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The metastable two-phase region in the zirconia-rich part of the ZrO_2–Y_2O_3 system

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ZrO_2–Y_2O_3 alloys with yttria contents between 2.0 and 6.3 mol % were prepared by arc-melting. The microstructure of the alloys after isothermal ageing was examined by electron microscopy. It was found that a modulated structure was formed in alloys aged at appropriate temperatures. The modulated structure resembles the structure of spinodally decomposed metallic alloys and ceramics. The range in which the modulated structure is developed is inside the cubic–tetragonal two-phase region of the ZrO_2–Y_2O_3 system. The modulated structure is associated with metastable phase decomposition.

1. Introduction

Partially-stabilized zirconia (PSZ) is toughened by the stress-induced martensitic transformation of tetragonal phase (t-phase) into monoclinic phase (m-phase) in the process zone around a propagating crack [1–9]. The fracture toughness of PSZ is, therefore, controlled by the amount and dispersion of t-phase [10, 11]. The precipitation of t-phase occurs during firing or ageing in the cubic–tetragonal two-phase region, which results in a change in fracture toughness and other mechanical properties [11, 12]. In addition to the precipitation of t-phase, the modulated structure is sometimes developed in PSZ by heat treatment [13, 14]. Marder, Mitchell and Heuer [14] have postulated that the structure originates from aligned tetragonal particles along the ⟨1 0 0⟩ direction in the cubic matrix (c-phase) in ZrO_2–CaO. However, as pointed out by themselves [14], it is anomalous for the particles to align in the ⟨1 0 0⟩ direction, which is elastically hard in cubic zirconia [15]. The present authors have recently suggested that the modulated structure developed in ZrO_2–5.2 mol % Y_2O_3 alloy has the following features characteristic of spinodal decomposition [16].

1. The normal direction of bright and dark lamellae is nearly parallel to the elastically soft ⟨1 1 1⟩ direction.
2. The log–log plot of the wavelength of the modulated structure and the undercooling gives a straight line with a slope of $-1/2$ as predicted from the theory of spinodal decomposition [17].
3. X-ray diffraction studies have revealed that 4 0 0 peaks from t- and c-phases are clearly separated in as-cast ZrO_2–5.2 mol % Y_2O_3 alloy, but a single broad 4 0 0 peak is obtained in aged alloy with a modulated structure.

Spinodal decomposition in ZrO_2–Y_2O_3 alloys, however, may not have been generally accepted yet, because the phase diagram of the ZrO_2–Y_2O_3 system does not have a miscibility gap. In the present study, the temperature and composition range in which the modulated structure is developed was determined by examining the microstructure of aged ZrO_2–Y_2O_3 alloys with various compositions. On the basis of the result, discussion is devoted to whether or not spinodal decomposition possibly occurs in ZrO_2–Y_2O_3 alloys.

2. Experimental procedure

Zirconia and yttria powders with 99.9% purity supplied by Rare Metallic Co. Ltd (Ishikaura Building, Chiyodaku Misakicho 2-20-1, Tokyo 101) were used for preparing ZrO_2–2.0, 2.9, 4.0, 5.0 and 6.3 mol % Y_2O_3 alloys by arc-melting. Experimental details of the alloy preparation were the same as those described in previous reports [16, 18]. Alloys with a uniform composition were obtained by arc-melting; the local compositional change was within about 10% of the average composition of each alloy. Disc specimens cut from the arc-melted buttons were aged at various temperatures between 1800 and 1200° C. They were thinned by ion bombardment and examined with a JEM 200B electron microscope (Gaton Co. Ltd, USA) operated at 200 kV.

3. Results

It has been shown in a previous paper that a modulated structure is developed in ZrO_2–5.2 mol % Y_2O_3 alloy at ageing temperatures between 1600 and 1400° C [16]. The modulated structure is formed not only in this alloy but also in other alloys with different compositions. Fig. 1 shows an example of modulated structure formed at 1700° C in ZrO_2–4.0 mol % Y_2O_3 alloy. A typical modulated structure with bright and dark lamellae is seen. The structure is clearly different from ellipsoidal [11, 13] or plate-shaped t-phase [16] precipitated in a cubic matrix. It has been shown that similar bright and dark lamellae in TiO_2–SnO_2 are associated with local compositional fluctuations formed by spinodal decomposition [19–23].

