same tetragonal polymorph; however, the t' phase is the product of cubic-to-tetragonal (t') diffusionless transformation.³ In this study, X-ray diffraction, along with the quenching technique, is used to determine the phase relationships of the $\text{ZrO}_2\text{--Sc}_2\text{O}_3$ system.

The thermal expansion method is used to determine the tetragonal solubility in this study. This method is based on a tetragonal-to-monoclinic first-order martensitic transformation with a volume change and with its transformation temperature being composition- and grain-size-dependent.^{15,16} In the cubic plus tetragonal composition range, a tetragonal phase exists with the same composition at a constant temperature. Because

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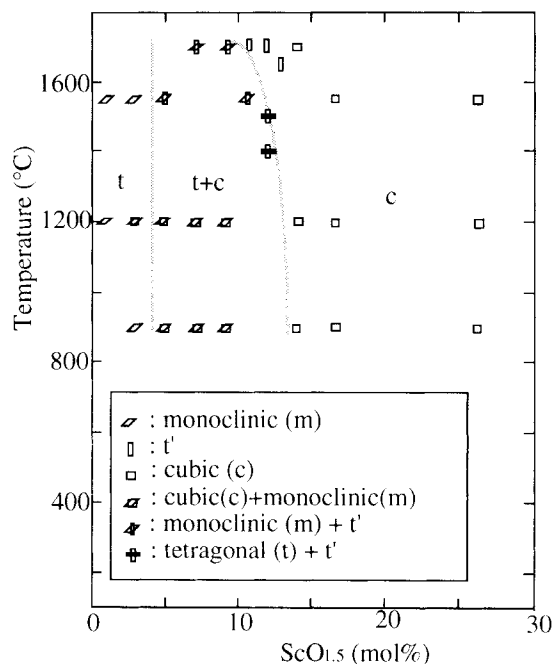


Fig. 2. Tentative zirconia-rich part of $\text{ZrO}_2\text{-Sc}_2\text{O}_3$ phase diagram determined by the X-ray diffraction method. Symbols represent phases existing at room temperature after samples were quenched from the heat-treated temperatures. Phase relationships at high temperatures are defined by three phase regions: tetragonal (t), tetragonal plus cubic ($c + t$), and cubic (c).

of the same composition of the tetragonal phase, the relationships between the transformation temperature of tetragonal-to-monoclinic and Sc_2O_3 composition are expected to be unique. Subsequently, through these unique relationships, the tetragonal solubility limit is defined.

The EDX composition analysis method is used to determine the tetragonal and cubic solubility limits. Combined with the backscattered electron image and energy dispersive X-ray spectrum (EDX), the compositions of the tetragonal and cubic phases in the cubic plus tetragonal phase region at high temperatures are analyzed. This method is based on the fact that the parent phase (c or t) and the transformed phase (t' or m) have the same composition even though their crystal structures are different before and after quenching. Tentatively, for determining the tetragonal and cubic solubility limits, the EDX composition analysis method is more convenient than the other two

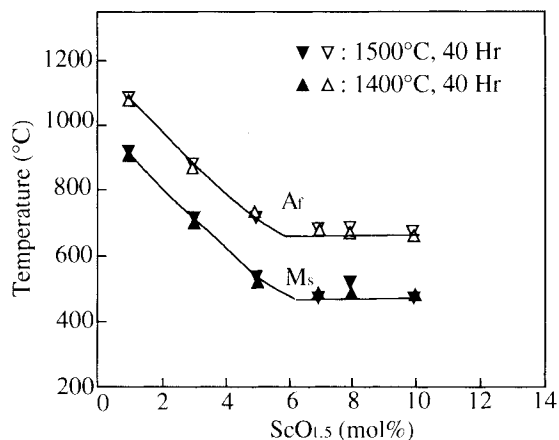


Fig. 3. Relationships among A_i , M_s , and composition. A_i is the final transformation temperature of monoclinic-to-tetragonal during the heating cycle, and M_s is the starting transition temperature of tetragonal-to-monoclinic during the cooling cycle.

