

Thermal stability and mechanical properties of yttria-doped tetragonal zirconia polycrystals with dispersed alumina and silicon carbide particles

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Yttria-doped tetragonal zirconia polycrystals in which were dispersed various amounts of Al_2O_3 and SiC particles were sintered at 1500°C for 3 h, and the mechanical properties and the thermal stability of the sintered bodies were evaluated. Dispersion of Al_2O_3 caused no significant effect on sinterability, and increased the hardness and elasticity of the composites. Dispersion of SiC particles decreased the relative density and the grain size of composites. Elasticity and hardness increased by dispersing less than 10 vol% SiC, but decreased above 10 vol% SiC due to the decrease of relative density. Dispersion of both Al_2O_3 and SiC particles slightly increased the fracture toughness of ZrO_2 -3 mol% Y_2O_3 ceramics but significantly decreased that of ZrO_2 -2 mol% Y_2O_3 ceramics. The rate of the tetragonal-to-monoclinic phase transformation decreased by dispersing both Al_2O_3 and SiC particles. The transformation depth increased rapidly and then slowly with increasing the annealing time. The rate of increase in the transformation depth greatly decreased by dispersing Al_2O_3 particles.

1. Introduction

Yttria-doped tetragonal zirconia polycrystals (Y-TZP) have received great attention because of their high sinterability and superior mechanical properties [1-7]. Many studies [8-14] have been done on the thermal stability of Y-TZP, since the degradation of the fracture strength by annealing at low temperature such as 150 to 300°C was reported [15]. It was believed that the degradation of strength was caused by the formation of microcracks accompanied with the tetragonal-to-monoclinic phase transformation during annealing. The free energy change of the tetragonal-to-monoclinic phase transformation ($\Delta G_{t \rightarrow m}$) can be described by

$$\Delta G_{t \rightarrow m} = \Delta G_c + \Delta G_{sc} + \Delta G_s \quad (1)$$

$$\Delta G_{sc} = E_c(\Delta V/V)^2/6 \quad (2)$$

$$\Delta G_s = 6(\gamma_m - g_s\gamma_t)/d \quad (3)$$

where ΔG_c , ΔG_{sc} , ΔG_s , are the chemical free energy change, the strain free energy change and the surface free energy change, respectively, and E_c , ΔV , V , γ , g_s and d are Young's modulus, volume expansion by the phase transformation, transformed volume, specific interfacial surface energy, ratio of the interfacial surface area of monoclinic ZrO_2 and tetragonal ZrO_2 , and the grain size [1], respectively. It was reported that the structural modification, in which these three free energy changes increased by alloying CeO_2 , dispersing Al_2O_3 particles and decreasing the grain size of zirconia particles, were effective to control the tetragonal-to-monoclinic phase transformation

[10, 11]. However, it should be noted that the increase in the thermal stability of TZP often resulted in a loss of fracture toughness. The contribution of the stress-induced phase transformation to fracture toughness can be written as

$$K_c = \left[K_0^2 + 2(|\Delta G_c| - \Delta G_{sc}) \frac{E_c V_i R}{1 - \nu_c^2} \right]^{1/2} \quad (4)$$

where K_c , K_0 , V_i , R , ν_c are the critical stress-intensity factor of the composite, the critical stress-intensity factor of the material without the transformation phenomenon, the volume fraction of the tetragonal phase, the size of the transformed zone and Poisson's ratio, respectively. Since dispersion of second-phase particles with high elasticity may increase the values of both ΔG_{sc} and E_c , it is expected that thermal stability could be controlled without loss of the fracture toughness. Al_2O_3 and SiC particles are good candidates to improve the thermal stability of TZP because they have much higher elasticity such as 400 GPa and 450 GPa, respectively. In the present study, Y-TZP in which was dispersed various amounts of Al_2O_3 and SiC was fabricated and the characteristics of sintered bodies such as sinterability, mechanical properties and thermal stability were evaluated.

