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The modulated structure formed by isothermal ageing in ZrO_2–5.2 mol% Y_2O_3 alloy

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The modulated structure produced by isothermal ageing of ZrO_2–5.2 mol% Y_2O_3 alloy was examined mainly by electron microscopy. It was found that the modulated structure was formed at ageing temperatures between 1400 and 1600° C, but not at 1700° C. The structure is developed by spinodal decomposition, which produces compositional fluctuation in the elastically soft ⟨1 1 1⟩ direction in cubic zirconia. The hardness increase caused by the development of modulated structure during ageing is larger than the hardening by precipitation of tetragonal phase in the cubic matrix.

1. Introduction

It is well know that a suitable dispersion of tetragonal particles in cubic zirconia causes an improvement of fracture toughness of zirconia [1–5]. The toughness increase is believed to be due to the stress-induced transformation of tetragonal particles into a stable monoclinic structure during crack propagation [6–11]. Zirconia with such a dispersion is obtained by an addition of cubic-stabilizing oxides, such as CaO, MgO and Y_2O_3 and termed partially-stabilized zirconia (PSZ). One of the interesting properties of PSZ is that the strength and toughness change with ageing treatment [3, 5]. The structural change during isothermal ageing has recently been examined in several PSZ [2, 12, 13]. One of the characteristic features of the as-fired or aged PSZ is that a modulated structure with a tweed-like contrast is sometimes developed [12,13]. However, the nature of the structure and also the role of such a structure on the strength and toughness of PSZ have not been clarified yet. In the present study, the modulated structure developed by isothermal ageing of ZrO_2–Y_2O_3 alloy was examined in detail and the nature of the structure is discussed.

2. Experimental procedures

Zirconia and yttria powders with 99.9% purity produced by Rare Metallic Co., Ltd were used for preparing ZrO_2–5.2 mol% Y_2O_3 alloy. The oxide powders were mixed in a ball mill followed by pelleting in a steel die. The pellet was sintered at 1400° C for 1 h and then melted in an argon atmosphere using an electric arc furnace with a water-cooled copper hearth. EPMA analysis, by Shimazn ARL-EMX microanalyser, has revealed that the local compositional change in the arc-melted alloys is less than 0.5 mol%. The ageing treatment was made isothermally in the two-phase region (cubic/tetragonal) of the ZrO_2–Y_2O_3 system [14, 15]. Hardness measurements and X-ray diffraction studies were carried out in the heat-treated alloys. Thin foils were prepared by ion-beam thinning and examined by a JEOL 200B electron microscope operated at 200 kV.

3. Results

3.1. Hardness measurements

Fig. 1 shows the change in microhardness with ageing time. The alloy has an age-hardening character at all temperatures examined and the

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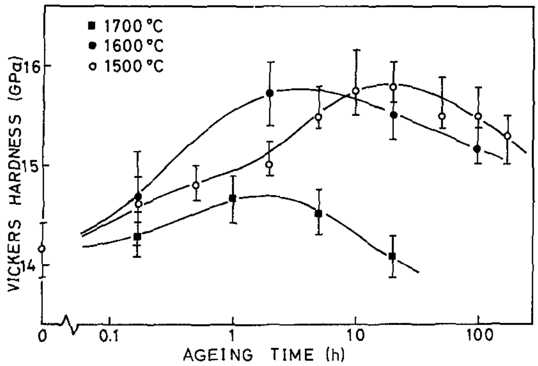

Figure 1 Microhardness of aged materials as a function of ageing time.

time to reach the peak hardness decreases with increasing temperature, as commonly found in metallic alloys. The peak hardness is 15.8 GPa at 1600 and 1500° C, which is about 1.6 GPa higher than that in the alloy without any heat treatments after arc-melting. On the other hand, the hardness increase with ageing at 1700° C is about 0.5 GPa and is much smaller than that at lower temperatures. The increase in fracture strength and/or fracture toughness has already been reported in magnesia-PSZ (Mg-PSZ) [15] and calcia-PSZ (Ca-PSZ) [2]. However, Garvie *et al.* have found that there is little significant change in hardness during ageing except for a drop which occurred on overageing, but the modulus of rupture increases to a peak and then drops off rapidly. They have suggested that PSZ should not be referred to as age-hardened but age-toughened [12]. The result shown in Fig. 1 is different from that reported in Ca-PSZ. Yttria and calcia may have a different role in the structure and strength of aged PSZ.

