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Effect of Ta₂O₅, Nb₂O₅, and HfO₂ Alloying on the Transformability of Y₂O₃-Stabilized Tetragonal ZrO₂

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The addition of Ta₂O₅, Nb₂O₅, and HfO₂ enhanced the transformability of Y₂O₃-stabilized tetragonal ZrO₂ polycrystal (Y-TZP), which was indicated by an increase in phase transformation temperatures and fracture toughness of Y-TZP. Comparison of the alloying effects of these oxides on the transformability and crystal structure of Y-TZP suggested that an alloying oxide which increases the c/a axial ratio (tetragonality) of TZP also increases the transformability. Empirical equations to predict the tetragonality are proposed. Calculated tetragonalities showed good agreement with measured values in the systems ZrO₂-Y₂O₃-Ta₂O₅, –Nb₂O₅, and –HfO₂. [Key words: yttria, zirconia, alloys, transformations, fracture toughness.]

I. Introduction

IT IS well-known that for ZrO₂ to be utilized for technical applications the high-temperature polymorphs, namely, cubic (c) and tetragonal (t) phases, should be stabilized at ambient temeprature by the formation of solid solutions which prevent deleterious tetragonal-to-monoclinic (m) phase transformation. The alloying oxides which lead to the stabilization are alkaline-earth, rare-earth, and actinide oxides and some transition-element oxides such as In₂O₃.[1] Although there is no theoretical basis to select the stabilizer, it has been suggested that the factors which may influence the stabilization are size, valency, and concentration of solute cations and crystal structure of the solute oxide,[2] where the valency and concentration determine the number of oxygen vacancies created by the formation of substitutional solid solutions.

Y₂O₃ is a very effective stabilizer for t-ZrO₂, which possesses high values of strength and fracture toughness with an optimum amount of Y₂O₃ concentration.[3,4] The t-ZrO₂ phase retention at room temperature in this system depends on the composition, grain size, and density of the Y₂O₃-stabilized t-ZrO₂ polycrystal (Y-TZP).[5] For a given grain size and density, the addition of Y₂O₃ to ZrO₂ lowers the transformation temperatures of t → m (M_s) and m → t (A_s),[6] so that the chemical driving force for the transformation is reduced with increasing Y₂O₃ concentration.[7] Thus the transformability or instability of Y-TZP decreases as the Y₂O₃ content increases. This lowered transformability is manifested by a small amount of m-ZrO₂ fraction observed on the fracture surface of Y-TZP and is accompanied by a decrease in the fracture toughness.[8]

Schubert[9] has related the compositional dependence of the stability of TZP in this system to its dependence on the thermal expansion anisotropy ($\Delta\alpha$), which decreases with increasing Y₂O₃ concentration. $\Delta\alpha$ is known to govern the residual stress in t-ZrO₂ so that the increased residual stress enhances the transformability.[7,9] Since the $\Delta\alpha$ of Y-TZP decreases with

increasing Y₂O₃ content, it was expected that the composition at which the $\Delta\alpha$ becomes zero would coincide with that at which c-ZrO₂ becomes stable.[9] However, the composition determined from the linear extrapolation of the $\Delta\alpha$ to zero was very different from the composition for c-ZrO₂ obtained from the measurement of lattice parameters.[10] Consequently, the effect of alloying on the transformability cannot be predicted by the effect on the $\Delta\alpha$ alone. On the other hand, the alloying of HfO₂ into ZrO₂ raises the A_s and M_s temperatures,[11] which is attributed to an increase in the driving force for the t → m transformation.[12,13] The increased M_s due to HfO₂ alloying has been interpreted by Burke and Garvie[14] using the concept of the soft phonon mode. In their argument M_s increases with decreasing effective cation mass of the resulting solid solution, which is decreased by the addition of HfO₂. This simple interpretation is not applicable to changes in M_s in the other ZrO₂ solid solutions since these solid solutions cannot conform to the assumption that ZrO₂ and a solute are identical with the exception of cation masses.