2. Experimental procedures

Zirconia powders containing 2 and 3 mol% Y_2O_3 , Al_2O_3 powder and SiC powder were supplied by Toyo Soda Co Ltd. (Shinnanyo, Yamaguchi 746, Japan), Sumitomo Chemical Co. Ltd (Niigama, Ehime 792,

TABLE I Phase content of as-sintered bodies of $ZrO_2(Y_2O_3)$ with dispersed Al_2O_3 and SiC particles*

Substrate	Additive	Concentration of additive (vol %)			
		5	10	20	30
ZrO_2 -2 mol % Y_2O_3	Al_2O_3	t \geq m	t \geq m	t \geq m	t \geq m
ZrO_2 -3 mol % Y_2O_3	Al_2O_3	t > c	t > c	t > c	t > c
ZrO_2 -2 mol % Y_2O_3	SiC	t	t	t \geq m	t \geq m
ZrO_2 -3 mol % Y_2O_3	SiC	t > c	t > c	t > c	t + c + m

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

Japan) and Hermann C. Starck Berlin Co. (Berlin, West Germany). These powders were mixed in the desired ratios by ball-milling with acetone and plastic balls in a plastic container and then dried. The powders were uniaxially pressed at 200 MPa to form pellets, 6 mm in diameter and 5 mm in thickness, and then sintered at 1500°C for 3 h. The sintering of Y-TZP- Al_2O_3 and Y-TZP-SiC composites was carried out in air and argon gas atmosphere, respectively. The fabricated pellets were put into 20 ml of sealed glass tubes with 10 ml of distilled water. Each tube was sealed, and then placed in a glycerol bath regulated to the desired temperature. The sealed tubes were removed from the bath at regular time intervals, and quickly cooled to room temperature. The bulk density of the sintered bodies was measured by the Archimedes technique. Average grain size was determined by the intercept method [16]. Vickers microhardness, Young's modulus and fracture toughness were determined by the indentation method [17]. The

concentration of monoclinic ZrO_2 on the surface was determined by the method of Garvie and Nicholson [18].

3. Results and discussion

3.1. Characteristics of as-sintered materials

The crystalline phase, grain size, relative density, Vickers microhardness, Young's modulus and fracture toughness of as-sintered materials are summarized in Table I and Figs 1 and 2. The phases of zirconia in ZrO_2 -2 mol % Y_2O_3 ceramics with dispersed Al_2O_3 and SiC were mixtures of tetragonal

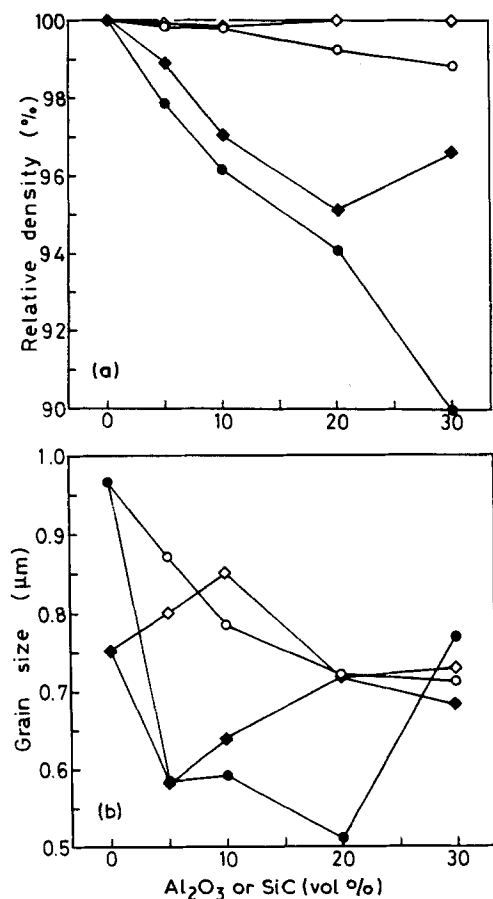


Figure 1 (a) Relative density and (b) grain size of (○, ●) ZrO_2 -2 mol % Y_2O_3 and (◇, ◆) ZrO_2 -3 mol % Y_2O_3 ceramics with various dispersed amounts of (○, ◇) Al_2O_3 and (●, ◆) SiC particles.