3.2. Electron microscopy

Fig. 2 shows the microstructure of the alloy before ageing treatment. The phase with lath-like morphology is present in the matrix in Fig. 2a. The diffraction patterns (b) and (c) were taken from the matrix and lath-like phase, respectively. The pattern (b) is indexed by an fcc lattice with a reported lattice parameter of cubic zirconia with fluorite structure [14]. The pattern (c) is very similar to (b), but forbidden reflections in the fcc lattice appear in (c). This fact suggests that the lath-like phase has a similar crystal structure but is slightly distorted from an fcc lattice. X-ray diffraction analysis mentioned later shows that the as-melted alloy is composed of cubic phase (c-phase) and tetragonal phase (t-phase). It is, therefore, concluded that the lath-like phase in Fig. 2a is t-phase, which has a lattice parameter very close to that of the c-phase. More details on the structure will be reported in a separate paper.

Fig. 3 shows the change in microstructure of the alloy with ageing at 1500° C. Ageing for 10 min results in the generation of faint dark and bright contrast, as seen in Fig. 3a. The regularly-spaced dark and bright lamellae, which is usually termed modulated structure, are more clearly found by ageing for 20 h (Fig. 3b). The ageing treatment leads to the peak hardness at the temperature. The result indicates that the hardness increase due to ageing is associated with the development of modulated structure. Fig. 3c is the structure of the overaged state, in which the modulated structure has disappeared and the tetragonal particles with an ellipsoidal shape are precipitated in the matrix. The morphology of tetragonal particles resembles that precipitated in Mg-PSZ [16]. Unidentified contrast was found in the cubic matrix in the overaged alloy.

Fig. 4 shows the modulated structure formed at 1500 and 1400° C. The lamella width decreases with decreasing ageing temperature. The modulated structure was found to be developed between 1600 and 1400° C, but not formed at 1700° C.

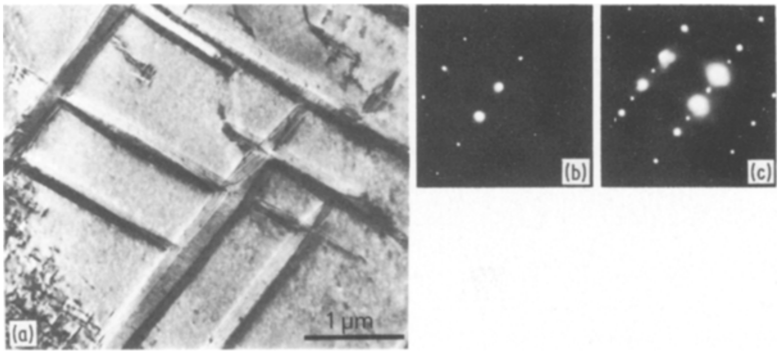

Figure 2 Microstructure of the arc-melted alloy without heat treatment (a). The diffraction patterns (b) and (c) were taken from matrix and lath-like phase, respectively. Note that the forbidden reflections in the fcc lattice appear in (c) but not in (b).