In the present paper, a systematic investigation of the effect of ternary element alloying on the transformability of Y-TZP was conducted in an effort to elucidate the origin of the compositional dependence of the transformability of t-ZrO₂. Primarily, the effect of Ta₂O₅ alloying on the transformation temperatures, fracture toughness, and lattice parameters of Y-TZP was investigated. In addition, Nb₂O₅ and HfO₂ were employed separately as ternary allowing oxides in Y-TZP to add to a generalization of the role of alloying oxides on the transformability. An effort was made to predict the alloying effect on the transformability which leads to a selection criterion for the stabilizer of t-ZrO₂.

II. Experimental Procedure

Starting powders were prepared by coprecipitation from aqueous solutions of Zr(SO₄)₂·4H₂O, Y(NO₃)₃·6H₂O, and TaCl₅, NbCl₅, or HfOCl₂·8H₂O with ammonia. For some compositions in the system ZrO₂-Y₂O₃-Nb₂O₅, ZrOCl₂·8H₂O was used for ZrO₂ because of the decomposition of Zr(SO₄)₂·4H₂O with high concentration of NbCl₅ solution in an aqueous mixture. The precipitates were dried for 20 h at 120°C after washing with distilled water and decomposed to the oxides by calcination for 3 h at 920°C. The oxide agglomerates which contained Ta₂O₅ or HfO₂ were dry-milled in a planetary mill using an alumina jar and balls. The powders in the system ZrO₂-Y₂O₃-Nb₂O₅ were obtained by attrition milling in isopropyl alcohol using ZrO₂ balls. Bend test specimens were prepared by pressing the powders isostatically at 170 MPa, and sintering for 1 h at 1500°C. The density of sintered specimens was determined by the Archimedes method.

The fracture toughness was determined by two methods. One method involved the fracture of polished four-point bend specimens of dimensions 2.5 mm × 3.0 mm × 30 mm containing three 147-N Vickers indentations on the tensile surface within the inner span after Cook and Lawn.[15] The dimensions of the inner and outer spans were 10 and 20 mm, respectively. The samples were tested at a crosshead speed of 0.5 mm/min.

The fracture toughness of each composition was obtained from an average value of three measurements. The other method employed the indentation technique applying the equation proposed by Anstis et al.,[16] where the value of 205 GPa was used for the modulus of TZP. For the indentation method the indent load was varied from 196 to 490 N and the value of the fracture toughness was determined again by the average of three measurements. Four-point bend strength was obtained from the fracture of the bend specimens also at a crosshead speed of 0.5 mm/min.

The monoclinic fraction on the specimens was determined from X-ray diffractometer (XRD) peak intensities after Garvie and Nicholson.[17] A dilatometer was used to measure the A_s and M_s transformation temperatures, which correspond to the starting points of the discontinuous volume shrinkage and expansion of the samples during heating and cooling, respectively. The dilatometry samples were heated from room temperature to 900°C and cooled at the same rate of 7.5°C/min. The average grain size was measured by the linear intercept method with the use of a correction factor of 1.56 after Mendelson.[18] The lattice parameters were determined by least-squares refinement of XRD data, obtained using $CuK\alpha$ with Si as a standard and utilizing the program LCLSQ.[19]

