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Transformation of yttria partially stabilized zirconia by low temperature annealing in air

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The tetragonal-to-monoclinic phase transformation of yttria partially stabilized zirconia by low temperature annealing in air was investigated in the temperature range 100 to 650° C using a sintered body of zirconia containing 2 to 4 mol% Y_2O_3. The amount of monoclinic phase formed was maximum at about 200° C. Both the decrease in grain size and increase in the yttria concentration were effective in decreasing the critical temperature below which the monoclinic phase was formed. The relationship between the critical temperature (T_c) and the grain size was experimentally determined.

1. Introduction

Recently, partially stabilized zirconia has been given attention because of its high strength and high fracture toughness. Stress induced transformation of the tetragonal phase zirconia to the monoclinic one is believed to increase the fracture toughness [1, 2]. Therefore, the retention of the tetragonal phase zirconia at room temperature is essential for toughening brittle materials based on zirconia. However, it has been reported that the tetragonal phase on the surface of partially stabilized zirconia rapidly transforms to the monoclinic phase by low temperature annealing at 200 to 300° C, and both fracture strength and fracture toughness greatly decrease [3–5]. In the previous study [5], we reported that both decreasing the grain size and dispersing the alumina in yttria partially stabilized zirconia are quite effective in resisting the tetragonal-to-monoclinic phase transformation. It would be instructive to determine the thermodynamic conditions to retain the tetragonal phase. In the present study, the phase transformation of yttria partially stabilized zirconia ceramics containing different concentrations of yttria and having different grain sizes was investigated. From the experimental results, both grain size and yttria content dependences of the critical temperature (T_c) were calculated.

2. Experimental procedure

Zirconia powders containing 2, 3, and 4 mol% yttria supplied from Toyo Soda Co, Ltd designated ZrO_22Y, ZrO_23Y, and ZrO_24Y, were used as the starting materials. Zirconia (yttria) powders were uniaxially pressed by 1000 kg cm^{-2} to form pellets, 5 mm diameter and 5 mm thick, then sintered at 1000 to 1600° C for 3 h in air. The pellets fabricated were placed in an electric furnace at the desired temperature and were withdrawn at regular time intervals. The bulk density of the sintered bodies was measured by Archimedes' technique. The bulk density of porous specimens was determined by coating the surfaces with dibutylhydroxyltoluene. The phases were identified by X-ray diffraction analysis. A scan of 2θ between 27 and 33° C was conducted to estimate the monoclinic/(tetragonal + cubic) zirconia ratio [6], and the scan between 55 and 62° C was used to confirm the presence of the tetragonal and/or the cubic phase. Average grain sizes were determined on scanning electron micrographs of the fracture surface by the intercept method [7]. Microstructures of the

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TABLE I Characteristics of as-sintered materials

Sintered body	Sintering temperature (°C)	Crystalline phase*	Grain size (μm)	Relative density (%)	Monoclinic ZrO_2 (mol%)	
					As-sintered	Annealed at 200° C for 50 h
$ZrO_2$2Y	1000	m + t	0.22	55.5	28.5	28.5
	1200	t	0.40	90.7	0	88.1
	1400	t	0.49	97.4	0	73.2
	1450	t	0.61	98.4	0	78.7
	1500	t	0.72	99.6	0	85.7
	1600	t	1.55	99.2	0	96.9
$ZrO_2$3Y	1400	t	0.45	98.2	0	0
	1450	t	0.59	98.9	0	6.7
	1500	t	0.66	99.3	0	23.4
	1600	t	1.10	99.9	0	72.4
$ZrO_2$4Y	1400	t + c	0.34	98.0	0	0
	1450	t + c	0.44	98.0	0	0
	1500	t + c	0.64	98.7	0	4.7
	1550	t + c	0.75	98.8	0	38.2
	1600	t + c	1.08	98.8	0	44.3

*m, monoclinic; t, tetragonal; c, cubic.

cut surface of an annealed sample were observed by electron probe microanalysis (EPMA).

3. Results and discussion

3.1. Characteristics of as-sintered materials

The phase, grain size and relative density of as-sintered bodies and the amount of monoclinic phase on the surface of zirconia ceramics both before and after annealing at 200° C for 50h are summarized in Table I.