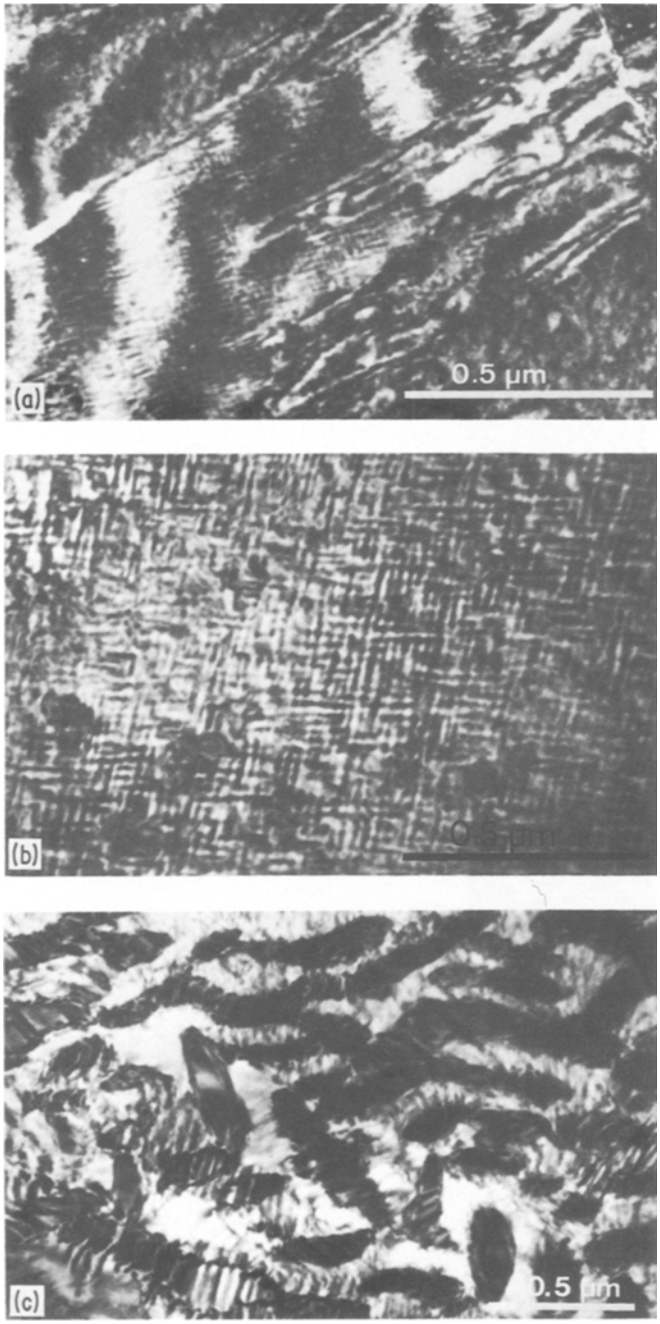

Figure 3 Change in microstructure during ageing at 1500° C. The ageing was made for (a) 10 min, (b) 20 h and (c) 200 h, respectively.

Fig. 5 shows the microstructure of the alloy aged at 1700° C for 1 h, which is the ageing time to get a peak hardness at the temperature. Plate-shaped precipitates, probably t-phase, are formed in cubix matrix. Some of the plate-shaped precipitates are inclined to the foil plane, showing the displacement fringe contrasts [17]. It has been verified in a number of solid–solid interfaces that the broad face of plate-shaped precipitates is coherent or semi-coherent and has a low interfacial energy [18]. The strain field is developed around the edge of coherent, plate-shaped precipitates, which induces dislocations at the periphery of the broad face during the growth of precipitates. Dislocations connected with precipitates in the cubic matrix in Fig. 5 are probably formed for relieving the strain field around the precipitates. It was found that a prolonged ageing resulted in a coherency