III. Results and Discussion

The effect of Ta_2O_5 alloying on the transformability of Y-TZP was examined by determining the effect on the transformation temperatures, A_s and M_s, of 2 and 3 mol% Y-TZP. As shown in Fig. 1, both A_s and M_s of each Y-TZP increase with the addition of Ta_2O_5, so that the chemical driving force for the $t \rightarrow m$ transformation of Y-TZP is enhanced because of the Ta_2O_5 alloying. This Ta_2O_5 alloying effect is contrasted to the effect of Y_2O_3, a stabilizer for TZP, whose addition decreases the transformation temperatures.[6] Figure 2 compares the alloying effect of Ta_2O_5 with that of HfO_2 on M_s of 2 mol% Y-TZP. The HfO_2 has been known as the only solute which increases the M_s temperature.[12] The increasing trend of M_s due to Ta_2O_5 alloying is steeper than that due to HfO_2 alloying, which implies that Ta_2O_5 is a more effective destabilizer for TZP than HfO_2. In Fig. 2, the M_s temperatures of TZP in the system ZrO_2–Y_2O_3–Ta_2O_5 were obtained from specimens sintered for 8 h at 1500°C. Those in the system ZrO_2–Y_2O_3–HfO_2 were determined after sintering for 18 h at the same temperature. With these sintering schedules, the influence of grain size on the comparison in Fig. 2 becomes
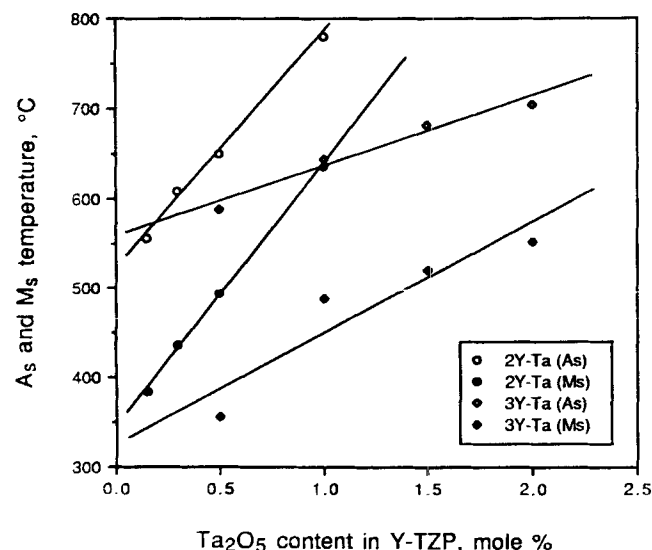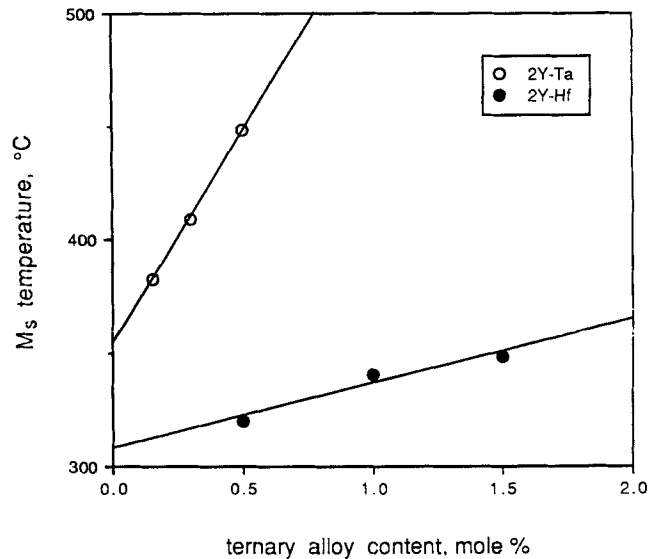
Fig. 2. Comparison of Ta_2O_5 and HfO_2 alloying effects on $t \rightarrow m$ transformation temperature of 2 mol% Y-TZP. Specimens were prepared to have grain sizes of about 1.0 μm by sintering at 1500°C for different times.

negligible, with both systems having a grain size of about 1.0 μm. The grain size dependence of the transformability of TZPs in the systems ZrO_2–Y_2O_3–Ta_2O_5 and –HfO_2 is documented in detail elsewhere.[20]

The alloying effect on the fracture toughness of Y-TZP was investigated and the result is shown in Fig. 3, where Ta_2O_5 is added to both 2 and 3 mol% Y-TZP, HfO_2 is added to 2 mol% Y-TZP, and Nb_2O_5 is added to 3 mol% Y-TZP. The toughness value of the specimen of 2 mol% Y-TZP with ≥0.5 mol% Ta_2O_5 could not be obtained since most of the t-ZrO_2 phase transformed to m-ZrO_2 phase during sample preparation. The alloying showed little effect on the microstructure of the specimens sintered at 1500°C for 1 h. Typically, the grain size of TZPs in the system ZrO_2–Y_2O_3–Ta_2O_5 was determined to be about 0.5 μm for all alloy additions.[20] The density of the specimens was ≥97% of the theoretical density. No m-ZrO_2 phase was detected in the as-sintered specimens, except in the sample with 1.5 mol% Ta_2O_5 which contained about 8% m-ZrO_2. The fracture toughness increases from 5 to about

