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Dependence of Phase Stability of Tetragonal Zirconia Polycrystal on Dopants

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The effect of aliovalent dopants, Nb_2O_5 and MnO, on the phase stability of 12 mol% ceria partially-stabilized zirconia (Ce-TZP) polycrystals was studied. Both dopants (MnO and Nb_2O_5) significantly increased the stability of the tetragonal zirconia phase (M_b temperature lower than liquid nitrogen temperature). The enhancement of the stability of the tetragonal phase in Ce-TZP doped with 1 mol % of MnO (Ce-TZP/MnO) and Ce-TZP doped with 1 mol % of Nb_2O_5 (Ce-TZP/Nb_2O_5)were explained by the significant reduction of the driving force, $-\Delta G_{chem}$, for the tetragonal-to-monoclinic phase transformation caused by the addition of MnO and Nb_2O_5. The enhanced stability of the tetragonal phase in the Ce-TZP and Al_2O_3 composite (Ce-TZP/Al_2O_3) is believed to be caused by smaller grain size, moderate reduction in the chemical driving force and increase in the strain energy barrier to the transformation. Mechanical properties of the Ce-TZP and the Ce-TZP/Al_2O_3 with (i) the same grain size and (ii) the same M_b temperature were examined by measuring stress-strain behavior in 3 point bending. The Ce-TZP/Al_2O_3 composite doped with 1.3 w % MnO (Ce-TZP/Al_2O_3/MnO), which had the same grain size as the Ce-TZP and Ce-TZP/Al_2O_3 showed more transformation plasticity than either the Ce-TZP or the Ce-TZP/Al_2O_3 composite. The Ce-TZP which had the same M_b temperature as that of the Ce-TZP/Al_2O_3/MnO did not show any transformation plasticity.

Key words : Ce-TZP, Aliovalent dopant, Transformation, Phase stability

I. Introduction

In general there are optimum amount of stabilizer and grain size for maximizing strength and fracture toughness of zirconia ceramics. Zirconia ceramics stabilized with CeO_2 shows maximum fracture toughness at about 12 mol % CeO_2.[1)]

Grain size can affect various properties of ceramics. In partially-stabilized zirconias including PSZs and TZPs, the stress-induced martensitic transformation of the metastable tetragonal phase to the monoclinic phase, which is responsible for the enhanced fracture toughness via transformation toughening, is strongly affected by the grain size. This grain-size dependence is reflected in a variation of the transformation yield stress with grain size as well as the observation of a critical grain size above which the tetragonal phase can not be retained at room temperature. Therefore, the phase stability of tetragonal zirconia particles embedded in the matrix of Ce-TZP, which is very important to the mechanical properties of zirconia ceramics, depends strongly on grain size and impurities.[2,3)]

The stability of the tetragonal phase in zirconia ceramics is governed by both the kinetics of the nucleation and the energetics of the phase transformation including the chemical driving force, $-\Delta G_{chem}$, the strain energy, ΔU_{str}, and the change in the surface energy, $\Delta \gamma_i$.

The stabilizer content affects the phase stability via the chemical driving force, while the grain size influence arises through both nucleation (surface versus volume) and energetics (volume energy versus surface energy terms). Aliovalent dopants affect phase stability indirectly via its control of grain size as well as more directly via their effect on the chemical driving force.

The mechanical properties of partially-stabilized zirconia ceramics are largely controlled by the stability of the tetragonal phase.[4,5)] For zirconia ceramics it is well-established that higher stability of the tetragonal phase (lower M_b temperature) leads to higher transformation yield stress and lower fracture toughness and vice versa. An understanding of the interaction between phase stability and mechanical properties is critical in the design of strong and tough zirconia ceramics.

II. Experimental Procedure

1. A. Processing of the Ce-TZP, the doped Ce-TZPs and Ce-TZP/Al_2O_3 composites

For preparation of the base Ce-TZP, both 88 mol percent of zirconia and 12 mol% of ceria powders were weighed and put in a polyethylene bottle together with adequate zirconia milling media and ethyl alcohol, and milled for 24 hours. The milled slurry was dried in air. The dried powder was calcined in air at 950°C for 1 hour. For preparation of the doped Ce-TZPs, Ce-TZP/ Nb_2O_5 and Ce-TZP/MnO, dopings were achieved by adding 1 mol % of dopant oxides, MnO and Nb_2O_5 respectively, to the calcined powder of the base Ce-TZP, and then ball milling in ethanol for 24 hours, and drying in air. The powder for Ce-TZP/Al_2O_3 compostie were achieved by the addition of 10 w% of Al_2O_3 to the base Ce-TZP. Ce-TZP/Al_2O_3 with 1.3 w% of MnO was also made with addition of 1.3 w% MnO to the Ce-TZP/Al_2O_3. The dried powder mixture was screened through a 75 μm screen. The screened powder was pressed uniaxially in a die press at 35 MPa, followed by isostatic pressing at 207 MPa. The green compacts were sintered at 1550°C for 20 minutes and then annealed at 1475, 1550, and 1600°C for different time intervals. Bulk densities were measured after sintering using Archimedes method with distilled water as the immersion medium.