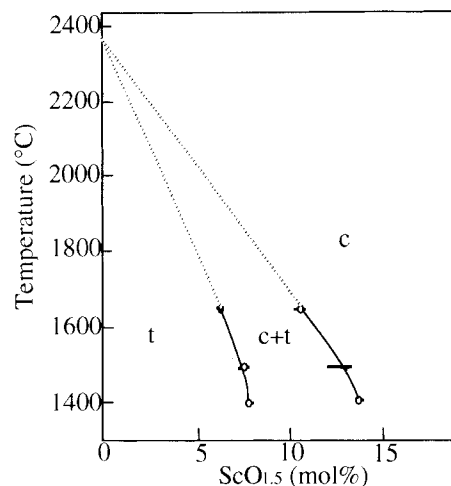


Fig. 4. Zirconia-rich part of $\text{ZrO}_2\text{-Sc}_2\text{O}_3$ phase diagram determined by the EDX method. Bars represent the compositional deviation for each phase. Symbols t and c represent tetragonal and cubic, respectively.

methods. Based on this assumption, the X-ray diffraction method and the thermal expansion method will not be repeated in the $\text{ZrO}_2\text{-In}_2\text{O}_3$ system. Only the EDX composition analysis method is discussed in this system to redefine the phase boundaries of the tetragonal and cubic phases.

II. Experimental Procedure

(1) Powder Preparation

The starting materials were 99.9% pure Sc_2O_3 , 99.9% pure In_2O_3 , and 93.1% pure $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (H_2O balance). A coprecipitation method was used to make different compositions of $\text{ZrO}_2\text{-Sc}_2\text{O}_3$ and $\text{ZrO}_2\text{-In}_2\text{O}_3$ powders. Sc_2O_3 and In_2O_3 were dissolved in a hot HCl solution, respectively. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was dissolved in distilled water. The above ScCl_3 (or InCl_3) and ZrOCl_2 solutions were proportionally mixed according to the compositions of $\text{ZrO}_2\text{-M}_2\text{O}_3$ ($M = \text{Sc}, \text{In}$). The mixed solution and NH_4OH solution (10% concentration) were added simultaneously and stirred continuously in a beaker to let metal hydroxide precipitate out by controlling the pH value at 9. Subsequently, the precipitates were filtered out from the gellike solution. These precipitates were consecutively water-washed and filtered three times to get rid of the chlorine ion. To prevent

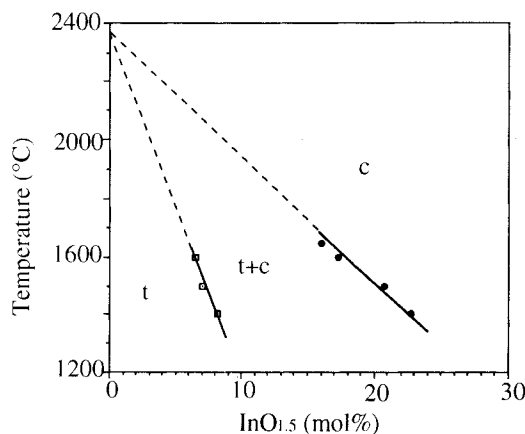


Fig. 5. Tetragonal (t) and cubic (c) phase boundaries in the $\text{ZrO}_2\text{-In}_2\text{O}_3$ system.