Fig. 1. Influence of Ta_2O_5 alloying on phase transformation temperatures of 2 and 3 mol% Y-TZP prepared by sintering at 1500°C for 15 h.
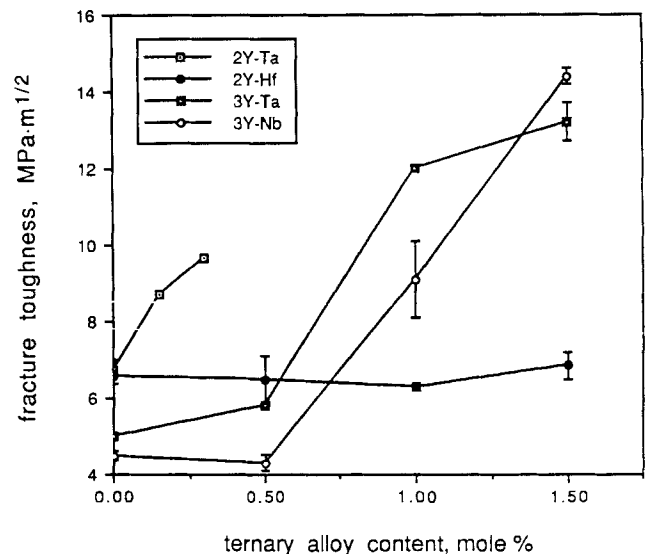
Fig. 3. Ta_2O_5, Nb_2O_5, and HfO_2 alloying effects on fracture toughness of 2 and 3 mol% Y-TZP prepared by sintering at 1500°C for 1 h.

14 MPa · m$^{1/2}$ as the Ta_2O_5 or Nb_2O_5 concentration in 3 mol% Y-TZP increases from zero to 1.5 mol%. This remarkable increase in the toughness is attributed to the enhanced transformability of t-ZrO_2 due to the alloying shown in Fig. 1. The influence of Nb_2O_5 alloying is similar to that due to Ta_2O_5 but the effect of HfO_2 alloying is not noticeable as compared with that of Ta_2O_5 alloying. The trends of Ta_2O_5 and HfO_2 alloying effects on the fracture toughness of 2 mol% Y-TZP are analogous to those on the M_s temperature shown in Fig. 2. Thus, Ta_2O_5 and Nb_2O_5 are strong destabilizers which enhance the transformability of Y-TZP, as compared with HfO_2. Figure 4 shows the Ta_2O_5 alloying effect on the bending strength and m-ZrO_2 fraction on the polished surface of 3 mol% Y-TZP. The bending strength slightly increases with the addition of Ta_2O_5 up to 1.0 mol% and decreases with further addition of Ta_2O_5. This decrease in the bending strength of the samples with 1.5 mol% Ta_2O_5 is due to the presence of a large amount of m-ZrO_2 phase on the polished sample surface. Increasing the sintering time, which results in grain growth, causes a further drop in the strength of the samples with 1.5 mol% Ta_2O_5 due to the increased amount of m-ZrO_2 phase.[20] The alloying effect on the transformability has been demonstrated by measuring the m-ZrO_2 phase fraction on the fracture surface of the bend test specimens, where the increasing trend of m-ZrO_2 fraction after the fracture as a function of Ta_2O_5 content shows excellent correlation with the fracture toughness.[20] The fracture toughness values measured by the multiple-crack method were identical to those obtained by indentation as long as the minimum requirement of $c \geq 2a$ suggested by Anstis *et al.*[16] is met, where c and a are the half crack length from a Vickers diamond pyramid indent and the half diagonal of the indent, respectively. Otherwise, the values by the indentation technique are overestimated by about 10% to 15% as compared with the values by the multiple-crack method.[20] This is the case for the specimens with 1.0 and 1.5 mol% Ta_2O_5 or Nb_2O_5 after indentation with the maximum load of 490 N employed in the present study.