2. B. *Measurement of the martensitic transformation temperature*

A strain gauge technique was used to determine the phase stability of the tetragonal zirconia grain via the measurment of the transformation temperature, M_b. A strain gauge was mounted on a rectangular parallelepiped specimen and the specimen-strain gauge assembly was cooled gradually by using a liquid nitrogen cooling arrangement. The M_b temperature was indicated by a sudden discontinuity in the strain vs temperature record.

3. C. *Three point bend tests*

Three point bend tests with 40 mm support span were conducted to examine transformation yielding and plastic deformation of the base and the other Ce-TZPs. A screw-driven universal testing machine[1] was used to apply bending loads on beam specimens (4×3×45 mm). Stress-strain curves were recorded by using strain gauges[2] which were mounted in the center of the tensile surface. The cross-head speed for three-point bend test was 0.05 mm/min.

4. D. *Vickers microhardness measurements*

Vickers microhardness measurements were executed for the study of the effect of composition and grain size on hardness. A microhardness tester[3] with a Vickers diamond pyramid as indentor was used for indentation. Load for indentation and loading time were 200 gram and 15 seconds, respectively. Ten indentations were made on each specimen to get the mean Vickers microhardness.

III. Experimental Results

X-ray diffraction patterns obtained for the Ce-TZP (grain size=7.2 μm) and the doped Ce-TZPs, Ce-TZP/ Nb_2O_5 (grain size=19.4 μm) and Ce-TZP/MnO (grain size=3.5 μm), indicated only tetragonal phase. However Ce-TZP/Al_2O_3 (grain size=3.6 μm), and Ce-TZP/Al_2O_3/MnO (grain size=3.0 μm) consisted of the tetragonal and α-alumina phase as well as the tetragonal and second phase including Ce, Al, Mn, and O, respectively.

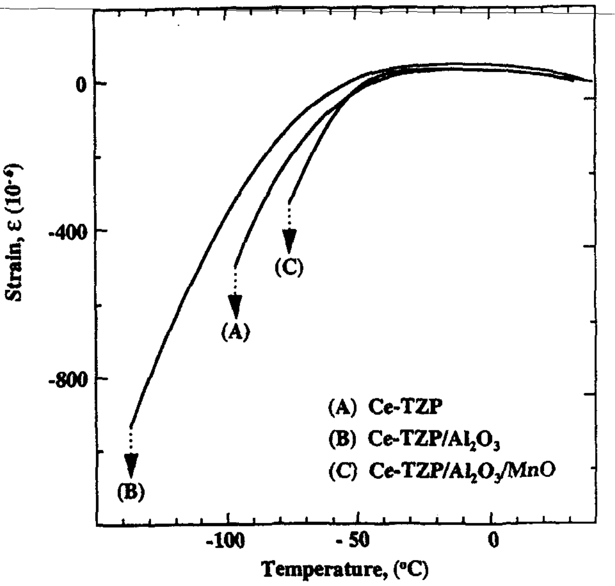

Fig. 1. Martensitic transformation temperature, M_b, indicated by the sudden change of strain observed on cooling of the Ce-TZP, Ce-TZP/Al_2O_3 and Ce-TZP/Al_2O_3/MnO.

The martensitic transformation temperatures of Ce-TZP/MnO and Ce-TZP/Nb_2O_5 could not be detected by using the liquid nitrogen apparatus because the M_b temperatures for these zirconia alloys were below the liquid nitrogen temperature (- 193°C).

Fig. 1 shows representative strain-temperature plots obtained in M_b temperature measurements. As the temperature decreased from room temperature the strain initially increased slightly because of the difference in thermal expansion coefficients between the constantan strain gauge and the Ce-TZPs and then decreased with further cooling. The martensitic transformation from tetragonal to monoclinic in the Ce-TZPs was indicated by a sudden strain change accompanied by specimen fracture or stripping of the strain gauge from the specimen. The corresponding temperature was recorded as the martensitic transformation temperature, M_b. The variation of M_b temperatures of the Ce-TZP, Ce-TZP/Al_2O_3, and Ce-TZP/Al_2O_3/MnO with mean grain size has been observed. This is shown in Fig. 2. Also the M_b temperatures depended strongly on composition. At the same grain size, for instance 2 μm, Ce-TZP/Al_2O_3/MnO showed the highest M_b temperature (-57°C), Ce-TZP/Al_2O_3 had the lowest M_b temperature (-127°C), and the Ce-TZP had intermediate value (-93°C). The sensitivity of the M_b temperature to the grain size was different for the three materials. Ce-TZP/Al_2O_3 showed almost the same sensitivity of the transformation temperature to the grain size as the Ce-

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[1] Model 1125, Instron Co., Canton, MA.