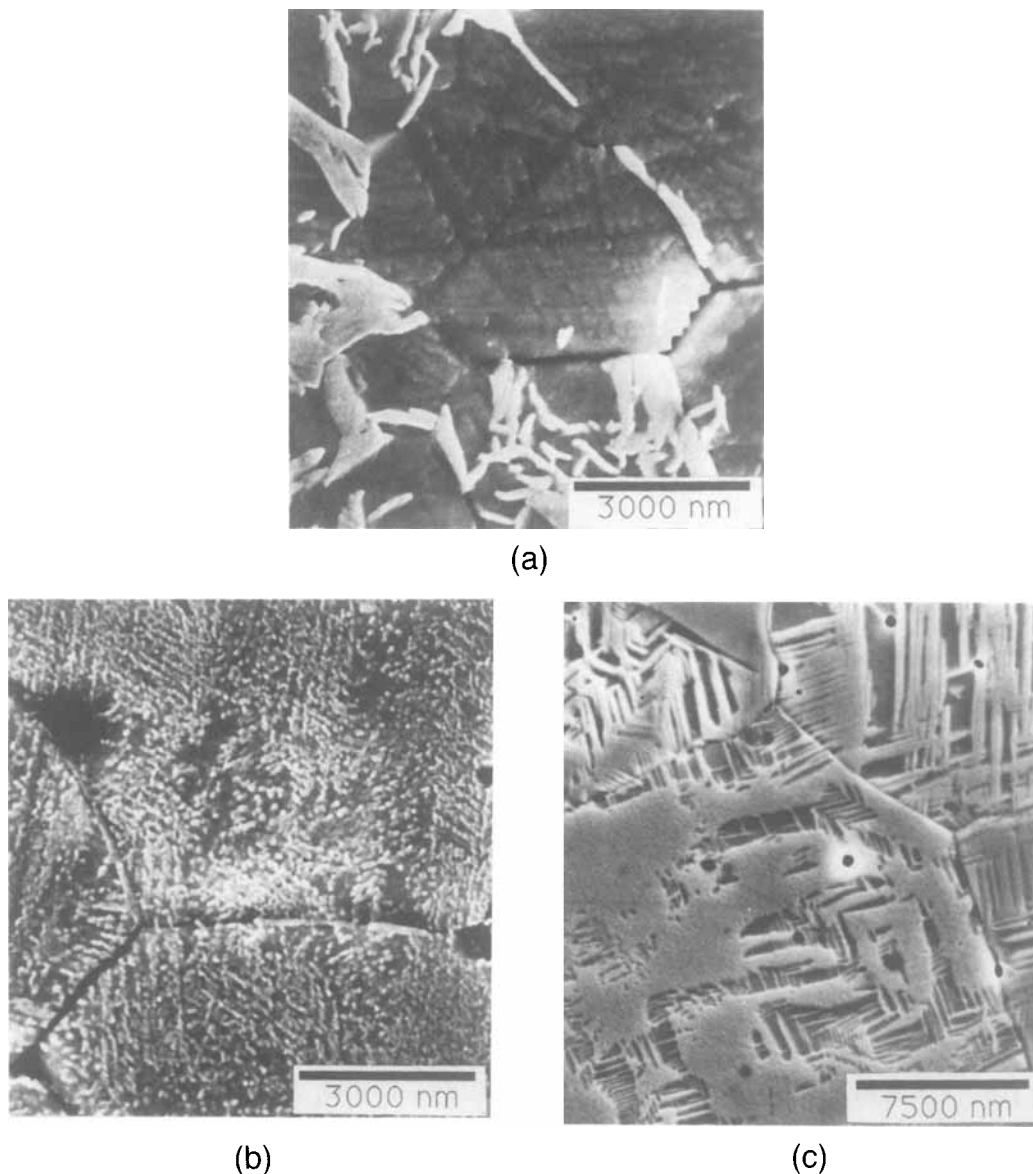


Fig. 6. Different SEM micrographs of 12.0 mol% $\text{ScO}_{1.5}$ samples: (a) heat-treated at 1500°C , and then air-quenched; (b) solution-treated at 1700°C , and then aged at 1400°C ; (c) solution-treated at 1700°C , and then air-quenched.

any metal hydroxide loss, a water-washed solution, distilled water with a small amount of NH_4OH , is controlled at a pH value of 9. After two consecutive washings with 100% pure ethyl alcohol and filtering procedures, the precipitates were dried in an oven below 80°C . Dried precipitates were calcined at 800°C for 2 h to convert their metal hydroxide to oxide. Green pellets were formed from the calcined powders under a uniaxial pressure and were then isostatically pressed at 340 MPa. Subsequently, the green pellets were sintered and heat-treated at high temperatures.

(2) Phase Relationships

Different compositions of green pellets were heat-treated at $900\text{--}1700^\circ\text{C}$ to reach phase equilibrium and then were air-quenched to room temperature. The phase existence of the quenched samples was determined by the X-ray diffraction method at room temperature. A dilatometric unit was used to measure the transformation temperatures of tetragonal-to-monoclinic. The dilatometric unit was operated within a temperature range of $25\text{--}1300^\circ\text{C}$ with both heating and cooling rates of $10^\circ\text{C}/\text{min}$. Different compositions of $\text{ZrO}_2\text{-Sc}_2\text{O}_3$ and $\text{ZrO}_2\text{-In}_2\text{O}_3$ standard samples were introduced in order to quantitatively calibrate the composition analysis of EDX. These standard samples were pellet forms made from a precise

mixing of a 99.9% pure ZrO_2 powder with either a 99.9% pure Sc_2O_3 or 99.9% pure In_2O_3 powder. A hydrofluoric acid (HF) solution was used as an etchant to reveal the microstructures. Microstructural observations were conducted either by SEM or by TEM.