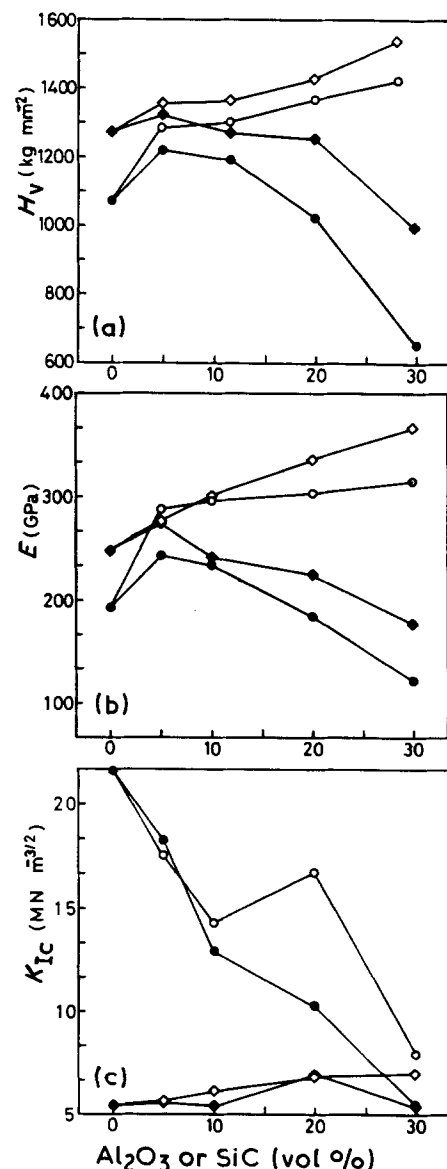


Figure 2 (a) Vickers microhardness, (b) Young's modulus and (c) fracture toughness of (○, ●) ZrO_2 -2 mol % Y_2O_3 and (◇, ◆) ZrO_2 -3 mol % Y_2O_3 ceramics with various dispersed amounts of (○, ◇) Al_2O_3 and (●, ◆) SiC particles.

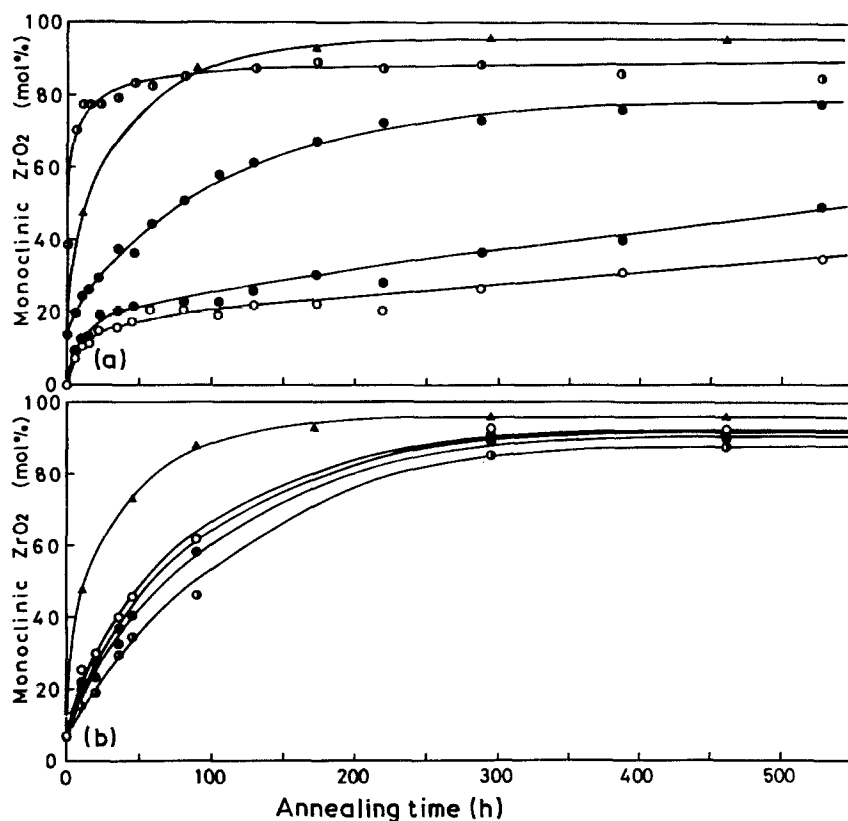


Figure 3 Time dependence of the monoclinic ZrO_2 formed on the surface of $ZrO_2-2\text{ mol \% } Y_2O_3$ with various dispersed amounts of (a) SiC and (b) Al_2O_3 particles. Annealing temperature: $120^\circ C$. Additive content (vol %): (○) 5, (●) 10, (⊗) 20, (⊙) 30.

phase and a small amount of monoclinic phase, and those in $ZrO_2-3\text{ mol \% } Y_2O_3$ were mixtures of tetragonal and cubic phases. Monoclinic phase coexisted in the composite of $ZrO_2-3\text{ mol \% } Y_2O_3$ with 30 vol % SiC. As seen in Fig. 1, the dispersion of Al_2O_3 into Y-TZP caused no significant change in the relative density and grain size of zirconia, while dispersion of SiC greatly decreased these values. As expected, dispersion of Al_2O_3 increased the elasticity and hardness of the composites. On the other hand, the elasticity and hardness increased by dispersing less than 10 vol % of SiC, but decreased by dispersing more than 10 vol % SiC due to an increase of the porosity. Dispersion of both Al_2O_3 and SiC slightly increased the fracture toughness of $ZrO_2-3\text{ mol \% } Y_2O_3$ ceramics but greatly decreased that of $ZrO_2-2\text{ mol \% } Y_2O_3$ ceramics.