[2] Type CEA-06-062UW-350, Meaurement Group Inc., Raleigh, NC.

[3] Type M, Shimadzu Seisakusho Ltd., Kyoto, Japan.

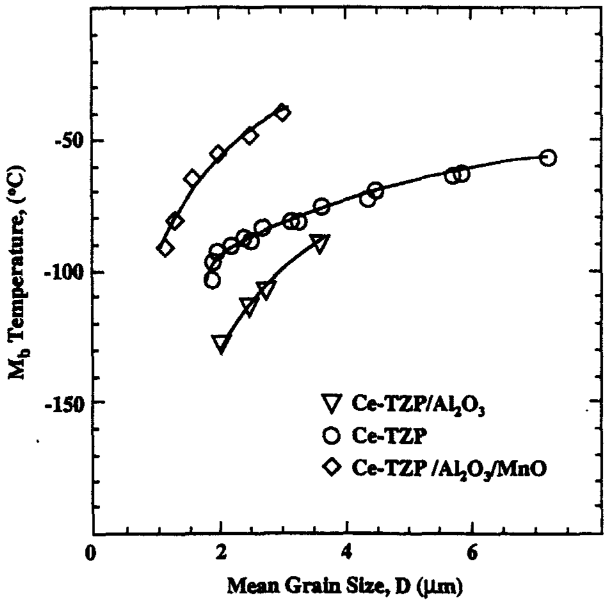

Fig. 2. The variation of the martensitic transformation temperature, M_b, of the Ce-TZP, Ce-TZP/Al$_2$O$_3$ and Ce-TZP/Al$_2$O$_3$/MnO with mean grain size.

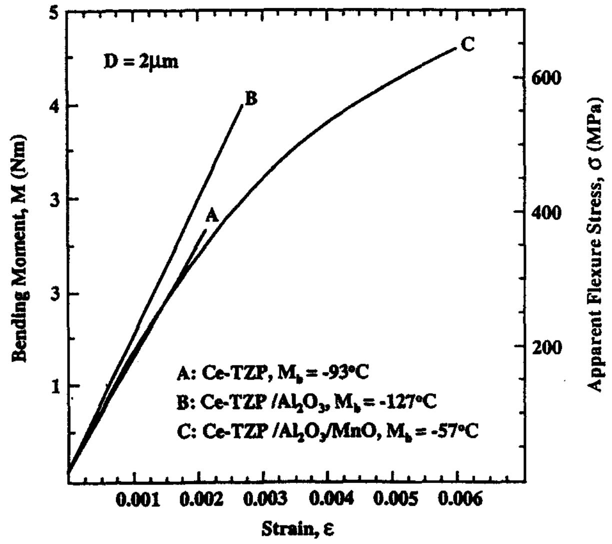

Fig. 3. The comparison of transformation yield, plasticity, and failure between the Ce-TZP, Ce-TZP/Al$_2$O$_3$ and Ce-TZP/Al$_2$O$_3$/MnO having same grain size and different phase stability.

TZP/Al$_2$O$_3$/MnO. The martensitic transformation of the Ce-TZP was relatively less sensitive to grain size than those in the Ce-TZP/Al$_2$O$_3$ and Ce-TZP/Al$_2$O$_3$/MnO.

Bending moment-strain curves, measured in three-point bending for the Ce-TZP (M_b=-93°C), Ce-TZP/Al$_2$O$_3$ (M_b=-127°C), and Ce-TZP/Al$_2$O$_3$/MnO (M_b=-57°C) at the same grain size (2 μm), were compared in Fig. 3. The strain was measured at the maximun stress location of the three-point bend specimen. Also the apparent flexure stresses calculated from the elastic bending formula are plotted on the Fig. 3. The stress-strain curves for Ce-TZP and Ce-TZP/Al$_2$O$_3$ consisted of only the elastic region. However, the stress-strain curve for Ce-TZP/Al$_2$O$_3$/MnO consisted of an initial elastic region where stress increased linearly and a region of plastic deformation. Addition of Al$_2$O$_3$ to the Ce-TZP increased Young's modulus and fracture strength of the Ce-TZP while addition of MnO to Ce-TZP/Al$_2$O$_3$ composite decreased the Young's modulus of Ce-TZP/Al$_2$O$_3$ and increased the transformation plasticity and fracture strength. Stress-strain behaviors of the Ce-TZP (grain size=7.1 μm) and Ce-TZP/Al$_2$O$_3$/MnO (grain size=2.0 μm) at the same M_b temperature (M_b=-57°C) were compared in Fig 4. The Ce-TZP/Al$_2$O$_3$/MnO showed significant amount of transformation plasticity and high fracture strength while the Ce-TZP with the larger grain size showed only elastic behavior and low fracture strength.

