Control of the tetragonal-to-monoclinic phase transformation of yttria partially stabilized zirconia in hot water

T. SATO, M. SHIMADA*
Department of Applied Chemsitry, Faculty of Engineering, Tohoku University, Sendai 980, Japan

The tetragonal-to-monoclinic phase transformation of yttria partially stabilized zirconia caused by annealing in hot water was investigated in the temperature range 80 to 200° C using sintered bodies in zirconia containing 2, 3 and 4 mol % Y_2O_3. Three approaches, alloying $ZrO_2(Y_2O_3)$ with 0 to 20 wt % CeO_2, dispersing 0 to 40 wt % Al_2O_3 into $ZrO_2(Y_2O_3)$ ceramics and decreasing the grain size of zirconia, were examined to inhibit the tetragonal-to-monoclinic phase transformation. The amount of monoclinic phase formed decreased with increasing concentrations of CeO_2 alloyed and Al_2O_3 dispersed, and with decreasing grain size of zirconia.

1. Introduction
Partially stabilized zirconia has excellent mechanical properties, such as high strength and high resistance to fracture. A martensitic transformation from the metastable tetragonal phase to the stable monoclinic phase is believed to relieve the fracture stress [1, 2]. Therefore, the retention of the tetragonal phase at room temperature is essential to increase the fracture toughness and fracture strength of partially stabilized 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 in air, and both fracture strength and fracture toughness are greatly reduced [3–5]. In a previous study [6] we reported that some solvents accelerated the tetragonal-to-monoclinic phase transformation, and that water was the most effective solvent to promote the phase transformation. In the present study, the tetragonal-to-monoclinic phase transformation of yttria partially stabilized zirconia containing different concentration of Y_2O_3 was investigated in hot water, in which three different approaches, alloying $ZrO_2(Y_2O_3)$ with CeO_2, dispersing Al_2O_3 into $ZrO_2(Y_2O_3)$ and decreasing the grain size of ZrO_2, were tested to inhibit the transformation.

2. Experimental procedure
Zirconia powder containing 2, 3 and 4 mol % Y_2O_3 (designated $ZrO_2 2Y$, $ZrO_2 3Y$ and $ZrO_2 4Y$) and alumina powder were supplied by Toyo Soda Co Ltd (Shinnanyo, Yamaguchi 746, Japan) and Sumitomo Chemical Co Ltd (Niihama, Ehime 792, Japan), respectively. All other chemicals were of analytical grade and were used without further purification. Starting powders were prepared by mixing $ZrO_2(Y_2O_3)$ powder and Al_2O_3 powder or CeO_2 powder by ball milling with acetone and Al_2O_3 balls in a plastic container; then all powders were dried. These powders were uniaxially pressed at 1000 kg cm^{-2} to form pellets, 5 mm in diameter and 5 mm in thickness, and then sintered at 1400, 1500 and 1600° C for 3 h in air. The fabricated pellets and 10 ml of distilled water were put into 20 ml sealed stainless tubes. Each tube was sealed, and then placed in an electric furnace regulated to the desired temperature. The sealed tubes were removed from the electric furnace at

*To whom all correspondence should be addressed.

regular time intervals, and quickly cooled to room temperature. The bulk density of the sintered bodies was measured by the Archimedes technique. The bulk density of porous specimens was determined by coating the surface with dibutylhydroxyltoluene. X-ray diffraction analysis was used for phase identification. Scans of 2θ between $27°$ and $32°$ were conducted to estimate the monoclinic/(tetragonal + cubic) zirconia ratio [7], and between $55°$ and $62°$ to confirm the presence of the tetragonal and/or cubic phase. Average grain size was determined on scanning electron micrographs of the fracture surface by the intercept method [8]. The concentrations of zirconium and yttrium dissolved in a solution were determined by a colourimetric method using xylenol orange [9] and by an atomic absorption method, respectively.