As is expected from the phase diagram of the ZrO_2–Y_2O_3 system [8, 9], phases of $ZrO_2$2Y and $ZrO_2$3Y ceramics, except $ZrO_2$2Y sintered at 1000° C, were fully tetragonal phase, and $ZrO_2$4Y was composed of a mixture of the tetragonal and the cubic phases. The microstructure of each sintered body was composed of the uniform grain size as listed in Table I. Relative densities of sintered bodies were easily achieved to more than 97% of the theoretical density by sintering for 3 h above 1400° C. As seen in Table I, it is noticeable that no monoclinic phase was formed by 200° C annealing for the sintered bodies of $ZrO_2$2Y, $ZrO_2$3Y and $ZrO_2$4Y sintered at 1000, 1400 and 1450° C, respectively.

3.2. EPMA-SEM image of the annealed ZrO_2

$ZrO_2$3Y fabricated at 1600° C was annealed at 200° C for 50 h. From the results of X-ray diffraction analysis for the surface of annealed $ZrO_2$3Y specimens, the formation of both monoclinic and cubic phases of zirconia was found. The EPMA–SEM image of the cut surface of the annealed $ZrO_2$3Y is shown in Fig. 1. As seen in this figure, the monoclinic and cubic phases of zirconia were formed on the surface and invaded the inside of the body accompanied by microcracks. The present authors observed that water and some nonaqueous solvents accelerate the growth of pre-existing flaws on the surface to release the surface strain, which stabilizes the tetragonal

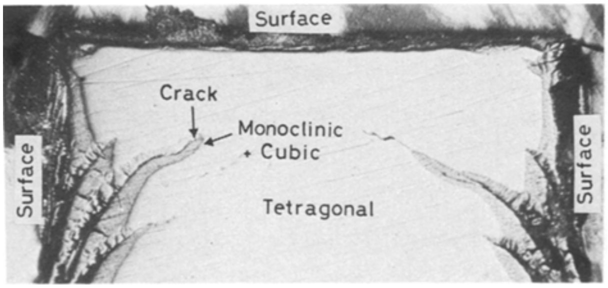

Figure 1 EPMA-SEM image of the cut surface of $ZrO_2$3Y annealed at 200° C for 50 h.

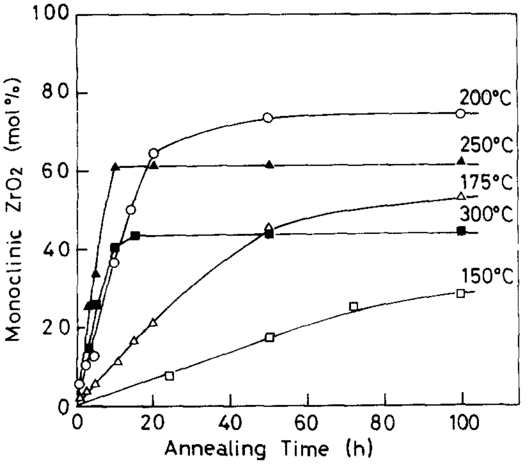

Figure 2 Relationship between the amount of the monoclinic phase and annealing time for ZrO_23Y fabricated at 1600° C.

phase, and consequently accelerates the tetragonal-to-monoclinic phase transformation [10]. Furthermore, the rate of the tetragonal-to-monoclinic phase transformation was very slow, when ZrO_23Y was annealed under vacuum. Therefore, the trace amount of water contained in air might play a significant role in the phase transformation.

3.3. Annealing of ZrO_2 ceramics at different temperature conditions

A series of experiments was conducted in which ZrO_23Y ceramics were annealed over the temperature range 150 to 300° C. The relationship between the amount of monoclinic phase formed on the surface and the annealing time is shown in Fig. 2. As seen in Fig. 2, equilibrium was attained within 50 h above 200° C, but was not attained even after 100 h below 175° C. The reason why the equilibrium rate decreased with decreasing annealing temperature, even though the tetragonal-to-monoclinic phase transformation was considered to be martensitic, might be due to the transformation rate being controlled by the rate of release of the surface strains. On the other hand, the decrease of the amount of monoclinic phase formed above 200° C might be attributed to the thermodynamics of the zirconia and that the tetragonal phase is stable at higher temperature [8, 9].