The effects of Ta_2O_5, Nb_2O_5, and HfO_2 alloying on the changes in the c/a axial ratio (tetragonality) of Y-TZP are illustrated in Fig. 5, and the lattice parameters of the resulting t-ZrO_2 solid solutions at room temperature are listed in Table I. As shown, the alloying of these oxides into Y-TZP increases the tetragonality. On the other hand, the addition of oxides such as Y_2O_3, Yb_2O_3, Gd_2O_3,[21] and CeO_2[22,23] to stabilize t-ZrO_2 is found to decrease the tetragonal distortion as summarized in Fig. 6. This is the exactly opposite effect of the alloying of Ta_2O_5, Nb_2O_5, and HfO_2 which enhances the
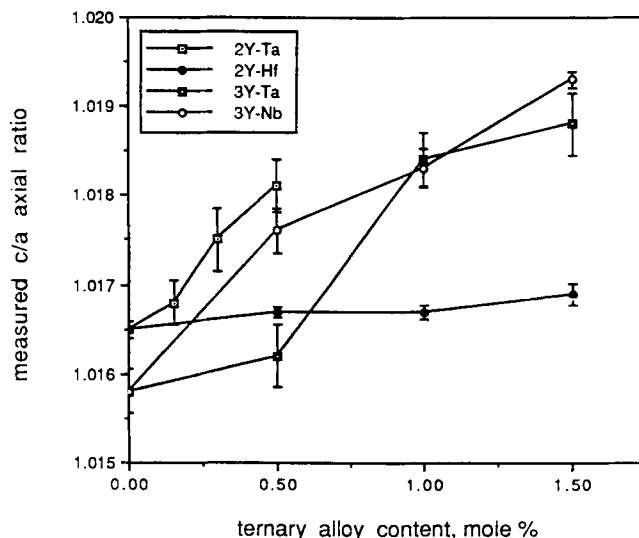
Fig. 5. Ta_2O_5, Nb_2O_5, and HfO_2 alloying effects on c/a axial ratio of 2 and 3 mol% Y-TZP.

transformability of Y-TZP. Thus the destabilizer and the stabilizer for the t-ZrO_2 might be differentiated depending on its role in the changes of the tetragonality of the resulting solid solution. Again, the effects of Ta_2O_5 and Nb_2O_5 alloying on the tetragonality are distinguished from the effect of HfO_2. In particular, the influences of Ta_2O_5 and HfO_2 alloying on the tetragonality of 2 mol% Y-TZP as shown in Fig. 5 are consistent with those on the M_s temperature and fracture toughness, as illustrated in Figs. 2 and 3, respectively. To see how the transformability of these ternary TZPs changes with the tetragonality, the M_s temperatures of the system ZrO_2–Y_2O_3–Ta_2O_5 shown in Fig. 1 are plotted as a function of the tetragonality in Fig. 7, where it can be seen that the M_s temperature of 2 and 3 mol% Y-TZP increases linearly with increasing tetragonality. The effect of the tetragonality on the transformability is apparent in Fig. 8, where the fracture toughness values are from Fig. 3. As a result, at least phenomenologically, the alloying effect on the transformability of TZP is closely related to the effect on the tetragonality of t-ZrO_2 solid solution in such a way that the transformability increases with the tetragonality.

The relationship between transformability and tetragonality is supported by consideration of t'-ZrO_2, which is known as nontransformable t-ZrO_2.[10,24] The c/a ratio of t'-ZrO_2 in the system Y_2O_3–ZrO_2 is closer to unity than that of transformable t-ZrO_2 with the same concentration of Y_2O_3 in the range from 10.9 to 13.0 mol% $YO_{1.5}$,[25] where the tetragonality of the transformable t-ZrO_2 is already small. The even smaller tetragonality of t'-ZrO_2 is likely responsible for its nontransformability. Another indication is in the system Y_2O_3–CeO_2–ZrO_2, where the substitution of Y_2O_3 for CeO_2 causes a decrease in the fracture toughness and an increase of the phase stability of Ce-TZP.[26] This Y_2O_3 alloying effect is predictable since the decrease in the tetragonality due to Y_2O_3 is more pronounced than that due to CeO_2, as shown in Fig. 6. The alloying effect of Y_2O_3 and CeO_2 on tetragonality is consistent with that on the $m \rightarrow t$ transformation temperature; that is, the decrease in A_s temperature per mole percent solute is reported to be 170.7°C for $YO_{1.5}$ and 71.2°C for CeO_2.[27] Evidently, t-ZrO_2 solid solutions become unstable as their tetragonality increases toward 1.020 (Fig. 6), which corresponds to the b/a axial ratio of m-ZrO_2 at room temperature.[28] On the other hand, they become stable as the tetragonality decreases toward unity, which corresponds to c-ZrO_2. This relationship allows the classification of oxides into either a stabilizer (decreasing tetragonality) or a destabilizer (increasing tetragonality) for the t-ZrO_2 phase at room temperature.
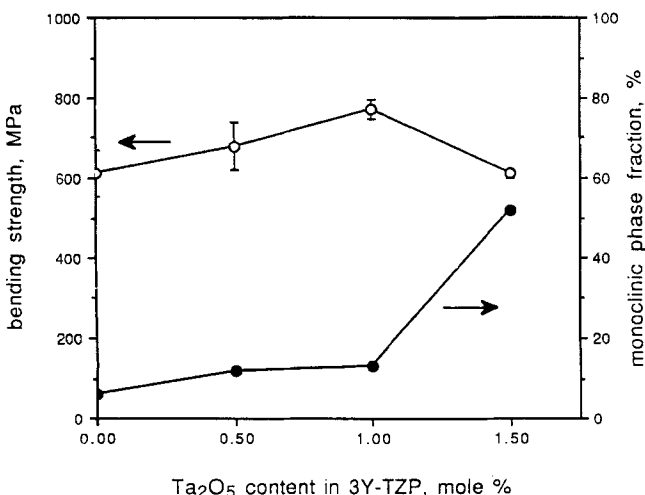
Fig. 4. Influence of Ta_2O_5 alloying on four-point bending strength and m-ZrO_2 phase content on polished surface of 3 mol% Y-TZP prepared by sintering at 1500°C for 1 h.