III. Results and Discussion

(1) Phase Relationships in the Zirconia-Rich Region

(A) $\text{ZrO}_2\text{-Sc}_2\text{O}_3$

(a) *X-ray Diffraction Method:* Figure 2 shows a tentative zirconia-rich part of the $\text{ZrO}_2\text{-Sc}_2\text{O}_3$ phase diagram. Three phase regions are defined at high temperatures: a single tetragonal (t), a tetragonal plus cubic ($t + c$), and a single cubic (c). Symbols in Fig. 2 represent the phases existing at room temperature after the samples were quenched from the heat-treating temperatures. The phase existence at room temperature is summarized as follows: (i) in the composition range from 0 to 5 mol% $\text{ScO}_{1.5}$, only the monoclinic phase existed; (ii) 5 to ~ 11 mol% $\text{ScO}_{1.5}$, two phases ($c + m$, or $m + t'$) coexisted and the amount of the monoclinic phase decreased with $\text{ScO}_{1.5}$ composition; (iii) 10 to ~ 15 mol% $\text{ScO}_{1.5}$, either

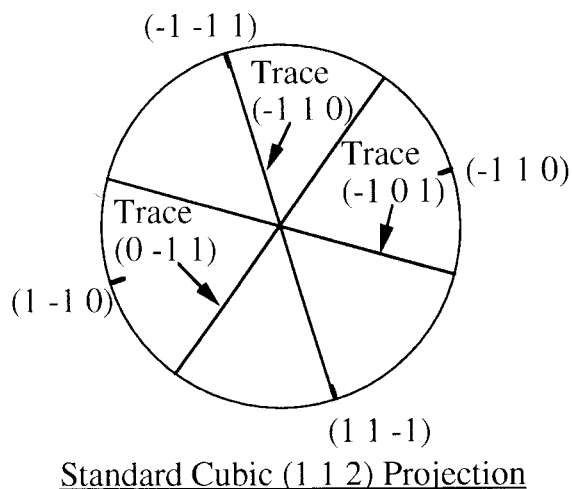
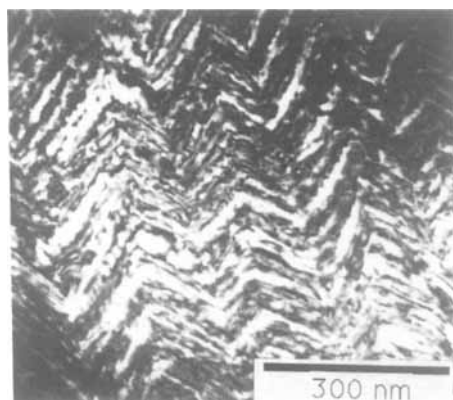


Fig. 7. Morphology of the Sc- t' phase which contains twinning structures. Twin boundaries were analyzed along $\{101\}$.

two phases ($t + t'$, or $t' + c$) or a single phase (t' or c) existed; (iv) $> \sim 15$ mol% $\text{ScO}_{1.5}$, a single cubic phase existed.

There were two diffusionless phase transformations, tetragonal (t)-to-monoclinic (m) and cubic (c)-to-tetragonal (t'), that occurred in the zirconia solid solutions during quenching. Therefore, the m phase and the t' phase being observed at room temperature should be defined as the t and the c phase at high temperatures, respectively.^{2,3,13,14} Based on these two diffusionless phase transformations, the phase relationships at 1200–1600°C were defined as follows: (i) a single tetragonal phase region in the 0–5 mol% $\text{ScO}_{1.5}$; (ii) a tetragonal plus cubic phase region in the 5–15 mol% $\text{ScO}_{1.5}$; (iii) a single cubic phase region in $> \sim 15$ mol% $\text{ScO}_{1.5}$. As a result, the tetragonal and the cubic phase boundaries could be tentatively drawn as indicated in Fig. 2.