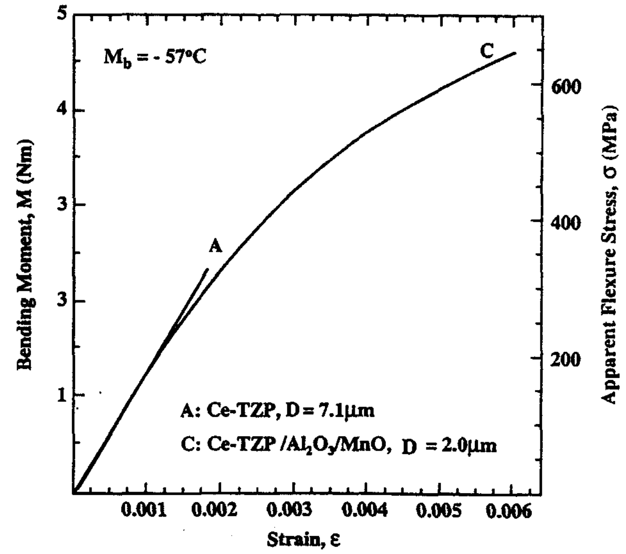

Fig. 4. The comparison of transformation yield, plasticity, and failure between the Ce-TZP and Ce-TZP/Al$_2$O$_3$/MnO having same phase stability and different grain size.

Variations of Vickers microhardnesses of the Ce-TZP, Ce-TZP/Al$_2$O$_3$, and Ce-TZP/Al$_2$O$_3$/MnO with grain size are shown in Fig 5. It was found from Fig. 5 that as grain size decreased, the microhardness for the three materials increased. Addition of Al$_2$O$_3$ to the Ce-TZP enhanced the microhardness of the Ce-TZP while the addition of MnO to Ce-TZP/Al$_2$O$_3$ composite reduced the microhardness of Ce-TZP/Al$_2$O$_3$. Thus, the microhardness was affected by both grain size and composition.

IV. Discussion

1. A. *Thermodynamics of tetragonal-monoclinic transformation in zirconia*

The structures of the Ce-TZP and the doped Ce-TZPs are described in terms of a tetragonal polycrystal. The factors controlling the stability of tetragonal zirconia grain in the Ce-TZP and in the doped Ce-TZPs are grain

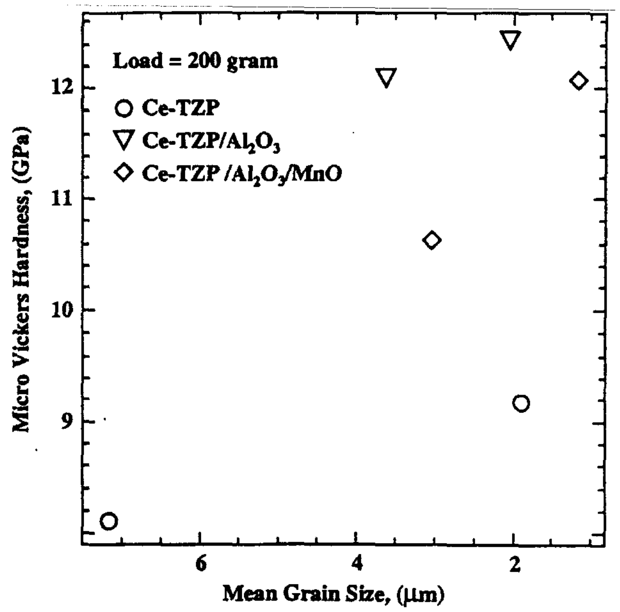

Fig. 5. The variation of the microhardness with grain size and composition.

