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Improvement of Thermal Stability of Yttria-Doped Tetragonal Zirconia Polycrystals by Alloying with Various Oxides

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SUMMARY

Yttria-doped tetragonal zirconia polycrystals doped with 0–12 mol% of CaO, MgO, CeO_2 and TiO_2 were sintered at 1400–1600°C for 3 h, and the mechanical properties and thermal stability of the sintered bodies were evaluated. The degree of the tetragonal-to-monoclinic phase transformation by annealing in humid air or hot water decreased with both increasing amounts of CeO_2 or TiO_2 and decreasing grain size of ZrO_2. Alloying with TiO_2 accelerated the grain growth and depressed densification, but alloying with less than 6 mol% of CeO_2 caused no significant changes in grain size and mechanical properties.

1. INTRODUCTION

Partially stabilized zirconia has excellent mechanical properties such as high strength and high fracture toughness. The martensitic phase transformation from the metastable tetragonal to the stable monoclinic phase is believed to relieve the fracture stress in the vicinity of a crack front.[1-3] Therefore, it is essential to retain the tetragonal phase at room temperature subsequent to sintering to obtain high strength and tough zirconia ceramics. Maximum strength and toughness have been attained with fully tetragonal zirconia polycrystals (TZP), fabricated by doping with 2–3 mol% of Y_2O_3.[3] However, it has been reported that both the strength and the fracture toughness of Y-TZP were greatly degraded by annealing at low temperatures (150–300°C) in air.[4] The loss of fracture

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toughness and strength by annealing is caused by the formation of microcracks accompanying the tetragonal-to-monoclinic phase transformation, which starts from the surface and is particularly enhanced in the presence of water.[5-9] The free energy change of the tetragonal-to-monoclinic phase transformation ($\Delta G_{t \to m}$) can be described by

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

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 of the monoclinic and tetragonal phases, respectively. It is expected that the tetragonal-to-monoclinic phase transformation can be controlled by increasing ΔG_c, ΔG_{se} and ΔG_s. It was reported that the degree of the phase transformation depended on the Y_2O_3 content, grain size, etc.; the rate of the phase transformation actually decreased[5-7] with increasing Y_2O_3 content, dispersing Al_2O_3 and decreasing the grain size of ZrO_2.[5-9] It should be noted, however, that increasing the thermal stability sometimes results in loss of strength and fracture toughness, i.e. increasing the Y_2O_3 content to more than 4 mol% prevents the phase transformation during low temperature annealing but causes a significant loss in the fracture toughness.[3] In the present study, Y-TZP doped with various amounts of CaO, MgO, CeO_2 and TiO_2 were fabricated and the characteristics of the sintered bodies such as thermal stability and mechanical properties were evaluated.

2. EXPERIMENTAL

Zirconia powders containing 0, 2, 3, 4 and 6 mol% of Y_2O_3 were supplied by Toyo Soda Co. Ltd. All other chemicals were of analytical grade and were used without further purification. Starting powders were prepared by mixing $ZrO_2(Y_2O_3)$ powders and CaO, MgO, CeO_2 and TiO_2 powders by ball milling with plastic balls in a plastic container in acetone; all powders were then dried. The powders were uniaxially pressed at 100 MPa to form pellets, 5 mm in diameter and 5 mm in thickness, and then sintered at 1400, 1450, 1500 and 1600°C for 3 h in air. The sintered bodies were annealed in a stream of humid air at 100–400°C for 50 h or in water at 130°C for 7 days. The partial pressure of water in air was adjusted to 1·54 and 3·35 kPa by bubbling air through the saturated aqueous solutions of $Ca(NO_3)_2 . 4H_2O$ at 25°C and distilled water at 25°C, respectively.