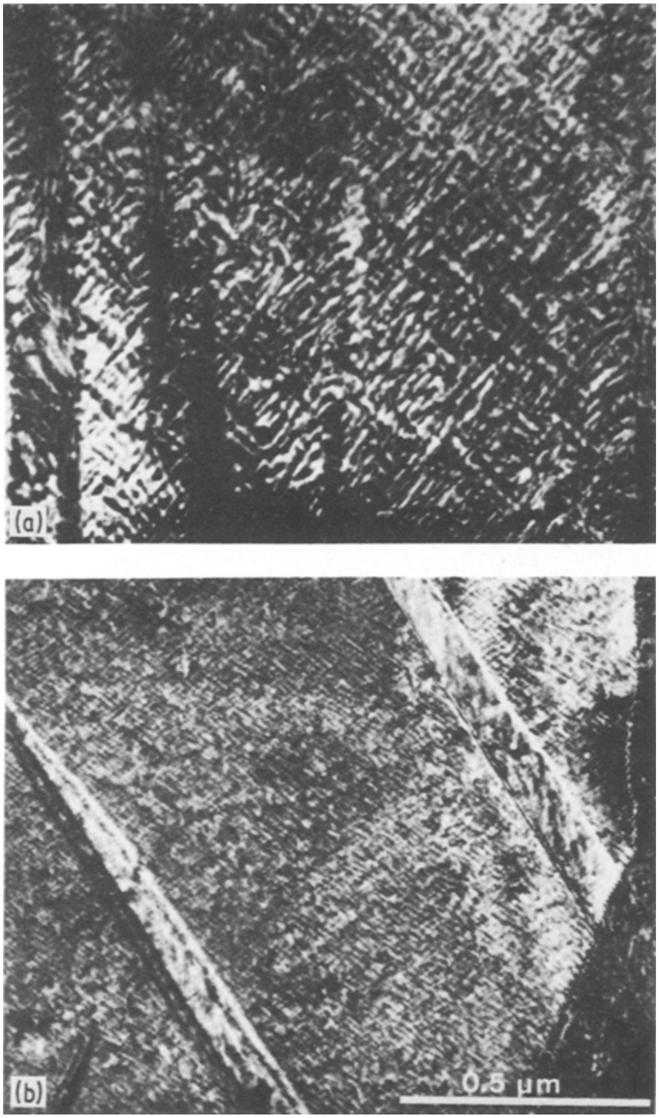

Figure 4 Modulated structure formed at (a) 1500° C and (b) 1400° C. The width of dark and bright lamellae changes with ageing temperature. Ageing time; 20 h.

loss of precipitates and a change in morphology from plate-shaped to ellipsoidal ones.

3.3. X-ray diffraction studies

Crushed powders of heat-treated specimens were examined by X-ray diffractometer at room temperature. Fig. 6 shows the X-ray intensity profiles around the 400 reflection of the cubic phase in (a) an as-melted specimen and (b) an aged specimen treated at 1500° C for 20 h. As can be seen from Fig. 3b, the modulated structure is formed by the ageing. In Fig. 6a, the peaks from c- and t-phases are separated, showing that the as-melted alloy is composed of the two phases, in agreement with electron microscopy. The peak becomes broad and the separation of peaks from c- and t-phases is not clear in the aged specimen in Fig. 6b. The broadening of the X-ray intensity profile by ageing is discussed in a later section.

Discussion

4.1. Nature of the modulated structure

Marder *et al.* have found that the tetragonal precipitates aligned in the ⟨100⟩ direction of the cubic matrix lead to a tweed-like contrast in aged ZrO_2–CaO alloy [13]. The contrast formed by the aligned precipitates is similar to the modulated structure. However, the detailed examination revealed that the modulated structure in the present alloy was not from closely-spaced precipitates

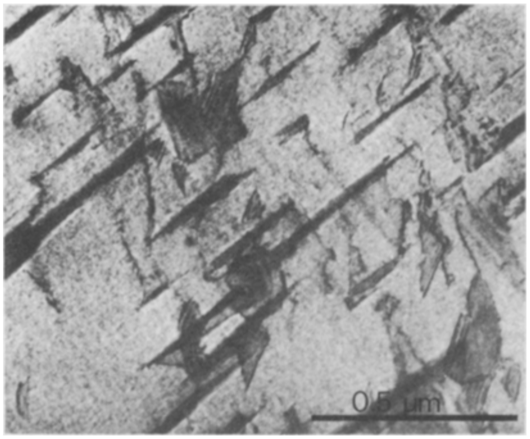

Figure 5 The microstructure of the alloy aged at 1700° C for 1 h. Modulated structure was not found at the ageing temperature. Plate-shaped precipitates and dislocations are seen.