(b) *Thermal Expansion Method:* From the X-ray diffraction method, the monoclinic phase was found to exist in the composition range of 0 to ~ 11 mol% $\text{ScO}_{1.5}$. Using a dilatometric unit to measure the thermal expansions of these samples, the phase transformation temperatures (A_t and M_s) of tetragonal-to-monoclinic were determined as shown in Fig. 3. A_t is the final transformation temperature of monoclinic-to-tetragonal during its heating cycle, and M_s is the starting transformation temperature of tetragonal-to-monoclinic during its cooling cycle. The thermal cycle in this thermal expansion measurement was in the temperature range of 25–1300°C. Samples with heat treatment at 1400°C for 40 h had the same M_s and A_t curves as samples with heat treatment at 1500°C for 40 h. In the composition range of 7 to ~ 10 mol% $\text{ScO}_{1.5}$, M_s and A_t temperatures were not found to be composition-dependent. This composition range was defined to be in the tetragonal plus cubic two-phase region at 1400° and 1500°C. Because the transformation temperature of $t \rightarrow m$ was fundamentally composition-

and grain-size-dependent,^{15,16} the only possibility for allowing it to be neither composition- nor grain-size-dependent in the composition range of 7 to ~ 10 mol% $\text{ScO}_{1.5}$ was for the tetragonal phase to have the same composition and a grain size large enough to have the phase transformation of $t \rightarrow m$ without any energy barrier. Based on the above measurements, the tetragonal solubility limits at 1400° and 1500°C were defined to be approximately 6.0 mol% $\text{ScO}_{1.5}$.

(c) *EDX Composition Analysis Method:* The quenched specimens which had been in the tetragonal plus cubic two-phase region at high temperatures were used to analyze the compositions of these two phases by EDX. One of the microstructures in these samples at room temperature is shown in Fig. 6(a). In Fig. 6(a), the area with the dark background represents the t' phase (which was cubic at 1500°C) and the bright area represents the t phase or the m phase (which was tetragonal at 1500°C) at room temperature. The compositions of the tetragonal and cubic phases at high temperatures are given in Fig. 4. These compositions represent the solubility limits of the cubic and tetragonal phases at 1400°, 1500°, and 1650°C, respectively. For determining these solubility limits at each temperature, a minimum of two different compositions of samples were prepared (for example, at 1500°C, samples with 10 and 12 mol% $\text{ScO}_{1.5}$). The composition variations in each phase were very small, as the deviation bars show in Fig. 4.

The phase boundaries determined by the EDX method were consistent with the other two methods. Since the EDX method easily defined the boundaries in a two-phase region, the phase diagram shown in Fig. 4 was used to represent a zirconia-rich part of the ZrO_2 - Sc_2O_3 phase diagram. Its tetragonal solubility limit was similar to that in Stricker's phase diagram,⁸ and the cubic phase boundary was close to that in Thorner's or in Spiridonov's phase diagram.^{9,10}

(B) ZrO_2 - In_2O_3

The EDX composition analysis method was also used to determine the tetragonal and cubic phase boundaries in the ZrO_2 - In_2O_3 system. The phase boundaries of the tetragonal and cubic phases were determined as shown in Fig. 5. In this phase diagram, the cubic phase boundary was similar to Morozova's but the tetragonal solubility limit, 9 mol% $\text{InO}_{1.5}$ at 1400°C, was higher than Morozova's.¹²

(2) Microstructure Observations

(A) ZrO_2 - Sc_2O_3

Different SEM micrographs of samples with a composition of 12.0 mol% $\text{ScO}_{1.5}$ are shown in Fig. 6. Figure 6(a) represents a two-phase microstructure. This sample was directly heat-treated in the cubic plus tetragonal two-phase region and then air-quenched to room temperature. Figure 6(b) is the typical microstructure of the partially stabilized zirconia, in which tetragonal precipitates are uniformly distributed in the cubic phase matrix. This sample was solution-treated in the cubic phase region and then heat-treated in the cubic plus tetragonal two-phase region. Figure 6(c) represents the microstructure of the t' phase. This sample was heat-treated in the cubic phase region and then air-quenched to room temperature. The crystal structure was identified to be tetragonal at room temperature by X-ray diffraction. This t' phase had lattice constants of $a = 5.0834$ Å and $c = 5.1334$ Å, as well as a tetragonality $c/a = 1.0098$, which is smaller than the regular tetragonal phase (t'). It indicated that a diffusionless phase transformation of cubic-to-tetragonal (t') occurred during cooling without formation of tetragonal precipitates. The TEM micrograph in Fig. 7 shows the characteristic twinning structures of the t' phase. These twin boundaries are $\{101\}$ planes. This Sc- t' phase had the same morphology as the t' phase in the ZrO_2 - Y_2O_3 system¹⁴ but was different from the regular tetragonal phase (t). From the above microstructure observations, a two-phase region existing in the 12.0 mol% $\text{ScO}_{1.5}$ sample at a temperature below 1700°C was further identified.