Fig. 2 shows an electron micrograph taken near the beam direction [0 1 1] in ZrO_2–4.0 mol % Y_2O_3 alloy.

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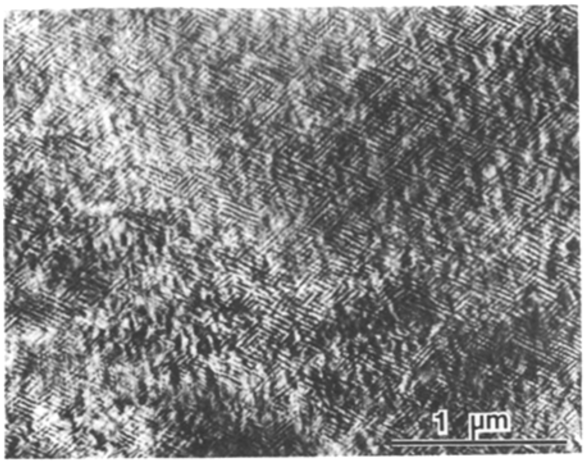

Figure 1 The modulated structure formed in ZrO_2–4.0 mol % Y_2O_3 alloy aged at 1700° C for 10 min.

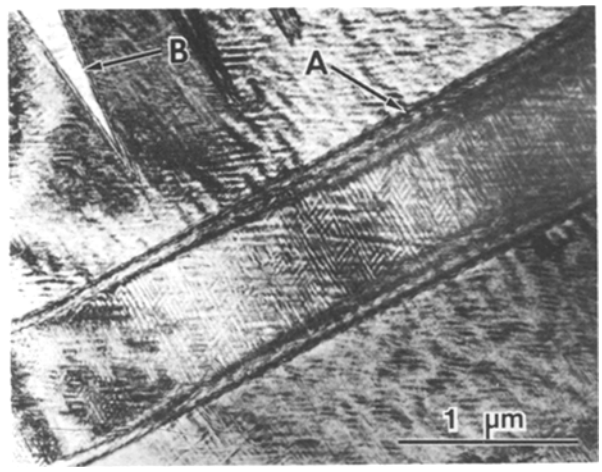

Figure 3 The microstructure of ZrO_2–2.9 mol % Y_2O_3 alloy aged at 1700° C for 10 min. The band A and lenticular phase B are t-phase, which exists in as-cast alloy without ageing. Modulated structure is developed in t-phase as well as in the cubic matrix.

The normal direction of bright and dark lamellae is nearly parallel to the $[1\,\bar{1}\,1]$ and $[1\,1\,\bar{1}]$ directions, and the 4 0 0 diffraction spot shown inserted in Fig. 2 has satellite spots appearing close to the two $\langle 1\,1\,1 \rangle$ directions. The $\langle 1\,1\,1 \rangle$ direction is elastically soft in cubic zirconia [15, 16], which is favourable for compositional fluctuations to be formed [17].

Fig. 3 shows the structure of ZrO_2–2.9 mol % Y_2O_3 alloy aged at 1700° C for 10 min. A modulated structure is seen both in the matrix and in a band marked A in Fig. 3. Judging from the microstructure of as-cast alloys [18], this band and the lenticular phase B are regarded as being t-phase in the cubic matrix. The lenticular t-phase in as-cast alloys has almost the same yttria content as the cubic matrix, which was formed by martensitic transformation during cooling from the melting temperature [18]. It was found that modulated structure was also formed in phase B, but it was not seen in Fig. 3 due to the Bragg reflecting condition. A slight tilting of the foil revealed the modulated structure in B, but results in the disappearance of the structure in A. It is noted that modulated structure is developed in the original t-phase as well as in c-phase during ageing.