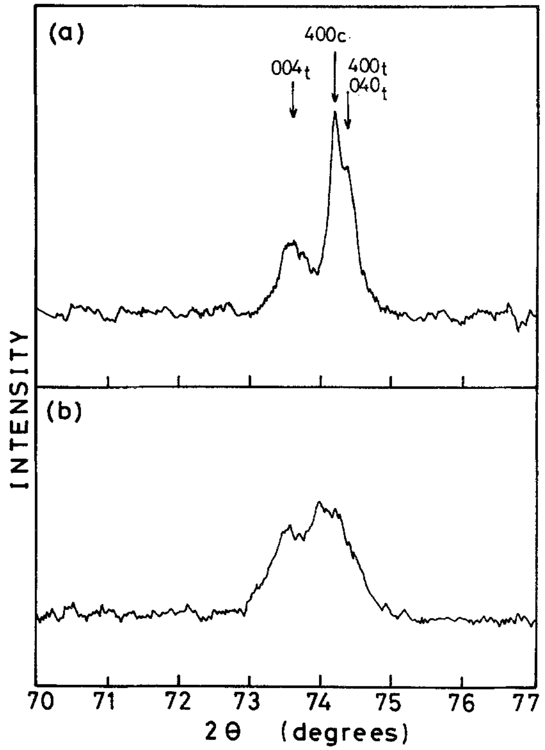

Figure 6 X-ray intensity profile around 400 peak of cubic zirconia. The profiles are obtained in the alloy without heat treatment after arc-melting (a) and the alloy aged at 1500° C for 20 h (b). Subscripts t and c in the figure shown the tetragonal and cubic phases, respectively.

but resembled the structure of spinodally-decomposed metallic alloys [19–23] or ceramics [24, 25]. It is known that the spinodal decomposition occurs inside the coherent spinodal curve by a continuous process when the two phases have the same crystal structure or only a slightly different structure [20]. The modulated structure in the ZrO_2–Y_2O_3 alloy was found in a region inside the cubic/tetragonal two-phase region, in agreement with the theory of spinodals [19, 20]. The coherent spinodal curve is expected to be inside the two-phase region in the ZrO_2–Y_2O_3 system. It is noted that the spinodal curve is inside the region of two phases, which have a slightly different crystal structure. Although such a decomposition is predicted by the theory [20], the spinodal decomposition is usually found when the two phases have the same crystal structure with a different composition [24, 25]. In yttria-stabilized PSZ (Y-PSZ), the tetragonality of the t-phase is very small and the t-phase has a very similar crystal structure to the c-phase [12]. It has also been pointed out that the tetragonal distortion of cubic crystals plays an important role in the spinodal decomposition of two cubic phases [26]. The distortion is produced to accommodate the misfit strain which is induced for maintaining the continuity of crystals with different lattice parameters [26]. It is, therefore, likely that the spinodal decomposition takes place in a region inside the cubic/tetragonal two-phase region in the ZrO_2–Y_2O_3 system.

The spinodal decomposition is also characterized by compositional fluctuation along a particular crystallographic direction [20]. The broad X-ray intensity profile from the aged alloy with modulated structure in Fig. 6b is expected from the continuous change in lattice parameter, i.e. compositional fluctuation as found in spinodally-decomposed TiO_2–SnO_2 [27]. Although the characteristic satellite reflections were not clearly found, the X-ray diffraction data supports the view that the modulated structure observed in the present alloy is associated with compositional fluctuation developed by spinodal decomposition.