3. Results and discussion
3.1. Characteristics of as-sintered materials

The phase, grain size and relative density of as-sintered bodies are summarized in Table I and Figs. 1 and 2. As expected from the phase diagram of the ZrO_2–Y_2O_3 system [10, 11], the phases of zirconia in $ZrO_2 2Y$–Al_2O_3 and $ZrO_2 3Y$–Al_2O_3 composites were fully tetragonal, and that in $ZrO_2 4Y$–Al_2O_3 composite was a mixture of tetragonal and cubic. On the other hand, the amount of cubic phase was increased by alloying $ZrO_2(Y_2O_3)$ with CeO_2, i.e. $ZrO_2 3Y$–CeO_2 ceramics containing more than 10 wt % CeO_2 were composed of a mixture of tetragonal and cubic phases. As seen in Figs. 1 and 2, the dispersion of Al_2O_3 into $ZrO_2(Y_2O_3)$ resulted in no significant difference in the relative density and grain size, and the relative densities of $ZrO_2(Y_2O_3)$–Al_2O_3 sintered bodies were

TABLE I Phase contents of sintered bodies of $ZrO_2(Y_2O_3)$ with added Al_2O_3 and CeO_2

Additive	(wt %)	Phase content*		
		$ZrO_2 2Y$	$ZrO_2 3Y$	$ZrO_2 4Y$
none	—	t	t	t + c
Al_2O_3	5–40	t + a	t + a	t + c + a
CeO_2	2	t	t	t + c
	5	t	t	t + c
	10	t	t + c	t + c
	15	t	t + c	t + c
	20	t	t + c	t + c

*t, tetragonal ZrO_2; c, cubic ZrO_2; a, α-Al_2O_3.
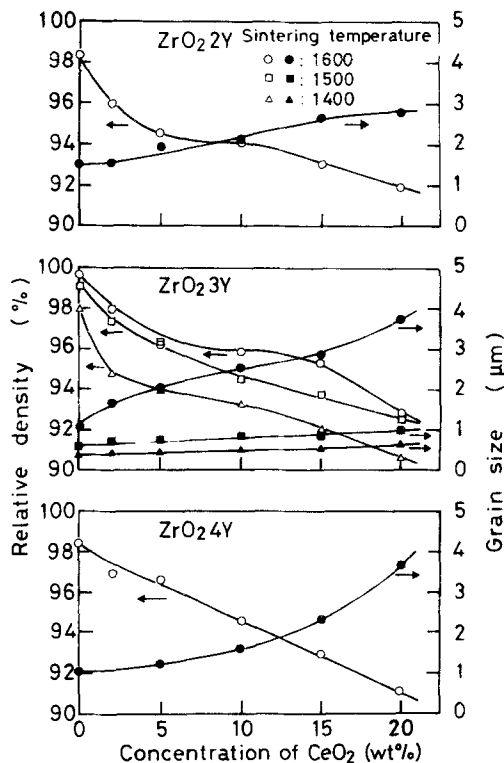

Figure 1 Relative densities and grain sizes of $ZrO_2(Y_2O_3)$ ceramics alloyed with different concentrations of CeO_2.
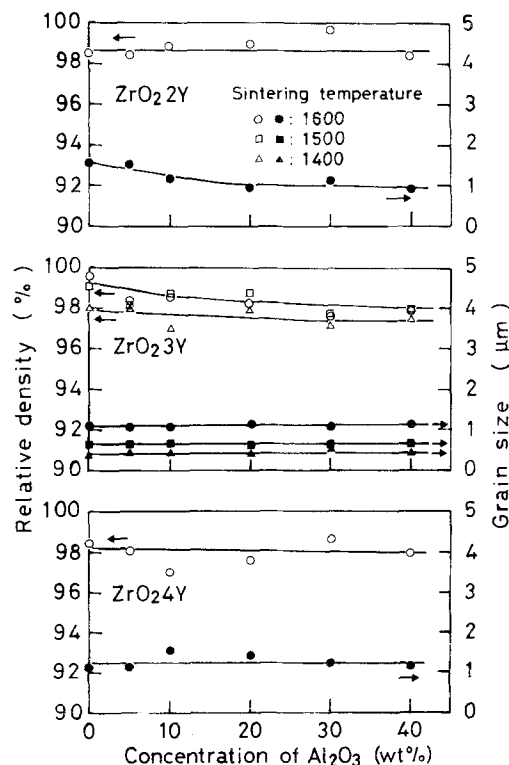

Figure 2 Relative densities and grain sizes of $ZrO_2(Y_2O_3)$ ceramics dispersed with different concentrations of Al_2O_3.