The phases in the surface of the sample were identified by X-ray diffraction analysis using Ni-filtered Cu–Kα radiation. Scans of 2θ between

27° and 33° were conducted to estimate the monoclinic to (tetragonal + cubic) zirconia ratio, and those between 55° and 62° were used to discriminate between the tetragonal and cubic phase. The bulk density of the sintered bodies was measured by Archimedes' technique. The average grain size was determined from scanning electron micrographs of the fracture surface using the intercept method.[10] Vickers microhardness (H_v) was measured by Vickers indentation with loads from 2 to 5 N. Young's modulus (E) was determined by Knoop indentation with loads of 5 N. Fracture toughness (K_{IC}) was measured using the indentation technique[11] at loads from 10 to 20 N.

3. RESULTS AND DISCUSSION

3.1. Characteristics of as-sintered materials

The phase, grain size, relative density and mechanical properties of as-sintered bodies of ZrO_2–3 mol% Y_2O_3 alloyed with various amounts of CaO, MgO, CeO_2 and TiO_2 sintered at 1500°C for 3 h in air are summarized in Table 1 and Fig. 1. The phases of zirconia in ZrO_2–3 mol% Y_2O_3 alloyed with CeO_2 and TiO_2 were fully tetragonal and those in ZrO_2–3 mol% Y_2O_3 alloyed with CaO and MgO were mixtures of tetragonal

TABLE 1
Phase, Grain Size and Relative Density of As-sintered Bodies of ZrO_2–3 mol% Y_2O_3 Ceramics Alloyed with Various Oxides Sintered at 1500°C for 3 h

Additive	*Content/mol%*	*Phase*[a]	*Grain size/μm*	*Relative density/%*
None	—	t	1·1	99·0
	—	t	0·8	99·3
TiO_2	2	t	2·4	98·1
	5	t	5·1	98·4
	10	t	10·6	96·5
CeO_2	2	t	1·1	99·7
	5	t	1·3	99·3
	10	t	1·4	99·0
CaO	2	t + c	0·5	99·0
	4	t < c	0·5	98·4
	6	t ≪ c	—	95·4
MgO	2	t + c	0·9	98·3
	4	t < c	—	98·5
	6	t ≪ c	—	96·3

[a] t: tetragonal, c: cubic.

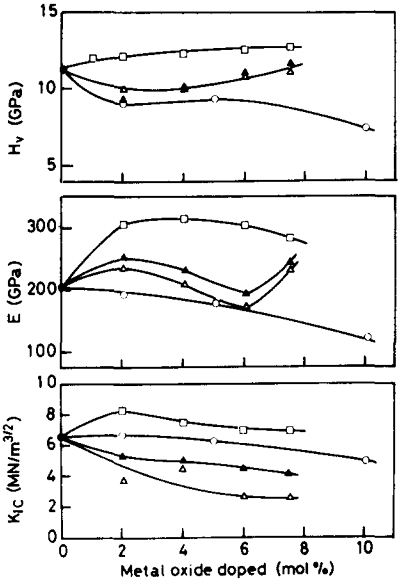

Fig. 1. Vickers microhardness, Young's modulus and fracture toughness of ZrO_2–3 mol% Y_2O_3 ceramics alloyed with various oxides. Metal oxide: CeO_2, □; TiO_2, ○; MgO, ▲; CaO, △.

and cubic. Alloying with CeO_2 resulted in no significant difference in the relative density and grain size, but the values of H_v, E and K_{IC} increased a little. Alloying with TiO_2 resulted in a great increase of grain size and a decrease of relative density. It caused no significant change in K_{IC}, but the values of H_v and E decreased. Alloying with CaO and MgO degraded the value of K_{IC} due to decreasing the tetragonal-ZrO_2 content.