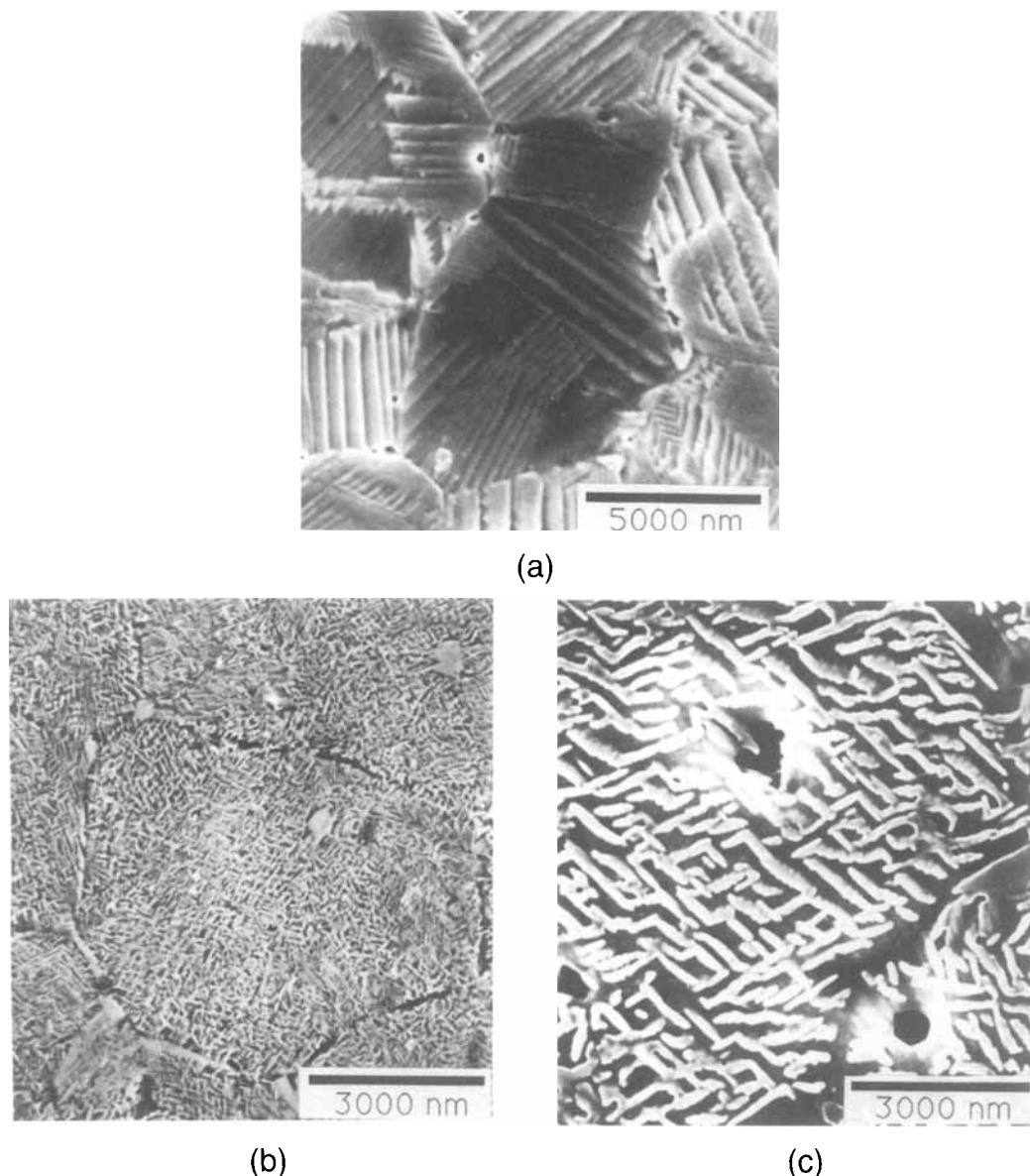


Fig. 8. Different SEM micrographs of 8.0 mol% In_2O_3 samples: (a) solution-treated at 1720°C for 2 h, and then air-quenched; (b) solution-treated at 1720°C for 2 h, then aged at 1400°C for 21 h and air-quenched; (c) solution-treated at 1720°C for 2 h, then aged at 1400°C for 100 h.

(B) $\text{ZrO}_2\text{-In}_2\text{O}_3$

Different SEM micrographs of samples with a composition of 8.0 mol% In_2O_3 are shown in Fig. 8. Figure 8(a) represents a typical morphology of the t' phase. This sample was solution-treated in the cubic phase region and then air-quenched to room temperature. Figure 8(b) represents the microstructure of the partially stabilized zirconia, in which the tetragonal precipitates were in the cubic phase matrix. The sample in Fig. 8(c) had the same heat treatment as that in Fig. 8(b). However, the aging period in Fig. 8(c) was longer than that in Fig. 8(b). Because of larger tetragonal precipitates being transformed into the monoclinic phase to form twin structures during cooling, a zigzag structure of precipitates can be seen in Fig. 8(c).

(3) Discrepancies of Phase Relationships

Figure 1 shows the distorted tetragonal phase of α_2 in Ruh's phase diagram.¹¹ This distorted phase α_2 was the product of the cubic-to-tetragonal (t') transformation. Samples in Ruh's experiment were heat-treated at 2000°C and then cooled to room temperature before they were soaked at different temperatures to identify equilibrium phases. Apparently, under those conditions, the diffusionless phase transformation of cubic-to-tetragonal (t') had already occurred in some

composition ranges. Even though a further heat treatment was applied, samples had difficulty reaching phase equilibrium again at temperatures below a certain value. This phenomenon was noted by Scott in the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ system.¹⁷ Also, the starting composition of the α_2 phase was nearly equal to the cubic solubility limit at 2000°C . This coincidence suggests that the α_2 phase in Ruh's phase diagram was the t' phase, not an equilibrium phase.