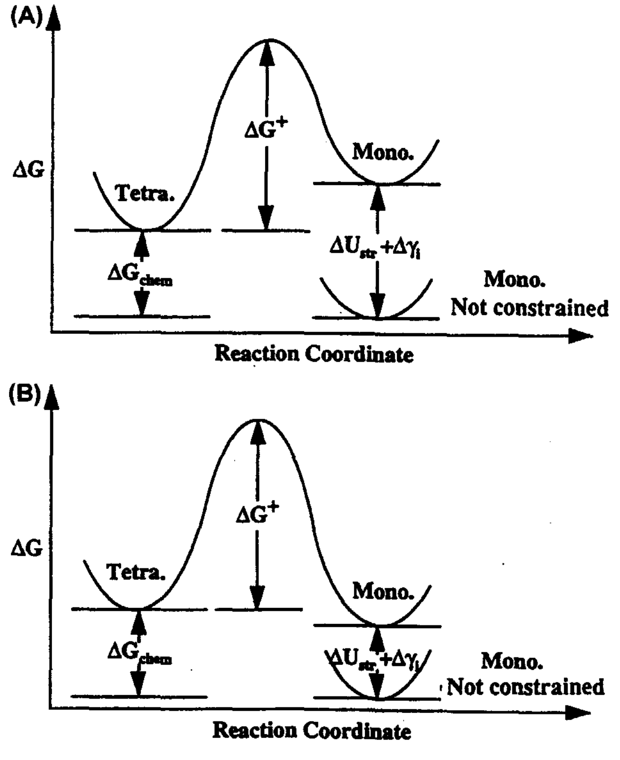

Fig. 6. Reaction coordinate diagram showing energetics of a constrained ZrO_2 tetragonal and monoclinic grain at (A) $M_b<T<T_e$(B)$T<M_b$.

size, amount of dopant, and kind of dopant.

On supercooling the total free energy change of the system caused by the martensitic transformation from tetragonal to monoclnic phase can be expressed by

$$\Delta G_T=(-\Delta G_{chem}+\Delta U_{str})\Delta V+\Sigma\Delta A_i\Delta\gamma_i \qquad (1)$$

where ΔG_T is the total change in free energy of the system, ΔG_{chem} is the chemical driving force dependent on temperature and composition, ΔU_{str} is a change in the strain energy associated with transformed particle and surrounding matrix, ΔV is a volume change associated with the martensitic transformation, ΔA_i is a change in the surface area of the transformed volume if there are no additional interfaces, such as twin boundaries within the transformed volume and $\Delta\gamma_i$ is a change in the interfacial energy associated with transformed particle and surrounding matrix. When the temperature decreases below the equilibrium transformation temperature (T_e) of the Ce-TZPs the chemical free energy difference between the tetragonal and the monoclinic phases increases. For a tetragonal zirconia grain in a solid matrix, the martensitic transformation leads to a strain energy due to the volume change and shape change associated with the transformation. Fig. 6 compares energetics of TZP grain at the temperatures lower and higher than the martensitic transformation temperature. As shown in Fig. 6 (A), when the sum of increases in the strain and interfacial energies is greater than the decrease in the chemical free energy, the tetragonal grain will be stable against the transformation. If futher cooling is supplied to the system an increment of the chemical driving force will be greater than that of the strain energy and the interfacial energy as shown in Fig. 6 (B). Thus, activation energy barrier for the martensitic transformation will be overcome. Therefore, the condition for the martensitic transformation from tetragonal to monoclinic phase is

$$\Delta G_T \leq 0 \qquad (2)$$

or

$$\Delta V|-\Delta G_{chem}|>\Delta V\Delta U_{str}+\Sigma\Delta A_i\Delta\gamma_i \qquad (3)$$

2. B. Dependence of the martensitic transformation temperature of the Ce-TZPs on Grain Size

Phase stability of zirconia grain in the Ce-TZP, Ce-TZP/Al_2O_3, and Ce-TZP/Al_2O_3/MnO is dependent on a grain size of tetragonal zirconia. That is, a critical grain size exists, below which a retention of the tetragonal zirconia phase can be achieved and above which it can not.

ΔU_{str} in Equation 1 consists of a dilatational strain energy (ΔU_{str}^{dil}), a twinning strain energy (ΔU_{str}^{twin}), and a shear strain energy (ΔU_{str}^{shr}).[4] The dilatational strain energy, ΔU_{str}^{dil}, can be expressed in the following equation.[6,7]

$$\Delta U_{str}^{dil}=\frac{0.33E_mE_p\Delta^2}{E_p(1+\nu_m)+2E_m(1-2\nu_p)} \qquad (4)$$

where Δ (=0.04) is the volume strain, which is calculated from the difference between the unit cell volumes of the tetragonal and the monoclinic phases, E_m and E_p are the Young's moduli of the matrix and particle phases following Eshelby's notation and n_m and n_p are the poisson's ratio of the matrix and particle phases (In the case of the

Ce-TZP $E_m=E_p=E_t$ and $n_m=n_p=n_t$).