3.2. Tetragonal-to-monoclinic phase transformation in $ZrO_2(Y_2O_3)$ ceramics alloyed with various oxides

ZrO_2–3 mol% Y_2O_3 ceramics alloyed with various amounts of CaO, MgO, CeO_2 and TiO_2 sintered at 1500°C for 3 h were annealed in a stream of air with a partial water vapor pressure of 1·540 kPa at 200°C for 50 h or in water at 130°C for 15–140 h. The amount of monoclinic ZrO_2 formed on the surface of the samples is shown in Figs 2 and 3. Figure 2 shows that the tetragonal-to-monoclinic phase transformation was depressed with increasing amounts of metal oxides added. However, the mechanism controlling the phase transformation seemed to be different. Since no decrease in the rate of the phase transformation to attain equilibrium was found in the ZrO_2–3 mol% Y_2O_3 ceramics alloyed with CaO and MgO, the depression of the phase transformation might be attributed to the

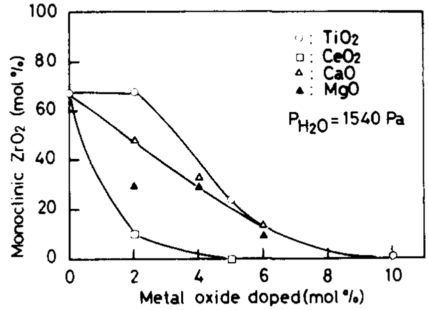

Fig. 2. Amount of monoclinic ZrO_2 formed in ZrO_2–3 mol% Y_2O_3 ceramics alloyed with various oxides by annealing in humid air at 200°C for 50 hours.

smaller amount of the tetragonal-ZrO_2 content in the sintered bodies. It should be noted that the cubic-ZrO_2 content increased with increasing amounts of CaO and MgO added. On the other hand, since ZrO_2–3 mol% Y_2O_3 ceramics alloyed with CeO_2 and TiO_2 were composed entirely of the tetragonal phase as listed in Table 1, CeO_2 and TiO_2 seem to stabilize the tetragonal phase. CeO_2 appeared to be the best oxide for stabilizing the tetragonal ZrO_2 because it caused no significant degradation in sinterability and mechanical properties.

ZrO_2–3 mol% Y_2O_3 ceramics alloyed with various amounts of CeO_2 were sintered at 1400, 1450, 1500 and 1600°C for 3 h to fabricate sintered bodies having different grain sizes. The sintered bodies were annealed in moist air with a partial water vapor pressure of 3·35 kPa at 100–400°C for 50 h. The amount of monoclinic ZrO_2 formed on the surface of the sample is shown in Fig. 4 as a function of annealing temperature. The amount of monoclinic ZrO_2 was at a maximum around 200°C. Both the amount of

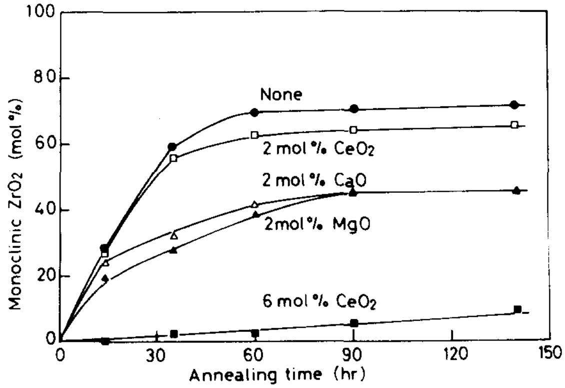

Fig. 3. Time dependence of the amount of monoclinic ZrO_2 formed in ZrO_2–3 mol% Y_2O_3 ceramics alloyed with various oxides by annealing in water at 130°C.