For determining high-temperature phase relationships of ceramic materials, the method which used the quenching technique to retain high-temperature phase at ambient temperature was unsuccessful in the zirconia-containing systems. Two diffusionless phase transformations, cubic-to-tetragonal (t') and tetragonal-to-monoclinic occurring during cooling, have caused several phase controversies in the past. As a result, we believe that establishing phase relationships is dependent not only on the crystal structure determination by the X-ray diffraction technique but also on other techniques such as microstructural observation and composition analysis. In some cases, *in situ* high-temperature phase determinations, such as by high-temperature X-ray diffractometry, must be introduced to solve some phase controversies. However, even using this *in situ* method, the thermal history of the sample must be noted.

IV. Conclusions

(1) The zirconia-rich parts of $\text{ZrO}_2\text{--Sc}_2\text{O}_3$ and $\text{ZrO}_2\text{--In}_2\text{O}_3$ phase diagrams were determined. In the $\text{ZrO}_2\text{--Sc}_2\text{O}_3$ system, the tetragonal solubility limit was found similar to Stricker's⁸ and the cubic phase boundary was close to Thornber's or Spiridonov's.^{9,10} In the $\text{ZrO}_2\text{--In}_2\text{O}_3$ system, the cubic phase boundary was similar to Morozova's.¹² However, a larger tetragonal solubility limit, 9 mol% $\text{InO}_{1.5}$ at 1400°C , was observed in this study.

(2) A diffusionless phase transformation from cubic to tetragonal (t') was observed in the $\text{ZrO}_2\text{--Sc}_2\text{O}_3$ and $\text{ZrO}_2\text{--In}_2\text{O}_3$ systems. With a maximum heat treatment temperature at $\sim 1700^\circ\text{C}$, a complete tetragonal phase (t') appeared in a composition range of 10.0 to ~ 15.0 mol% $\text{ScO}_{1.5}$.

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