4.2. Crystallographic direction of compositional fluctuation

Fig. 7 shows the modulated structure taken in the beam direction close to [001] in the cubic lattice. The direction of dark and bright lamellae is not parallel to the [100] or [010] direction, being different from the modulated structure in TiO_2–SnO_2 [24, 25]. The structure was taken in various beam directions to determine the direction of compositional fluctuation, which is in the "normal"

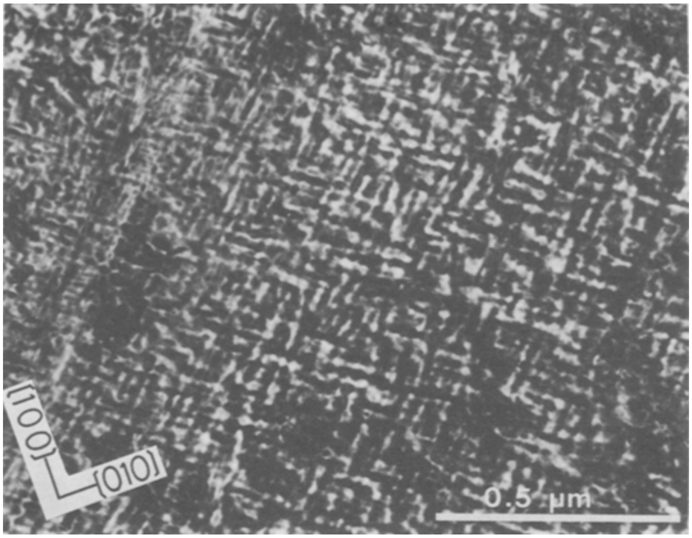

Figure 7 Modulated structure taken in the beam direction close to [001] in the cubic phase. Image rotation with respect to diffraction pattern was carefully corrected. The direction of dark and bright lamellae is not parallel to the [100] or [010] directions. Ageing treatment; 1500° C, 20 h.

direction of each lamella in modulated structure. The normal direction was determined by conventional trace analysis [17, 28], and the result is shown in the standard stereographic triangle in Fig. 8. The great circles, which include the normal direction, intersect in the (111) pole of cubic lattice. The result means that the compositional fluctuation is in the ⟨111⟩ direction of the c-phase. It has theoretically been clarified that the spinodal decomposition occurs in a particular crystallographic direction, being dependent on the anisotropy constant of the crystals [20],

$$A = \frac{2C_{44}}{(C_{11} - C_{12})} \quad (1)$$

where C_{11}, C_{12} and C_{44} are the elastic stiffnesses. The ⟨100⟩ becomes the soft direction if A is larger than unity, and the ⟨111⟩ is the soft direction if A is less than unity in cubic crystals. The compositional fluctuation is developed in a soft direction of crystals to minimize the elastic strain energy during decomposition. Table I shows the elasticity data of cubic zirconia [29]. The value of A is calculated to be 0.31 to 0.37 in cubic zirconia with yttria content between 8 and 12 mol %. The ⟨111⟩ direction is, therefore, the soft direction in cubic zirconia and the compositional fluctuation is likely to occur in the direction experimentally confirmed in the present alloy. The result also seems reasonable from the theory of spinodal decomposition [20].

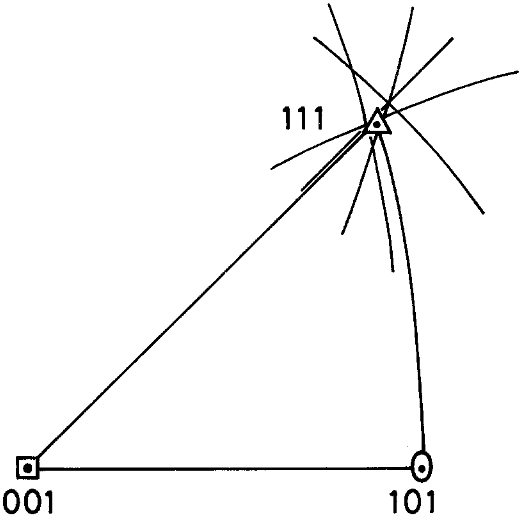

Figure 8 Standard stereographic triangle showing the normal direction of dark and bright lamellae in the modulated structure. Part of great circles including the normal direction are shown on the triangle. Great circles intersect along the (111) pole showing that the normal direction is close to the ⟨111⟩ in cubic crystal.