3.2. Phase transformation on the surface

The time dependence of the molar concentration of monoclinic ZrO_2 , formed on the surface of $ZrO_2-2\text{ mol \% } Y_2O_3$ in which was dispersed various amounts of Al_2O_3 and SiC by annealing in water at $120^\circ C$, is shown in Fig. 3. The rate of the phase transformation decreased by dispersing both Al_2O_3 and SiC particles. Since the plots of $\ln(1-\alpha)^{-1}$ against time was linear as shown in Fig. 4, where α is fractional conversion of the tetragonal phase to the monoclinic one, the rate of the phase transformation was first-order with respect to the tetragonal ZrO_2 concentration. Arrhenius plots of the rate constants for $ZrO_2-2\text{ mol \% } Y_2O_3$ ceramics with dispersed Al_2O_3 and SiC particles are shown in Fig. 5. The apparent activation energies calculated were 85 to 100 kJ mol^{-1} , and no noticeable difference was observed between these specimens. These results indicated that dispersion of Al_2O_3 and SiC particles

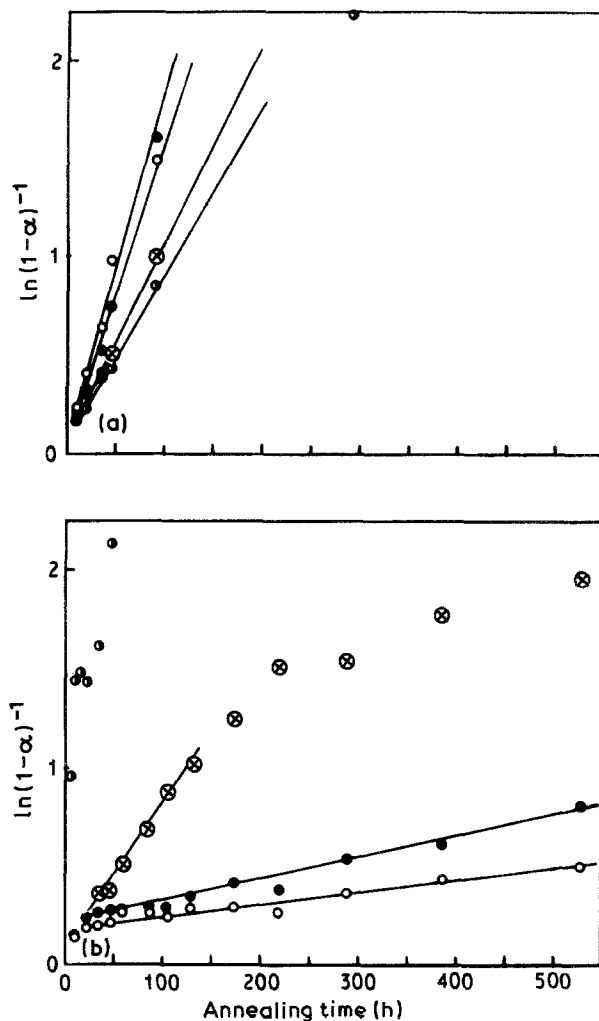


Figure 4 Plots of $\ln(1-\alpha)^{-1}$ against time for the phase transformation in $ZrO_2-2\text{ mol \% } Y_2O_3$ with various dispersed amounts of (a) Al_2O_3 and (b) SiC particles. Annealing temperature: $120^\circ C$. Additive content (vol %): (○) 5, (●) 10, (⊗) 20, (⊙) 30.