The ceramics of ZrO_22Y, ZrO_23Y and ZrO_24Y fabricated above 1400° C were annealed under various temperature conditions for 50 h. The results are shown in Fig. 3. It is noticeable that the amount of monoclinic phase formed and the critical temperature (T_c), below which the monoclinic phase was formed, decreased with decreasing sintering temperature. No monoclinic phase was formed in samples of ZrO_23Y and ZrO_24Y fabricated below 1400 and 1450° C, respectively.

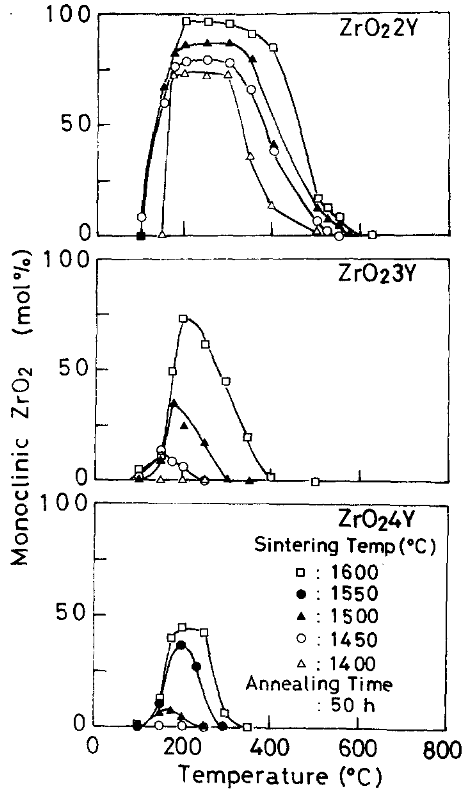

Figure 3 Relationship between the amount of the monoclinic phase and annealing temperature.

These results may be due to the effect of the surface energy of the grain, remembering that the grain size was smaller at lower sintering temperature, i.e. the free energy change of the tetragonal-to-monoclinic transformation ($\Delta G_{t\rightarrow m}$) can be described by Equation 1 [11],

$$\begin{aligned}\Delta G_{t\rightarrow m} &= (G_c^m - G_c^t) + (G_{se}^m - G_{se}^t) \\ &\quad + (G_s^m - G_s^t) \\ &= \Delta G_c + \Delta G_{se} + \Delta G_s \qquad (1)\end{aligned}$$

where G_c^m and G_c^t, G_{se}^m, and G_{se}^t, and G_s^m and G_s^t are the chemical free energies, the strain free energies and the surface free energies in the monoclinic and the tetragonal states. Since the surface free energy of the tetragonal phase is less than that of the monoclinic phase [12], the surface free energy change (ΔG_s) is always positive, and is

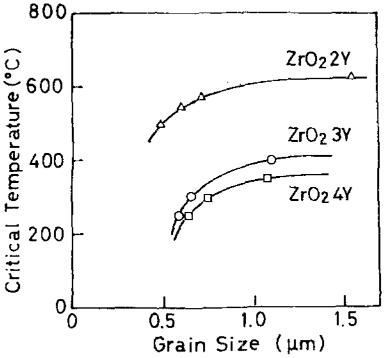

Figure 4 Relationship between the critical temperature and grain size.

inversely proportional to the grain size as given by Equation 2,

$$\Delta G_s = (A_m\gamma_m - A_t\gamma_t)/V = 6(\gamma_m - g_s\gamma_t)/d \qquad (2)$$

where A_m and A_t are the interfacial surface areas, γ_m and γ_t are the specific interfacial surface energies in the monoclinic and the tetragonal states, $V(V = \pi d^3/6)$ is the transformed volume, d is the diameter of the transformed grain and $g_s = A_t/A_m$. Therefore, the resistance to the phase transformation increases with decreasing the grain size. The critical temperatures (T_c) shown in Fig. 3 are replotted against the grain size in Fig. 4. It is obvious that the critical temperature (T_c) decreased rapidly with decreasing the grain size, especially below a grain size of 1.0 μm. Assuming that the value of ΔG_{se} is zero at equilibrium condition, Equation 1 can be expressed as

$$\Delta G_c + 6(\gamma_m - g_s\gamma_t)/d = 0 \qquad (3)$$

If the chemical free energy change and the surface energies are expressed as a function of temperature by Equations 4, 5 and 6 [13], and if ΔH_{c298} is not zero, Equation 3 can be expressed as Equation 7, in which we obtain the relationship between the critical temperature (T_c) and the grain size,