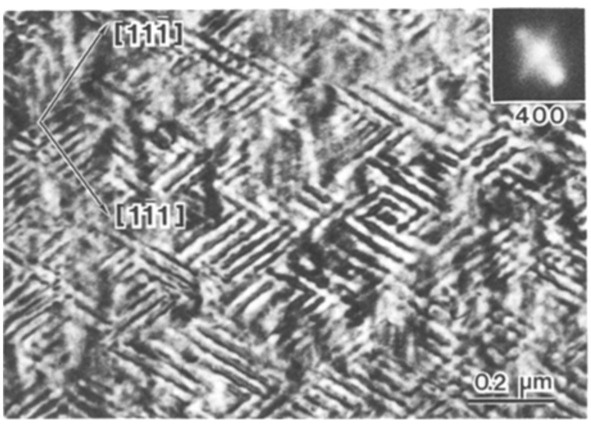

Figure 2 Electron micrograph taken near the beam direction [0 1 1]. Note that bright and dark lamellae are nearly normal to the $[1\,\bar{1}\,1]$ or $[1\,1\,\bar{1}]$ direction. Satellite spots appear in the two [1 1 1] directions around the 4 0 0 reflection of the c-phase.

Fig. 4 shows the microstructure of five alloys aged at 1500° C for 20 h. The microstructure of ZrO_2–2.0 mol % Y_2O_3 alloy (Fig. 4a) is composed of twinned m-phase without any precipitates and modulated structure. The modulated structure is developed in ZrO_2–2.9, 4.0 and 5.0 mol % Y_2O_3 alloys at the ageing temperature as seen in Figs. 4b, c and d. A precipitate with displacement fringe contrast is formed in ZrO_2–6.3 mol % Y_2O_3 alloy (Fig. 4e), being different from other alloys. Fig. 4 indicates that the modulated structure is formed in a particular composition range in ZrO_2–Y_2O_3.

The range was determined from microstructural observations such as Fig. 4, and the result is shown in Fig. 5. The zirconia-rich region of the ZrO_2–Y_2O_3 phase diagram in Fig. 5 is that reported by Scott [24]. In each alloy, the modulated structure was found at ageing temperatures shown by open circles, but not at temperatures shown by filled circles. The boundary between open and filled circles is shown by broken lines. The lines are probably linked at a high temperature, although observations at ageing temperatures above 1800° C were not made in this work because of experimental limitations. It seems, however, reasonable to say from Fig. 5 that the modulated structure is formed in a region inside the cubic–tetragonal two-phase region.

4. Discussion

Spinodal decomposition in crystalline oxides was first found in TiO_2–SnO_2 [19], which has a miscibility gap in the phase diagram [25]. The decomposition occurs between two tetragonal phases with a rutile-type structure. It is expected that spinodal decomposition occurs in a region inside the miscibility gap. Chemical and coherent spinodals have been predicted from a regular solution model in TiO_2–SnO_2 [22]. The modulated structure in aged TiO_2–SnO_2 alloys is believed to be formed by spinodal decomposition, which occurs inside the coherent spinodal.

In the case of ZrO_2–Y_2O_3 the situation is very complicated, because a miscibility gap is not present in