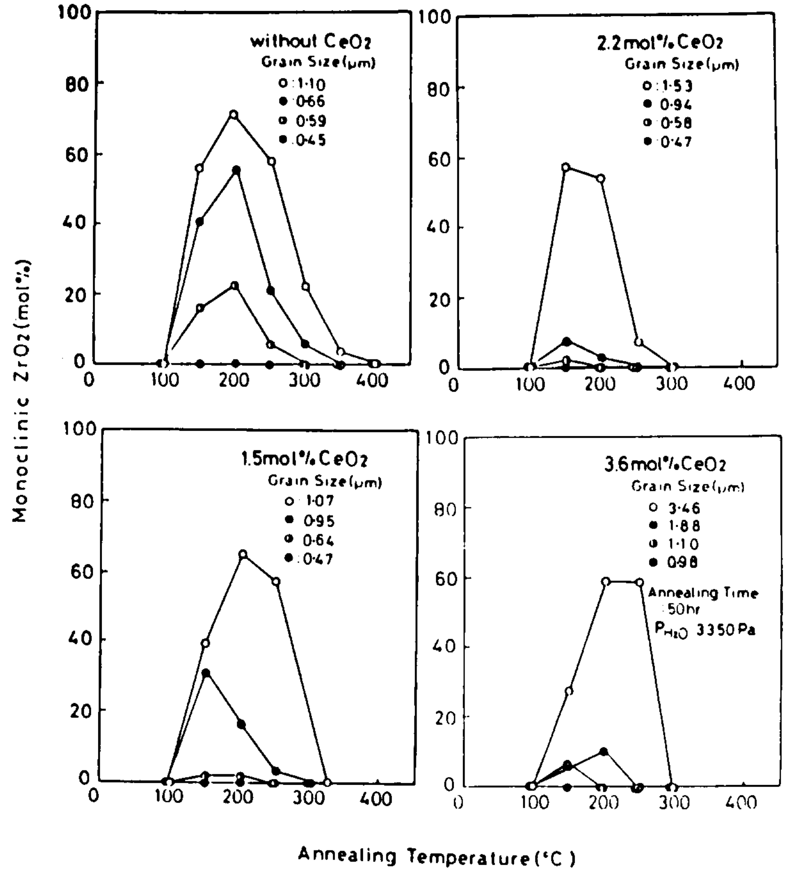

Fig. 4. Relationship between the amount of monoclinic ZrO_2 formed in ZrO_2–3 mol% Y_2O_3 ceramics alloyed with different concentrations of CeO_2 and annealing temperature as a function of grain size.

monoclinic ZrO_2 and the critical temperature (T_c), below which the monoclinic phase was formed, decreased with increasing amount of CeO_2 added and decreasing grain size, as was expected from eqn (1), i.e. ΔG_c increases with increasing amount of CeO_2 added and ΔG_s is inversely proportional to the grain size as given by eqn (2):

$$\begin{aligned}\Delta G_s &= (A_m\gamma_m - A_t\gamma_t)/V \\ &= 6(\gamma_m - g_s\gamma_t)/d \qquad (2)\end{aligned}$$

where A_m and A_t are the interfacial surface areas and γ_m and γ_t are the specific surface energies of the monoclinic and tetragonal states, respectively; $V(V = \pi d^3/6)$ is the transformed volume, d is the diameter of the transformed grain and $g_s = A_t/A_m$.

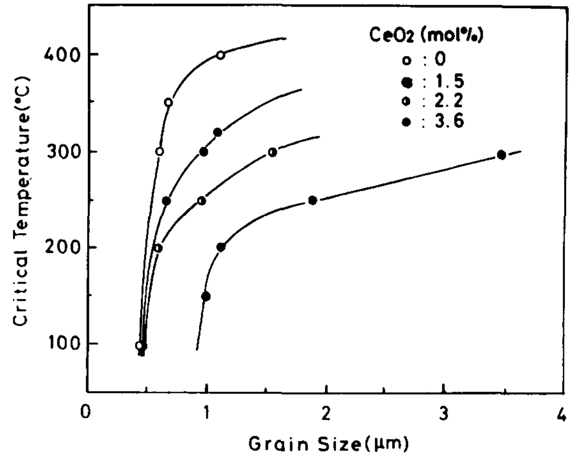

Fig. 5. Relationship between critical temperature and grain size.