$$\Delta G_c = \Delta H_{c298} - T\Delta S_{c298} \qquad (4)$$

$$\gamma_m = \gamma_m^{\circ} - \Gamma_m T \qquad (5)$$

$$\gamma_t = \gamma_t^{\circ} - \Gamma_t T \qquad (6)$$

$$T_c = (d - B)/(dA + C) \qquad (7)$$

where ΔH_{c298} is the standard enthalpy change, ΔS_{c298} the standard entropy change, γ_m° and γ_t° are the surface energies at 0 K, Γ_m and Γ_t are constants, T is the absolute temperature, $A = \Delta S_{c298}/\Delta H_{c298}$, $B = -6(\gamma_m^{\circ} - g_s\gamma_t^{\circ})/\Delta H_{c298}$ and $C = 6(\Gamma_m - g_s\Gamma_t)/\Delta H_{c298}$. Note that Equation 7 can be used only when $dA > C$. The constants of A, B and C determined using the values of T_c and d shown in Fig. 4, and the values of d corresponding to $T_c = 298$ K are listed in Table II. These results indicate that if the grain sizes of $ZrO_2$2Y, $ZrO_2$3Y and $ZrO_2$4Y ceramics were less than 0.38, 0.50 and 0.53 μm, respectively, the tetragonal phase in those ceramics might be thermodynamically stable above 298 K. The present calculation results are consistent with experimental results in that no monoclinic phase was formed by annealing the ceramics of $ZrO_2$2Y, $ZrO_2$3Y and $ZrO_2$4Y having grain sizes of 0.22, 0.45 and 0.44 μm, respectively (see Table I and Fig. 3). Using the values listed in Table II, it is possible to construct a modified phase diagram indicating whether or not the tetragonal-to-monoclinic phase transformation would occur from the surface of the sintered body. The relationship between the critical temperature and the concentration of yttria as a function of grain size is shown in Fig. 5. The values calculated were in good agreement with the experimental values. It is noticeable that both decreasing the grain size and increasing the yttria concentration are very effective in decreasing the critical temperature.

4. Conclusions

1. The tetragonal phase on the surface of partially stabilized zirconia ceramics transformed to the monoclinic and cubic phases by annealing in the temperature range 150 to 600° C.

2. Decreasing the grain size and increasing the yttria concentration are useful for decreasing the critical temperature below which the monoclinic phase is formed.

TABLE II Values of constants in Equation 7 and the grain sizes corresponding to $T_c = 298$ K

Concentration of of Y_2O_3 (mol %)	A (10^{-3} K^{-1})	B (μm)	C (10^{-4} μm K^{-1})	d(μm) ($T_c = 298$ K)
2	1.10	0.369	−3.85	0.378
3	1.37	0.467	−5.70	0.503
4	1.50	0.477	−6.41	0.514

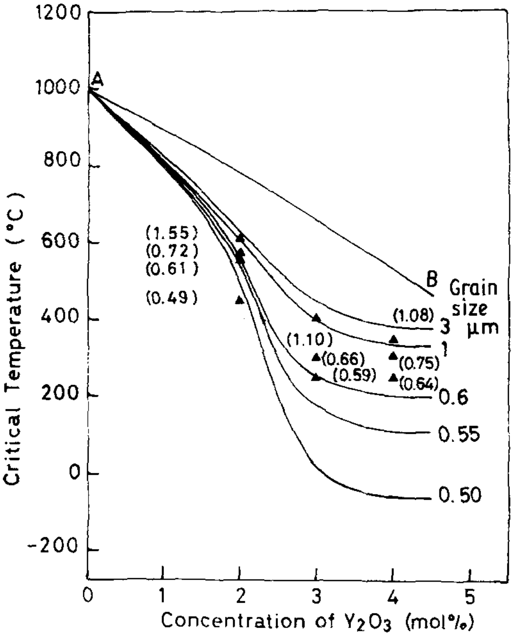

Figure 5 Relationship between the critical temperature and concentration of yttria as a function of the grain size. ——, Calculated value: △, experimental value, the values in parentheses are the grain sizes (µm): line AB, Pascual and Duran [9].

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