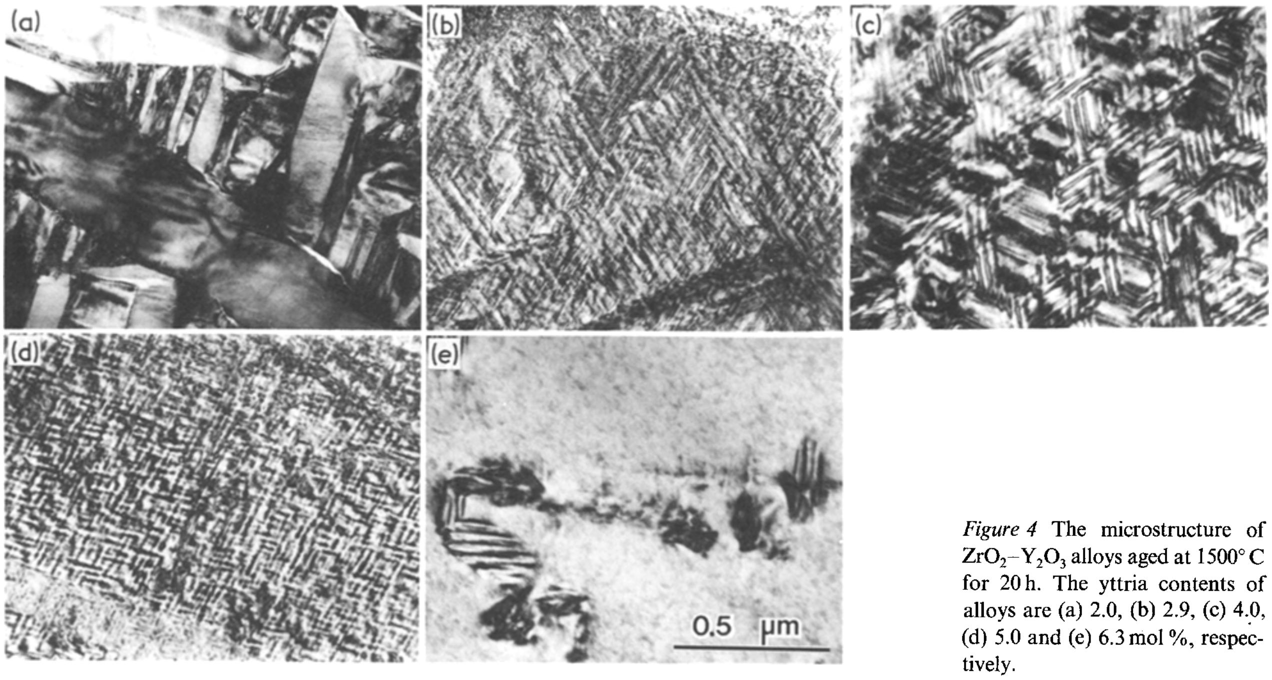

Figure 4 The microstructure of ZrO_2–Y_2O_3 alloys aged at 1500° C for 20 h. The yttria contents of alloys are (a) 2.0, (b) 2.9, (c) 4.0, (d) 5.0 and (e) 6.3 mol %, respectively.

the equilibrium phase diagram [24, 26]. The present result shows that the decomposition accompanying modulated structure takes place inside the cubic–tetragonal two-phase region in the ZrO_2–Y_2O_3 system. This fact means that the modulated structure is associated with metastable phase decomposition [27]. It is known that such a metastable miscibility gap exists in the system $Na_2B_8O_{13}$–SiO_2. The metastable phase decomposition is skilfully used for preparing

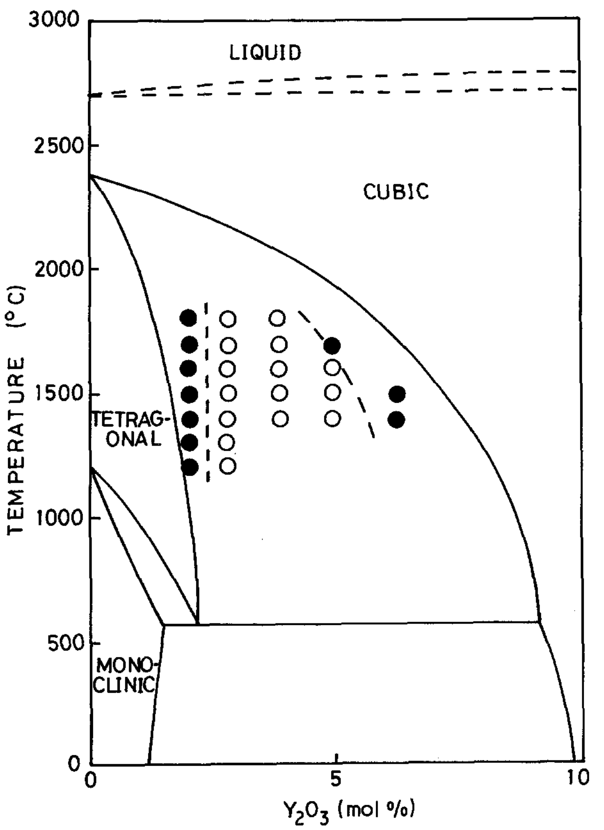

Figure 5 Zirconia-rich part of the ZrO_2–Y_2O_3 phase diagram [24]. The modulated structure was found at ageing temperatures shown by open circles but not at temperatures shown by filled circles.

glasses by the commercial Vycor process [28]. If there is a metastable binodal, it is possible for the metastable phases to decompose spinodally in a particular region inside the binodal as in commercial glass. In the following, the question of what type of metastable phase decomposition possibly occurs in ZrO_2–Y_2O_3 is discussed.