3989

achieved to more than 97% of the theoretical density. However, alloying $ZrO_2(Y_2O_3)$ with CeO_2 resulted in increase of grain sizes and decrease of relative density.

3.2. Phase transformation of $ZrO_2$3Y sintered bodies in hot water and in air at different temperature conditions

The molar concentration of the monoclinic phase formed on the surface annealed at 65 to 400° C in air and in hot water were determined for $ZrO_2$3Y ceramics fabricated at 1600° C. The results are shown in Fig. 3. As seen in Fig. 3, the rate of the tetragonal-to-monoclinic phase transformation increased with increasing temperature until 250° C. Although the rate of transformation in hot water was much faster than that in air, as reported earlier [6], the maximum concentration of the monoclinic phase formed in both air and hot water was almost the same. The concentrations of zirconium dissolved in the solution were less than 0.1 ppm and those of yttrium were not detectable in the present experimental conditions. Therefore, it was confirmed that the effect of dissolution of both zirconium and yttrium on phase transformation was negligible, and that the tetragonal-to-monoclinic phase transformation was accelerated by the reaction between water and zirconia ceramics on the surface.
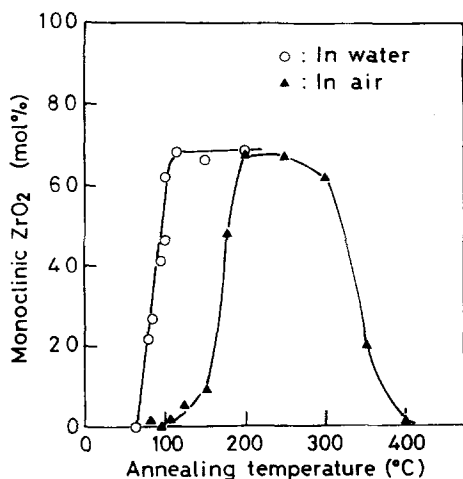
100

Figure 3 The tetragonal-to-monoclinic phase transformation in $ZrO_2$3Y ceramics fabricated at 1600° C by 50 h annealing in hot water and air.

3.3. Control of the tetragonal-to-monoclinic phase transformation

The free energy change of the tetragonal-to-monoclinic phase transformation ($\Delta G_{t \to m}$) can be described [12] by

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

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 tetragonal phases. Therefore, the tetragonal-to-monoclinic phase transformation can be controlled by increasing ΔG_c, ΔG_{se} and ΔG_s. It is well known that ΔG_c can be increased by alloying ZrO_2 with Y_2O_3, CeO_2, etc.; CeO_2 is a good candidate material for the present investigation, since it lowers the transformation temperature drastically [13]. On the other hand, since ΔG_{se} is dependent on the elastic properties of the transformed inclusion and surrounding matrix, ΔG_{se} is increased with increasing elastic modulus of the constraining matrix [12]. It is expected that the dispersion of Al_2O_3 (Young's modulus, 400 GPa) into zirconia might be suitable for control of the tetragonal-to-monoclinic phase transformation. Further, ΔG_s can be increased with decreasing grain size of ZrO_2, since the surface energy of the tetragonal phase is less than that of the monoclinic phase [14].

A series of experiments on the phase transformation in $ZrO_2$2Y, $ZrO_2$3Y and $ZrO_2$4Y with added 0 to 20 wt % CeO_2 or 0 to 40 wt % Al_2O_3 were performed in hot water at different temperature conditions. The results are shown in Figs. 4 and 5. As expected, the amount of monoclinic phase formed decreased with increasing concentrations of both CeO_2 and Al_2O_3. It is noticeable that no monoclinic phase was formed in $ZrO_2$3Y and $ZrO_2$4Y alloyed with more than 10 wt % CeO_2 and $ZrO_2$2Y alloyed with more than 15 wt % CeO_2. On the other hand, although the dispersion of Al_2O_3 decreased the transformation rate, it was effective only below 100° C, and could not inhibit the transformation completely.