The twinning strain energy, ΔU_{str}^{twin}, has been written in the following equation 2.

$$\Delta U_{str}^{twin} = \frac{\lambda_1}{\lambda_2 + \eta} \mu \gamma_T^2 \tag{5}$$

where λ_1 and λ_2 are constants, μ is the number of twins per spherical grain, μ is the shear modulus and λ_T is the unconstrained shear strain associated with each twin.

Garvie and Swain[8)] roughly estimated the shear strain energy, ΔU_{str}^{shr}, as

$$\Delta U_{str}^{shr} = \frac{0.16 c \mu \gamma^2}{r} \tag{6}$$

where c is a constant spacing of twins, γ (=0.16) is a constraint-free deviatoric shear strain due to the lattice change from tetragonal to monoclinic phase and r is a radius of tetragonal zirconia grain.

ΔU_{str}^{shr} in Equation 6 is inversely proportional to the grain size. Therefore, the magnitude of ΔU_{str} increases as the grain size decreases.

$\Sigma\Delta\gamma_i$ includes an excess surface energy for the monoclinic-tetragonal (t/m) interface ($\gamma_{t/m}$), a twin boundary energy ($\gamma_{t.w}$) and a microcrack formation energy (γ_{crack}). Since grain-boundary area increases as grain size decreases, a contribution of $\gamma_{t/m}$ increases. Generally most microcracks form either the termination of twins within the grains or the interface between the transformed grains and the matrix. Due to a character of the formation of microcracks, contribution of γ_{crack} increases as grain size decreases. Therefore, a magnitude of $\Sigma\Delta\gamma_i$ increases as grain size decreases.

Thus, the magnitudes of a positive terms (ΔU_{str} ΔV and $\Sigma\Delta A_i$ $\Delta\gamma_i$),which suppress the martensitic transformation increase as the grain size decreases. That is, the phase stability of tetragonal zirconia grain in the Ce-TZP is enhanced as the grain size decreases.

Yu[4] derives the equation for the dependence of the martensitic transformation temperature of the Ce-TZP on grain size

$$M_b = 401.4 - \frac{3.314 \times 10^{-4}}{D_c} \tag{7}$$

where M_b is the martensitic transformation temperature, and D_c is the critical mean grain size. Fig. 7 compares the experimental results and the theoretical prediction. The differences between the theoretical prediction and the experimental results may results from the poor choice of thermodynamic parameters.

3. C. *Effect of the aliovalent dopants on the phase stability of the Ce-TZP*

Both Ce-TZP/Nb_2O_5 (grain size=19.4 μm) and Ce-TZP/MnO (grain size=3.5 μm) did not show the martensitic transformation by the liquid nitrogen temperature. Thus, from a comparison of the Ce-TZP and Ce-TZP/MnO at same grain size (2 μm) have shown very different M_b temperatures and the Ce-TZP and Ce-TZP/Nb_2O_5 at same grain size (5.5 μm) also have shown very different M_b temperatures. Therefore, it was verified that the phase stability of the tetragonal zirconia grain in the Ce-TZPs was affected by both composition and grain size and the effect of composition on the phase stability was more profound than that of the grain size. From the fact that the Ce-TZPs at the same grain sizes as those of Ce-TZP/Nb_2O_5 and Ce-TZP/MnO had different M_b temperatures, it was assumed that $\Delta\gamma_i$ term in Equation 1 did not contribute to an enhancement of the phase stability of the Ce-TZP can be thought. It was expected the addition of small amount (1 mol %) of the aliovalent dopants (Nb_2O_5 and MnO) to the Ce-TZP did not change the Young's modulus, Possion's ratio, and shear modulus of the Ce-TZP significantly. Therefore, ΔU_{str} in Equation 1 also did not contribute to an enhancement of the phase stability of the Ce-TZP caused by the addition of the aliovalent dopants. Since $\Delta\gamma_i$ and ΔU_{str} did not contribute to the enhancement of the phase stability of the Ce-TZP caused by the addition of the aliovalent dopants, only factor caused the enhancement of the phase stability was a term of the chemical driving force, ΔG_{chem}. As described previously, ΔG_{chem}, can be affected by the temperature and composition. From the comparison of the phase stabilitis of the Ce-TZP and the doped Ce-TZPs it was verified that ΔG_{chem} term was affected by the addition of the small amount of the aliovalent dopants significantly. From classical nucleation theory the relationship between the chemical driving force, ΔG_{chem}, and the activation energy, ΔG^+, can be expressed in the following equation (8).