Table I.   Comparison of Measured and Calculated Lattice Parameters of t-ZrO_2 Solid Solutions

Composition (mol%)			a (nm)			c (nm)		
			Measd	Calcd	Δa (%)*	Measd	Calcd	Δc (%)*
ZrO_2	Y_2O_3	Ta_2O_5						
98.0	2	0.0	0.509 71	0.509 82	−0.02	0.518 12	0.517 85	0.05
97.85	2	0.15	0.509 66	0.509 79	−0.03	0.518 20	0.517 98	0.04
97.7	2	0.3	0.509 61	0.509 75	−0.03	0.518 51	0.518 11	0.08
97.5	2	0.5	0.509 30	0.509 71	−0.08	0.518 54	0.518 28	0.05
97.0	3	0.0	0.509 84	0.510 41	−0.11	0.517 92	0.517 35	0.11
96.5	3	0.5	0.510 24	0.510 30	−0.01	0.518 49	0.517 78	0.14
96.0	3	1.0	0.509 84	0.510 19	−0.07	0.519 24	0.518 19	0.20
95.5	3	1.5	0.509 89	0.510 07	−0.04	0.519 49	0.518 61	0.17
ZrO_2	Y_2O_3	Nb_2O_5						
96.5	3	0.5	0.509 62	0.510 30	−0.13	0.518 57	0.517 78	0.15
96.0	3	1.0	0.509 68	0.510 19	−0.10	0.519 03	0.518 19	0.16
95.5	3	1.5	0.509 67	0.510 07	−0.08	0.519 50	0.518 61	0.17
ZrO_2	Y_2O_3	HfO_2						
97.5	2	0.5	0.509 57	0.509 81	−0.05	0.518 10	0.517 84	0.05
97.0	2	1.0	0.509 60	0.509 80	−0.04	0.518 09	0.517 83	0.05
96.5	2	1.5	0.509 51	0.509 78	−0.05	0.518 13	0.517 82	0.06

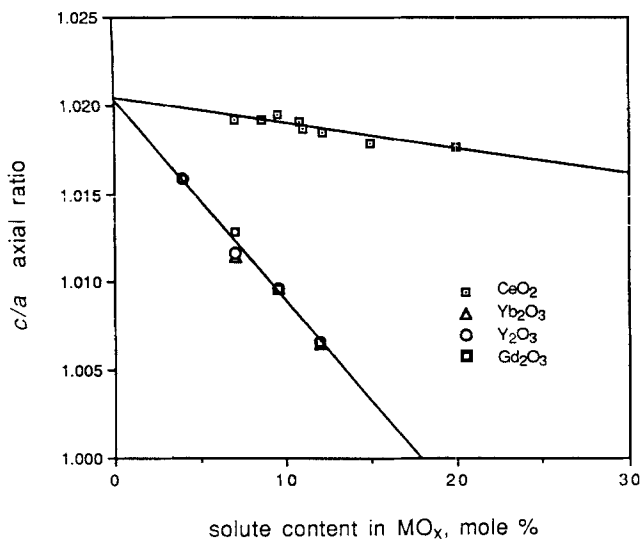*[(measured value − calculated value)/(measured value)] × 100.