Using $ZrO_2$3Y ceramics containing 0 to 20 wt % CeO_2 and 0 to 40 wt % Al_2O_3 with different grain sizes of ZrO_2 fabricated at 1400,
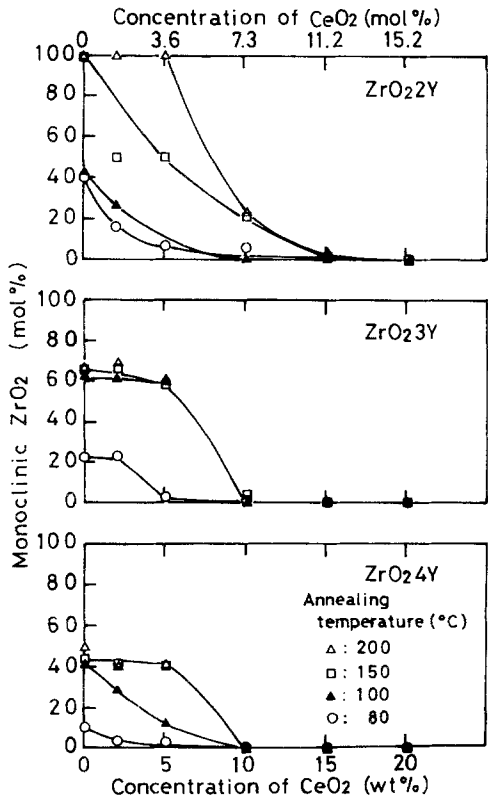
3990

Figure 4 The tetragonal-to-monoclinic phase transformation in $ZrO_2(Y_2O_3)$ ceramics alloyed with different concentrations of CeO_2 and fabricated at 1600° C by annealing in hot water for 7 days.
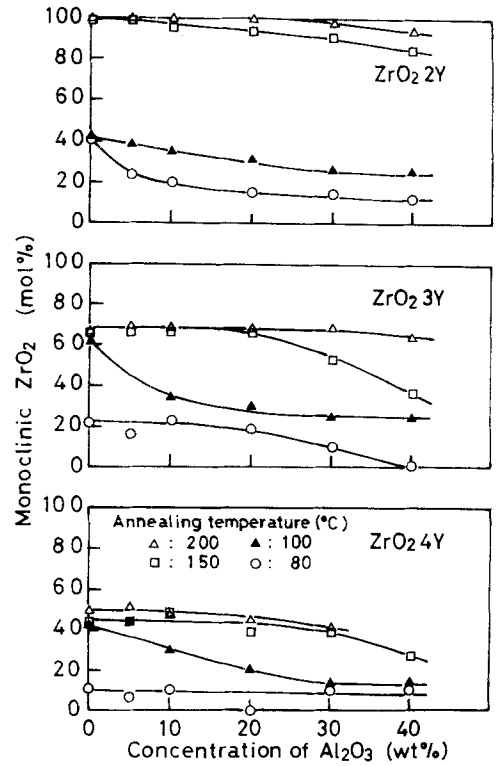
Figure 5 The tetragonal-to-monoclinic phase transformation in $ZrO_2(Y_2O_3)$ ceramics dispersed with different concentrations of Al_2O_3 and fabricated at 1600° C by annealing in hot water for 7 days.

1500 and 1600° C, the tetragonal-to-monoclinic phase transformation behaviour was tested in hot water at 100° C. The results are shown in Figs. 6 and 7. As seen in both figures, the amount of monoclinic phase formed decreased with decreasing grain size of ZrO_2. Under the present experimental conditions, the dispersion of Al_2O_3 into zirconia ceramics showed only limited control of the tetragonal-to-monoclinic phase transformation. On the other hand, alloying $ZrO_2(Y_2O_3)$ with CeO_2 could completely inhibit the phase transformation. The amount of CeO_2 alloyed with $ZrO_2(Y_2O_3)$, which could inhibit the phase transformation completely, decreased with decreasing sintering temperature, i.e. 10 wt % at 1500 and 1600° C, and 2 wt % at 1400° C. Another notable result shown in Figs. 6 and 7 was that the tetragonal-to-monoclinic phase transformation did not occur in $ZrO_2 3Y$ ceramics with grain size less than 0.45 μm by annealing in air [15], but a significant amount of the monoclinic phase was detected when
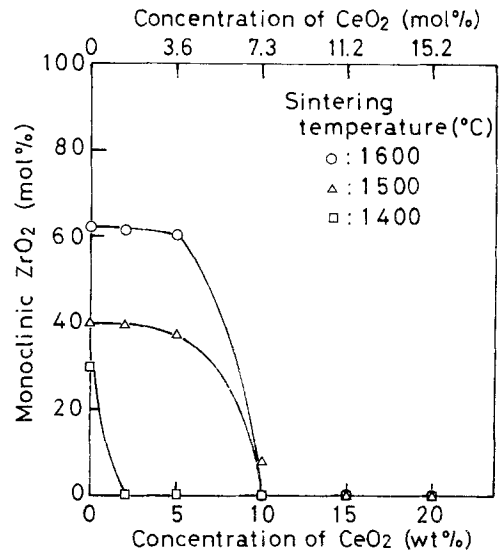