By assuming that the value of ΔG_{se} is zero at equilibrium, eqn (1) can be expressed as

$$\Delta G_{\mathrm{c}} + 6(\gamma_{\mathrm{m}} - g_{\mathrm{s}}\gamma_{\mathrm{t}})/d = 0 \tag{3}$$

If ΔG_{c}, γ_{m} and γ_{t} are expressed as a linear function of temperature (eqns (4)–(6)), eqn (7) can be obtained for the relationship between T_{c} and the grain size:

$$\Delta G_{\mathrm{c}} = \Delta H_{\mathrm{c}}^{\circ} - T\Delta S_{\mathrm{c}}^{\circ} \tag{4}$$

$$\gamma_{\mathrm{m}} = \gamma_{\mathrm{m}}^{\circ} - \Gamma_{\mathrm{m}}T \tag{5}$$

$$\gamma_{\mathrm{t}} = \gamma_{\mathrm{t}}^{\circ} - \Gamma_{\mathrm{t}}T \tag{6}$$

$$\begin{aligned} T_{\mathrm{c}} &= \{d + 6(\gamma_{\mathrm{m}}^{\circ} - g_{\mathrm{s}}\gamma_{\mathrm{t}}^{\circ})/\Delta H_{\mathrm{c}}^{\circ}\}/\{d\Delta S_{\mathrm{c}}^{\circ}/\Delta H_{\mathrm{c}}^{\circ} + 6(\Gamma_{\mathrm{m}} - g_{\mathrm{s}}\Gamma_{\mathrm{t}})/\Delta H_{\mathrm{c}}^{\circ}\} \\ &= (d - B)/(dA + C) \end{aligned} \tag{7}$$

The relationship between T_{c} and the grain size is plotted in Fig. 5 and the constants A, B and C determined using the values of T_{c} and the grain size

TABLE 2

Values of Constants in Eqn (7) and the Grain Sizes Corresponding to $T_{\mathrm{c}} = 298\,\mathrm{K}$

Concentration of CeO$_2$/mol%	*A/m K^{-1}*	*B/μm*	*C/nm K^{-1}*	*d/μm* ($T_{\mathrm{c}} = 298$ K)
0	1·38	0·395	−0·474	0·431
1·5	1·55	0·387	−0·508	0·438
2·2	1·55	0·243	−0·118	0·431
3·6	1·70	0·774	−1·18	0·856

as listed in Table 2. Using these values, 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 T_c and the amount of CeO_2 in ZrO_2–3 mol% Y_2O_3 ceramics is illustrated in Fig. 6 as a function of grain size. It is seen that T_c decreases with decreasing grain size and increasing amount of CeO_2. To confirm these results, ZrO_2–3 mol% Y_2O_3 ceramics alloyed with various amounts of CeO_2 having various grain sizes were annealed in water at 100°C for 7 days; the amount of monoclinic ZrO_2 formed is shown in Fig. 7. The shaded part indicates the region where the tetragonal-to-monoclinic phase transformation did not occur at all. It is obvious that the stability of the tetragonal ZrO_2 strongly depends on both the amount of CeO_2 alloyed and the grain size, especially for grain sizes below 1 μm. It is important to note that the phase transformation is completely controlled by a grain size less than 0·4 μm without any addition of CeO_2. The thermal stability of the tetragonal phase was also evaluated by using zirconia ceramics alloyed with different concentrations of Y_2O_3 and CeO_2. The amount of the monoclinic phase formed by annealing in water at 100°C for 7 days is shown in Fig. 8. The degree of phase transformation decreased with increasing concentration of both Y_2O_3 and CeO_2, i.e. the amount of CeO_2 that could completely control the phase transformation decreased from 12 to 0 mol% on increasing the Y_2O_3 concentration from 0 to 6 mol%.