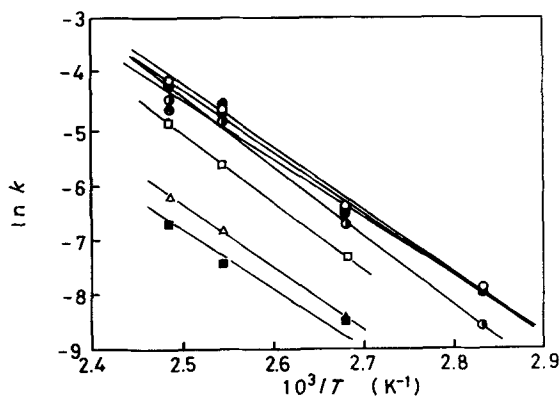


Figure 5 Arrhenius plots of the rate constant of the phase transformation in ZrO_2 -2 mol % Y_2O_3 . Content of Al_2O_3 (vol %): (○) 5, (●) 10, (⊗) 20, (◐) 30. Content of SiC (vol %): (■) 5, (△) 10, (□) 20.

decreased the transformation rate, but did not change the transformation mechanism. The relations between the rate constants and the contents of Al_2O_3 and SiC particles are shown in Figs 6 and 7. The rate of transformation simply decreased with increasing the Al_2O_3 content. This may be due to the increase of the strain free energy change caused by increasing the elasticity of composites. On the other hand, the rate of the transformation greatly decreased by dispersing 5 to 10 vol % of SiC, and above 10 vol % of SiC content the rate increased. These results agreed well with those of the compositional change in elasticity of as-sintered materials as shown in Fig. 2. The rates of the phase transformation in Y-TZP-SiC composites were much smaller than in Y-TZP- Al_2O_3 composites, which reflects the effect of the surface free energy change on the phase transformation. Note that the grain sizes of Y-TZP-SiC composites were smaller than those of Y-TZP- Al_2O_3 composites.

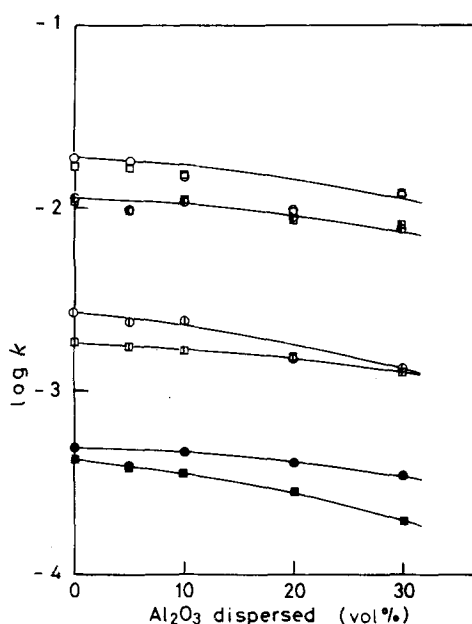


Figure 6 Relation between the rate constant of the phase transformation and the Al_2O_3 content. Circles, ZrO_2 -3 mol % Y_2O_3 ; squares, ZrO_2 -2 mol % Y_2O_3 . (●, ■) 80° C; (◐, □) 100° C; (◑, ▣) 120° C; (○, □) 130° C.

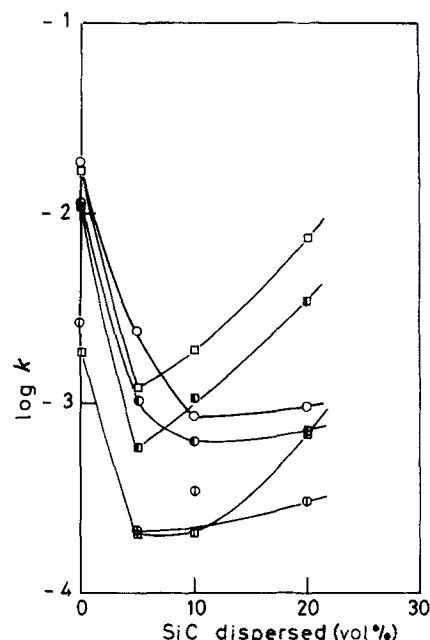


Figure 7 Relation between the rate constant of the phase transformation and the SiC content. Circles, ZrO_2 -3 mol % Y_2O_3 ; squares, ZrO_2 -2 mol % Y_2O_3 . (◐, □) 100° C; (◑, ▣) 120° C; (○, □) 130° C.