It is helpful to use a free energy–composition diagram (G–x diagram) for discussing the phase stability, and for thermodynamically predicting the possible reaction which occurs during heat treatment [29]. Thermodynamic data available for calculating the G–x diagram in ZrO_2–Y_2O_3, however, have not yet been obtained. It is, therefore, only possible to construct a G–x diagram compatible with the phase diagram. Such a G–x diagram has been depicted by Andersson and Gupta [5] for explaining phase stability and martensitic transformation in the ZrO_2–Y_2O_3 system. If the diagram for t- and c-phases are always concave upward as shown in their paper [5], binodal and/or spinodal decomposition will not take place. It is most probable that metastable binodal is present in the c-phase, because modulated structure is mainly formed in the c-phase.

Assuming that the G–x diagram for the c-phase inflects in a central region, the metastable binodal will appear as shown in Fig. 6b. A common tangent shown by the solid line in Fig. 6b makes contact with the G–x diagrams for t- and c-phases at compositions x_1^e and x_2^e, which correspond to equilibrium compositions of the two phases at a temperature T_1 in Fig. 6a. The broken line in Fig. 6b has two contact points at binodal compositions x_1^b and x_2^b with the G–x diagram for the c-phase. The compositions x_1^s and x_2^s are at the inflection points of the diagram, which define the chemical spinodal [17]. If the modulated structure is associated with spinodal decomposition, the compositions x_1^{mod} and x_2^{mod} determined experimentally would correspond to coherent spinodal which is inside the chemical spinodal. From the G–x

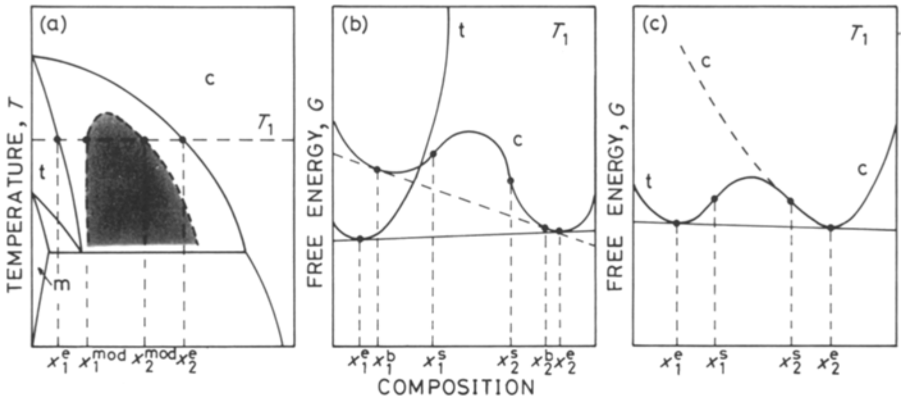

Figure 6 (a) ZrO_2–Y_2O_3 phase diagram and (b, c) the corresponding free energy–composition diagrams at a temperature T_1. A metastable binodal of the c-phase exists in (b), while metastable decomposition occurs spinodally between t- and c-phases in (c). For details see text.

diagram in Fig. 6b it is possible to predict the metastable binodal and also the spinodal decomposition in the c-phase.