4.3. Wavelength

It has theoretically been predicted that the wavelength of spinodal, λ, is a function of undercooling ΔT [20]. Fig 9 is the log–log plot of wavelength

TABLE I Elasticity data for cubic zirconia [29] (all values in GPa)

mol % Y_2O_3	C_{11}	C_{44}	C_{12}	A
8	394	56	91	0.37
10.3	403	58	83	0.36
12	449	62	55	0.31

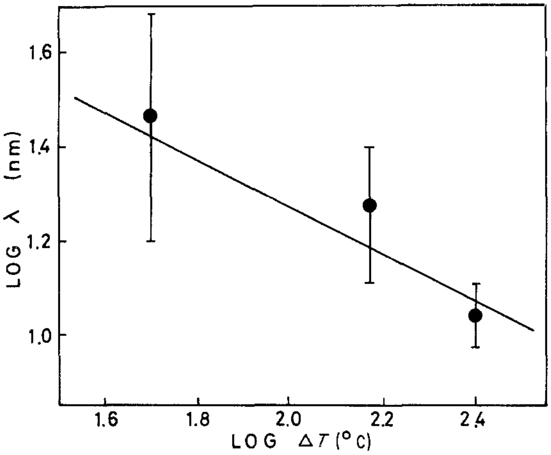

Figure 9 Log–log plot of wavelength of modulated structure and undercooling (see text).

of modulated structure and undercooling. The wavelength, which is twice as large as the width of the dark and bright lamellae in the modulated structure, was estimated at the ageing time of 20 h at each temperature. The spinodal temperature of the alloy was assumed to be 1650° C. The data in Fig. 9 show a considerable scatter, especially at high temperature, probably due to a change in wavelength with ageing time [24]. However, the average values are satisfactorily expressed by a straight line, which has a slope of $-1/2$, as theoretically predicted for an early stage of spinodal decomposition [20].

4.4. Relationship between hardness and microstructure

As found in earlier works [2, 5], PSZ has an age-hardening or age-toughening character. The present result shows that the development of modulated structure causes a hardening of Y-PSZ by ageing. The hardening caused by modulated structure is larger than the precipitation hardening by tetragonal particles in the cubic matrix. On the other hand, Porter and Heuer have clarified that the increase in bend strength and fracture toughness of aged Mg-PSZ is related to the volume fraction and coherency of tetragonal precipitates [5]. They have reported that the peak strength and toughness are obtained by the precipitation of maximum volume fraction of t-phase in the cubic matrix and the loss of coherency of precipitates caused by their growth is associated with overageing. The spinodal decomposition may not occur in Mg-PSZ, and the strengthening mechanism during ageing may be different between Y-PSZ and Mg-PSZ in spite of the fact that the $ZrO_2-Y_2O_3$ and ZrO_2-MgO systems have a similar phase diagram [14, 15, 30]. Further detailed works are required to make clear the relationship between microstructure and mechanical properties of PSZ.

5. Conclusion

The change in microstructure during ageing of ZrO_2–5.2 mol% Y_2O_3 alloy was examined. It was found that the modulated structure was developed in an early stage of ageing in a temperature range between 1400 and 1600° C. The modulated structure is associated with the compositional fluctuation in the elastically-soft ⟨1 1 1⟩ direction of the cubic phase, which is produced by spinodal decomposition. No decomposition was found by ageing at 1700° C. It is expected that the coherent spinodal curve is inside the cubic/tetragonal two-phase region. The development of modulated structure results in a larger hardening than the precipitation of t-phase in the cubic matrix.

Acknowledgements

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