3.3. Phase transformation inside the body

The surfaces of the annealed specimens were polished with emery paper, and the amount of the monoclinic phase was measured as a function of the depth from the original surface. The results are shown in Fig. 8. It is seen that the amount of the monoclinic phase decreased with increasing depth from the original surface. This result indicated that the phase transformation proceeded from the surface and supported the mechanism that the phase transformation was controlled by the chemical reaction between ZrO_2 and water on the surface. Time dependences of the amount of the monoclinic phase content and the transformation depth are shown in Fig. 9. Two-step development of the transformation layer was observed. The transformation depth increased rapidly at the first step, but increased slowly and linearly with time after completing the phase transformation on the surface. This result was due to the fact that the phase

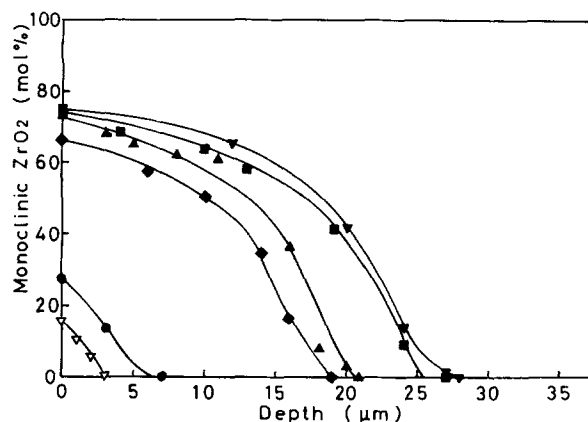


Figure 8 Relation between the monoclinic phase formed and the depth from the original surface. ZrO_2 -3 mol % Y_2O_3 with 10 vol % Al_2O_3 , annealing temperature 120° C. Annealing time (h): (▽) 50, (●) 100, (◆) 200, (▲) 300, (■) 400, (▼) 500.

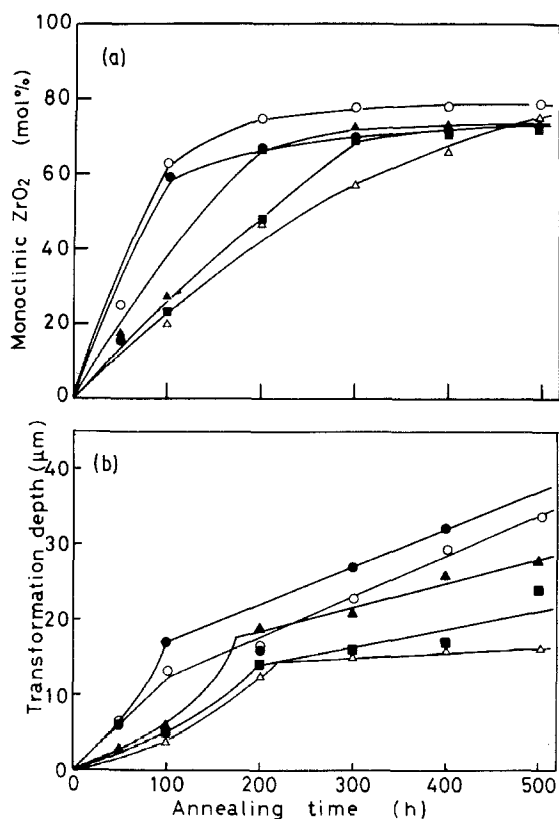


Figure 9 Time dependences of (a) the monoclinic phase formed on the surface and (b) the transformation depth. Annealing temperature: 120°C. ZrO₂-3 mol% Y₂O₃ with Al₂O₃ content (vol%): (○) 0, (●) 5, (▲) 10, (■) 20, (△) 30.

transformation on the surface proceeded faster, because the constraint by the surrounding particles on the surface was much smaller than it was inside the sintered body. It was noticeable that the rate of increase in transformation depth greatly decreased with increasing Al₂O₃ content. Since the fracture strength of the annealed samples depended on the transformation depth [19], dispersion of second-phase particles with high elasticity such as Al₂O₃ and SiC may be useful to control the degradation of the fracture strength by low-temperature annealing.

4. Conclusions

1. Dispersion of Al₂O₃ particles into Y-TZP caused no significant change in the sinterability, and increased the hardness and the elasticity.

2. Dispersion of SiC into Y-TZP decreased the relative density and the grain size.

3. Dispersing Al₂O₃ and SiC slightly increased the fracture toughness of ZrO₂-3 mol% Y₂O₃ ceramics but greatly decreased that of ZrO₂-2 mol% Y₂O₃.

4. Dispersing Al₂O₃ and SiC particles into Y-TZP was useful to depress the tetragonal-to-monoclinic phase transformation.

5. The rate of increase in the transformation depth greatly decreased by dispersing Al₂O₃ particles.

Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research of the Ministry of Education and by the General Sekiyu Research and Development Encouragement and Assistance Foundation. The authors are indebted to the management of Toyo Soda Co. Ltd and Sumitomo Chemical Co. Ltd for supplying the starting powders used in the present study.

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Received 14 April
and accepted 30 June 1986