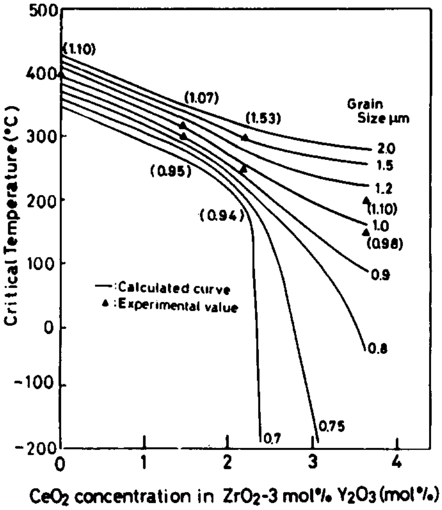

Fig. 6. Relationship between critical temperature and concentration of CeO_2 as a function of grain size.

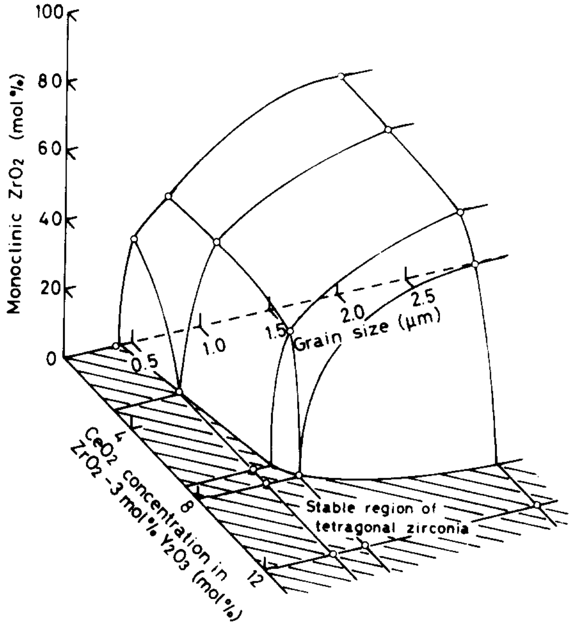

Fig. 7. Relationship of the amount of monoclinic phase formed in ZrO_2–3 mol% Y_2O_3 by annealing in water at 100°C for 7 days, grain size, and CeO_2 concentration.

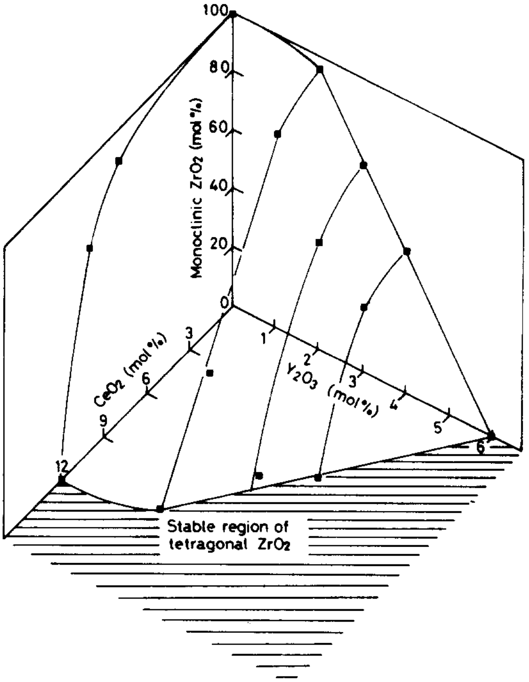

Fig. 8. Relationship of the amount of monoclinic phase formed by annealing in water at 100°C for 7 days and the concentrations of Y_2O_3 and CeO_2.

4. CONCLUSIONS

1. Alloying with TiO_2 stabilized the tetragonal-ZrO_2 phase in $ZrO_2(Y_2O_3)$ ceramics.
2. Alloying CeO_2 stabilized the tetragonal-ZrO_2 phase in $ZrO_2(Y_2O_3)$ ceramics without loss of the mechanical properties.
3. The stability of the tetragonal phase in $ZrO_2(Y_2O_3–CeO_2)$ ceramics increased with increasing amounts of Y_2O_3 and CeO_2 and decreasing grain size.

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