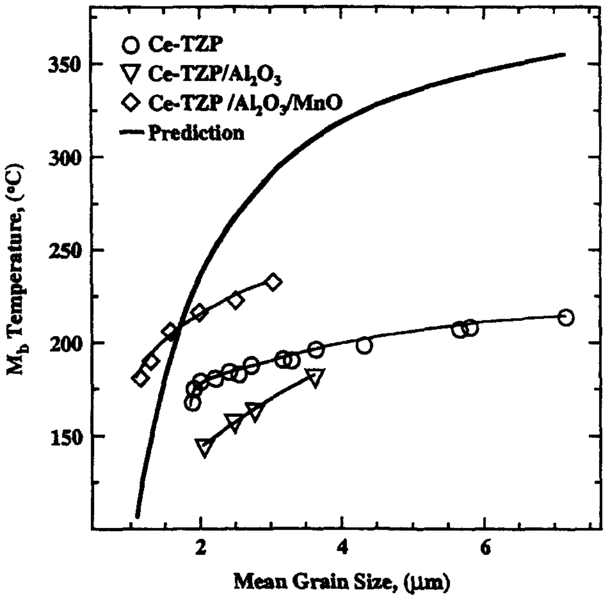

Fig. 7. Comparison of the dependence of the burst transformation temperature, M_b, on the critical mean grain size, d_c, between the theoretical prediction and the experimental results of the Ce-TZP, Ce-TZP/Al_2O_3 and Ce-TZP/Al_2O_3/MnO.

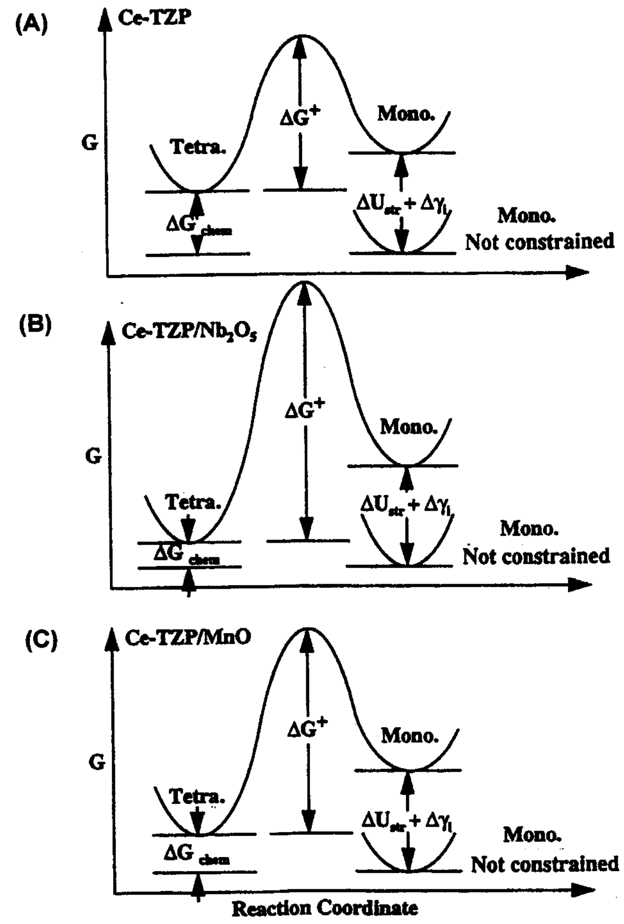

Fig. 8. Reaction coordinate diagram showing energetics of a constrained ZrO_2 tetragonal and monoclinic grain at M_b for (A) the Ce-TZP, (B) Ce-TZP/Nb_2O_5 and (C) Ce-TZP/MnO.

$$\Delta G^+ = \frac{1}{\Delta G_{chem}^2} \tag{8}$$

That is, the activation energy is inversely proportional to the square of chemical driving force. Thus, from the fact of the higher phase stability of the doped Ce-TZPs than the Ce-TZP, a reduction of the chemical driving force caused by the addition of the aliovalent dopants to the Ce-TZP induced the higher activation energy barrier for the martensitic transformation in the doped Ce-TZPs.

Fig. 8 compares energetic diagrams for the martensitic transformation in the Ce-TZP, Ce-TZP/Nb_2O_5 and Ce-TZP/MnO. Since the M_b temperature of Ce-TZP/Nb_2O_5 (grain size=19.2 μm) could not be detected even if the grain size of Ce-TZP/Nb_2O_5 was much greater than that of Ce-TZP/MnO (grain size=3.5 μm), it was found that the reduction of the chemical driving force caused by the addition of Nb_2O_5 was greater than that caused by the addition of MnO.