The present data, however, are not completely explained by postulating the presence of metastable binodal in the c-phase. First of all, the modulated structure always accompanies reflections that are forbidden for the fluorite structure and are characteristic of the t-phase. Fig. 7 is a diffraction pattern from the modulated structure in ZrO_2–4.0 mol % Y_2O_3 alloy, whose beam direction is close to [0 1 1]. Indexing is given for several principal reflections. Weak reflections between principal reflections are forbidden for c-phase with a fluorite structure, but appear in the t-phase [18]. The diffraction pattern seems to indicate that modulated structure accompanies the t-phase. Secondly, modulated structure is also developed in the t-phase which exists in as-cast alloys before ageing (Fig. 3). It is possible to propose that the G–x diagrams for c- and t-phases inflect in a central region. However, a difficulty still remains in explaining the appearance of reflections that are forbidden for the fluorite structure from modulated structure in the c-phase.

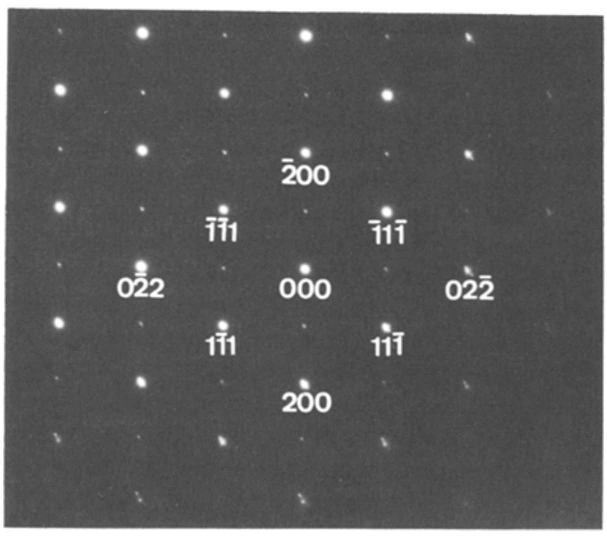

Figure 7 Electron diffraction pattern taken from ZrO_2–4.0 mol % Y_2O_3 alloy aged at 1700° C for 10 min. The zone axis is close to [0 1 1]. Indexing is given for principal reflections originating from the cubic fluorite structure. Weak reflections between the principal reflections are characteristic of t-phase, which are forbidden for fluorite structure.

Another possibility for spinodal decomposition in ZrO_2–Y_2O_3 exists in decomposition between c- and t-phases. It has been shown that the tetragonality of the t-phase decreases continuously with increasing Y_2O_3 content of alloys [25]. The t-phase would have a tetragonality with a miniumum free energy for each alloy. It is believed that the G–x diagram of the t-phase in Fig. 6b is made by linking the minimum free energy at each Y_2O_3 content of alloys. If the tetragonality continuously decreases to zero with an increase in Y_2O_3 content, the G–x diagrams for t- and c-phase will connect at a certain composition and becomes single curve as shown in Fig. 6c. Intersections between the G–x diagrams and a common tangent in Fig. 6c show equilibrium compositions of t- and c-phases x_1^e and x_2^e, respectively. The inflection points on the diagram are the compositions of chemical spinodal x_1^s and x_2^s. If this is the case, both t- and c-phases can decompose spinodally in a particular region inside the tetragonal–cubic two-phase region, and the structure formed by spinodal decomposition will always accompany reflections forbidden for fluorite structure in the diffraction pattern. It seems that the situation depicted in Fig. 6c is consistent with the present experimental observations. However, the G–x diagram in Fig. 6c is only at present a hypothetical one without thermodynamic backing. For verifying the situation, it is essential to confirm the continuous decrease in tetragonality to zero with increasing Y_2O_3 content. The data available for constructing the G–x diagram are also important to clarify the type of metastable decomposition and the origin of modulated structure.

5. Conclusion

A modulated structure with features characteristic of spinodally decomposed alloys is developed by isothermal ageing in ZrO_2–Y_2O_3 alloys. The structure is formed in a temperature and composition range inside the cubic–tetragonal two-phase region in the ZrO_2–Y_2O_3 system. The result suggests that a metastable phase decomposition causes the modulated structure. Several metastable phase decompositions possibly occur in the ZrO_2–Y_2O_3 system. However, it is not possible to specify the actual phase decomposition at present. Thermodynamic analysis in the ZrO_2–Y_2O_3 system is especially required to identify the phase decomposition accompanying the modulated structure.

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