Figure 6 The tetragonal-to-monoclinic phase transformation in $ZrO_2(Y_2O_3)$ ceramics alloyed with different concentrations of CeO_2 and fabricated at different temperatures by annealing in hot water at 100° C for 7 days.
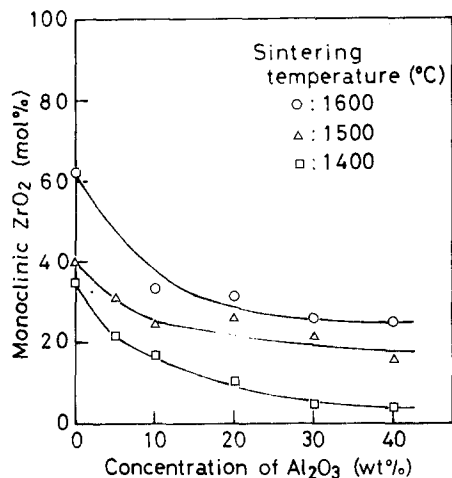
Figure 7 The tetragonal-to-monoclinic phase transformation in $ZrO_2(Y_2O_3)$ ceramics dispersed with different concentrations of Al_2O_3 and fabricated at different temperatures by annealing in hot water at 100°C for 7 days.

$ZrO_2 3Y$ ceramics with the same grain size were annealed in hot water. This might be due to a change in the surface energy of ZrO_2 with absorption of water.

4. Conclusions

(a) Alloying $ZrO_2(Y_2O_3)$ with CeO_2 was effective in inhibiting the tetragonal-to-monoclinic phase transformation.

(b) The dispersion of Al_2O_3 into $ZrO_2(Y_2O_3)$ ceramics slowed down the rate of the tetragonal-to-monoclinic phase transformation.

(c) Decreasing the grain size of zirconia reduced the degree of tetragonal-to-monoclinic phase transformation and lowered the concentration of CeO_2 alloyed with $ZrO_2(Y_2O_3)$ required to inhibit the transformation completely.

References
1. R. C. GARVIE, R. H. J. HANNINK and R. T. PASCOE, *Nature* **258** (1975) 703.
2. D. L. PORTER and A. H. HEUER, *J. Amer. Ceram. Soc.* **60** (1977) 183.
3. K. KOBAYASHI, H. KUWAJIMA and T. MASAKI, *Solid State Ionics* **3–4** (1981) 489.
4. Y. SHIGETO, T. FUSEKI and N. IGARASHI, Technical Paper no. 83052 (Toshiba Ceramics Co Ltd, 1983) p. 1.
5. T. SATO and M. SHIMADA, *J. Amer. Ceram. Soc.* **67** (1984) C 212.
6. *Idem. ibid.* **68** (1985) in press.
7. R. C. GARVIE and P. S. NICKOLSON, *ibid.* **55** (1972) 303.
8. R. L. FULLMAN, *J. Metals, Trans. AIME* **197** (1953) 447.
9. P. G. JEFFERY, "Chemical Methods of Rock Analysis" 2nd Edition (Pergamon Press, Oxford, 1975) Chap. 50.
10. V. S. STUBICAN, R. C. HINK and S. P. RAY, *J. Amer. Ceram. Soc.* **61** (1978) 17.
11. C. PASCUAL and P. DURAN, *ibid.* **66** (1983) 23.
12. F. F. LANGE, *J. Mater. Sci.* **17** (1982) 225.
13. *Idem, ibid.* **17** (1982) 255.
14. H. F. HOLMES, E. L. FULLER, Jr and R. B. GAMMAGE, *J. Phys. Chem.* **76** (1972) 1497.
15. T. SATO, S. OHTAKI and M. SHIMADA, *J. Mater. Sci.* **20** (1985) 1466.