As we showed previously, the Ce-TZP has single-phase microstructure while Ce-TZP/Al_2O_3/MnO and Ce-TZP/Al_2O_3 have two-phase microstructure. From the comparison of microstructures of the Ce-TZP and Ce-TZP/Al_2O_3/MnO the grain boundary between tetragonal zirconia grains in the Ce-TZP is fully coherent, whereas the tetragonal zirconia grains in Ce-TZP/Al_2O_3/MnO with second-phase particles ($CeMnAl_{11}O_{19}$) have incoherent grain-boundary locally. The tetragonal zirconia grains in the two systems are under different amounts of stress. In the Ce-TZP, a small thermal expansive mismatch between the tetragonal zirconia grains caused by diffference in orientation of the tetragonal zirconia grains causes a small strain on the tetragonal zirconia grain. In Ce-TZP/Al_2O_3/MnO, on the other hand, the thermal expansive mismatch caused by the two-phase microstructure is large. This large thermal expansion-mismatch increases the strain energy on supercooling relatively to that of the Ce-TZP. However, as we described before, the second-phase particle in Ce-TZP/Al_2O_3/MnO consists of Ce, Mn, Al and O. An extraction of the cerium ions acting as stabilizer from the tetragonal zirconia grain to the second phase particle should result in destabilization of the tretragonal zirconia phase. That is, ΔG_{chem} increases through the destabilization caused by the extraction of the stabilizer, Ce. From a comparison of the M_b temperatures of the Ce-TZP and Ce-TZP/Al_2O_3/MnO the increment of ΔG_{chem} caused by the destabilization of the TZP grain is larger than that of ΔU_{str}, caused by the termal expansive mismatch between the tetragonal zirconia grain and the second phase particle. Thus, the phase stability of Ce-TZP/Al_2O_3/MnO at the same grain size as that in the Ce-TZP is lower than that of the Ce-TZP.

In Ce-TZP/Al_2O_3, the second phase particle composes of only alumina (Al and O)[9] and dispersed intra- and intergranulally into the Ce-TZP matrix. Dispersion of alumina particles with higher elastic modulus than that of the tetragonal zirconia grain enhanced the elastic modulus of the Ce-TZP and restrict the martensitic transformation through the increment of magnitude of the strain energy term in Equation 1. Thus, the phase stability of Ce-TZP/Al_2O_3 is higher than those of the Ce-TZP and Ce-TZP/Al_2O_3/MnO.

4. Effect of Al_2O_3 and MnO on mechcnical properties of the Ce-TZP

As shown in Fig. 3, the Ce-TZP/Al_2O_3, with the same average grain size of 2 μm as the Ce-TZP, showed the same linear elastic behavior to fracture as that of the Ce-TZP and higher fracture strength than that of the Ce-TZP in the three point bending. It is expected from those results that a dispersion of the second phase particles of alumina with the higher Young's modulus than that of the TZP phase restricted the martensitic transformation of the TZP grains to fracture (linear elastic behavior) and supplied the stress resistent to fracture (higher fracture strength).

With the addition of MnO, the composite showed clear transition to ealstic-plastic behavior in the three point bending. Wang et al. have found that Ce-TZP/Al_2O_3 composite, which showed linear elastic stress-strain behavior in three point bending, showed no visible transformation zone on the SEBN specimen while Ce-TZP/Al_2O_3 with MnO had comparable wide but diffused transformation bands.[9] That is, the martensitic transformation of the TZP grains in Ce-TZP/Al_2O_3 assisted by the second phase particles of $CeMnAl_{11}O_{19}$ during the three point bending gave rise to the transformation plasticity and higher fracture strength than that of the Ce-TZP.

V. Summary

1. The phase stabilities of tetragonal zirconia particle in the Ce-TZP/MnO and Ce-TZP/Nb_2O_5 with the same grain size as that of the Ce-TZP are much higher than that in the Ce-TZP because the addition of MnO to the Ce-TZP enhances the activation energy barrier for the martensitic transformation.
2. The phase stability of TZP in the Ce-TZP/Al_2O_3 is enhanced as compared to that of the Ce-TZP because dispersion of alumina particles with higher elastic modulus restricts the martensitic transformation through the increment of magnitude of the strain energy.
3. The phase stability of TZP in the Ce-TZP/Al_2O_3/MnO is reduced, as compared to that of the Ce-TZP, because extraction of the cerium ions, acting as stabilizer, from the trtragonal zirconia grain to the second phase particle result in destabilization of the trtragonal zirconia phase.
4. The Ce-TZP/Al_2O_3/MnO with low phase stability shows a lot of plastic deformation in three-point bending test but other Ce-TZPs with relatively high phase stability shows small amount of plastic deformation or not.

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