Fig. 6. Compositional dependence of c/a axial ratio of t-ZrO_2 solid solutions stabilized by various oxides (Refs. 21 to 23).
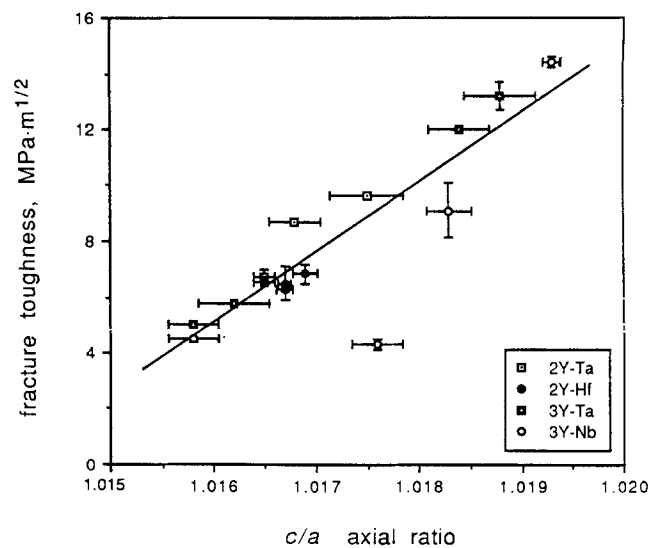

Fig. 7. Relationship between $t \rightarrow m$ transformation temperature and c/a axial ratio of Y(Ta)-TZP.

Fig. 8. Fracture toughness as a function of tetragonality.

In order to control the fracture toughness of TZP through alloying, besides the changes in the microstructure, it is desirable to formulate equations which predict changes in the lattice parameters of t-ZrO_2 as a result of compositional variations since the tetragonality is related to the transformability. The empirical equations for the changes in the lattice parameters, a and c, of t-ZrO_2 solid solutions at room temperature are expressed as follows:

$$a = 0.5086 + \sum_k (0.0255\Delta r_k + 0.00015\Delta z_k)m_k \tag{1}$$

$$c = 0.5189 + \sum_k (0.0213\Delta r_k + 0.00064\Delta z_k)m_k \tag{2}$$

where a and c are in nanometers, Δr_k (in nanometers) is the difference in ionic radius (r_k − 0.084) of the kth solute cation (r_k) and Zr^{4+} (0.084 nm) in eightfold coordination from Shannon's compilation,[29] Δz_k is the cation valency difference (z_k − 4), and m_k is the mole percent of the kth solute, in the form of MO_x, $x = z_k/2$. The term m_k, which corresponds to M_k for $n_k = 1$, is calculated by

$$m_k = \frac{n_k M_k}{100 + \sum_k (n_k - 1)M_k} \times 100 \tag{3}$$

where n_k is the number of cations in the kth solute oxide, and M_k is the concentration of the kth solute oxide in mole percent (e.g., n_k is 2 and M_k is 3 for 3 mol% Y_2O_3). The constants in Eqs. (1) and (2) were determined from regression analyses of t-ZrO_2 lattice parameters in the systems Y_2O_3-,[9,10,21,30] Yb_2O_3-,[21,30] Gd_2O_3-,[21,30] and CeO_2-ZrO_2.[22,23] The details of the formalism of Eqs. (1) and (2) are described elsewhere.[31] To illustrate, the changes in the lattice parameters of t-ZrO_2 in the system Y_2O_3-ZrO_2 as a function of the mole percent $YO_{1.5}$ can be represented as

$$a = 0.5086 + 0.00031 m_Y \tag{4}$$

$$c = 0.5189 - 0.00026 m_Y \tag{5}$$

by using $\Delta r_Y = 0.0179$ ($r_{Y^{3+}} = 0.1019$ nm) and $\Delta z_Y = -1$. Equations (4) and (5) are in excellent agreement with the equations determined experimentally by Toraya.[32] This suggests that the equations for the lattice parameters of t-ZrO_2 in the system Y_2O_3-CeO_2-ZrO_2, proposed by Urabe *et al.*,[27] should be

$$a = 0.5086 + 0.00031 m_Y + 0.00033 m_{Ce} \tag{6}$$

$$c = 0.5189 - 0.00026 m_Y + 0.00028 m_{Ce} \tag{7}$$

from $\Delta r_{Ce} = 0.013$ ($r_{Ce^{4+}} = 0.097$ nm) and $\Delta z_{Ce} = 0$. The only significant discrepancy between Eqs. (6) and (7) and those determined by Urabe *et al.* is the coefficient of m_Y in Eq. (6), which was 0.000 52.

The calculated lattice parameters using Eqs. (1) and (2) are compared with the measured values in Table I. Considering the standard error (0.000 30 nm) from the regression analyses in Eqs. (1) and (2) and the experimental error in the measurements, which ranges from 0.000 01 to 0.000 15 nm, the agreement between the calculated and measured lattice parameters is remarkable. Another good agreement can be found in the system MgO-Y_2O_3-ZrO_2,[33] where the measured values for a and c of t-ZrO_2 were reported to be 0.5114 and 0.5136 nm, respectively, for $M_{Mg} = 2.6$ and $M_Y = 4.5$ (i.e., $m_{Mg} = 2.5$ and $m_Y = 8.6$). These values are very close to the calculated a and c from Eqs. (1) and (2), which are 0.5108 and 0.5138 nm, respectively (here, $r_{Mg} = 0.089$ nm and $\Delta z_{Mg} = -2$). Accordingly, these equations can be applied to predict the effect of alloying on the tetragonality of t-ZrO_2 solid solutions as shown in Fig. 9. Comparison of Figs. 9 and 5 shows good qualitative agreement. In Fig. 9 the alloying effects of Ta_2O_5 and Nb_2O_5 on the tetragonality are estimated to be the same since the ionic radii in eightfold coordination
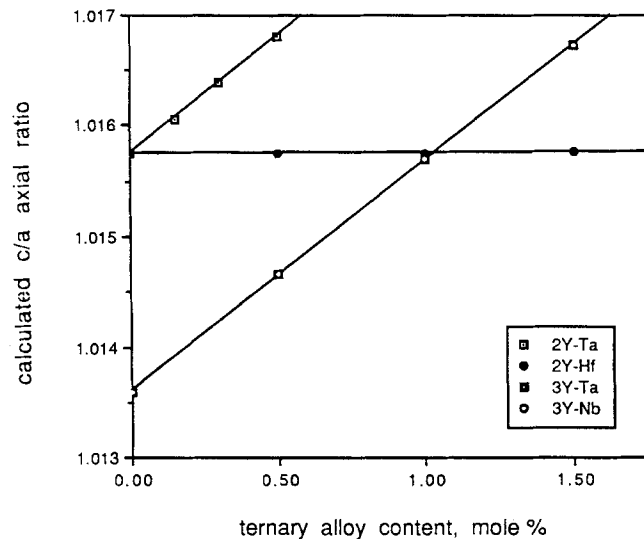
(0.074 nm) and valencies of Ta^{5+} and Nb^{5+} are identical. The small influence of HfO_2 alloying is clearly due to the same valency and the similar ionic radii of Zr^{4+} (0.084 nm) and Hf^{4+} (0.083 nm). It should be noted that the equations for the lattice parameters contain factors such as ionic radius, valency, and concentration of solute cation which are considered to influence the stabilization of the t-ZrO_2 phase, as discussed in the earlier section. Consequently, Eqs. (1) and (2) might be used to design TZP with a desired transformability by classifying solute oxides according to their influence on the tetragonality.

IV. Conclusion

The addition of Ta_2O_5, Nb_2O_5, and HfO_2 to Y_2O_3-stabilized tetragonal ZrO_2 (Y-TZP) gives rise to the high transformability of the resulting TZP. The enhanced transformability of Y-TZP is related to the alloying effect on the tetragonality of Y-TZP, so that the addition of these oxides increases the tetragonal distortion of the cubic fluorite lattice. The trend of increasing the tetragonality due to alloying is consistent with those of enhancing fracture toughness and $t \to m$ transformation temperature. The changes in the tetragonality due to the alloying are in remarkable agreement with the prediction by the proposed empirical equations.

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Fig. 9.   Calculated c/a axial ratio by using Eqs. (1) and (2) as a function of ternary element content in Y-TZP.

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