

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 temperature 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

Schubert⁹ 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 Garvie¹⁴ 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 alloying 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.

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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 α with Si as a standard and utilizing the program LCLSO.¹⁹

III. Results and Discussion

The effect of Ta₂O₅ 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 Ta₂O₅, so that the chemical driving force for the $t \rightarrow m$ transformation of Y-TZP is enhanced because of the Ta₂O₅ alloying. This Ta₂O₅ alloying effect is contrasted to the effect of Y₂O₃, a stabilizer for TZP, whose addition decreases the transformation temperatures.⁶ Figure 2 compares the alloying effect of Ta₂O₅ with that of HfO₂ on M_s of 2 mol% Y-TZP. The HfO₂ has been known as the only solute which increases the M_s temperature.¹² The increasing trend of M_s due to Ta₂O₅ alloying is steeper than that due to HfO₂ alloying, which implies that Ta₂O₅ is a more effective destabilizer for TZP than HfO₂. In Fig. 2, the M_s temperatures of TZP in the system ZrO₂-Y₂O₃-Ta₂O₅ were obtained from specimens sintered for 8 h at 1500°C. Those in the system ZrO₂-Y₂O₃-HfO₂ 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

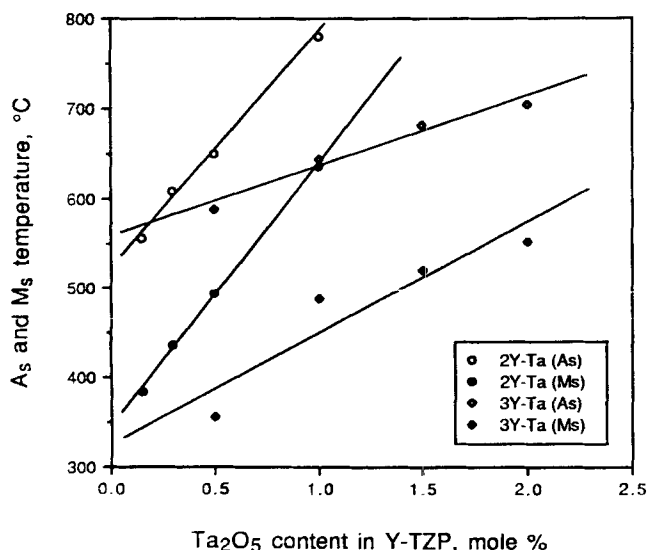


Fig. 1. Influence of Ta₂O₅ alloying on phase transformation temperatures of 2 and 3 mol% Y-TZP prepared by sintering at 1500°C for 15 h.

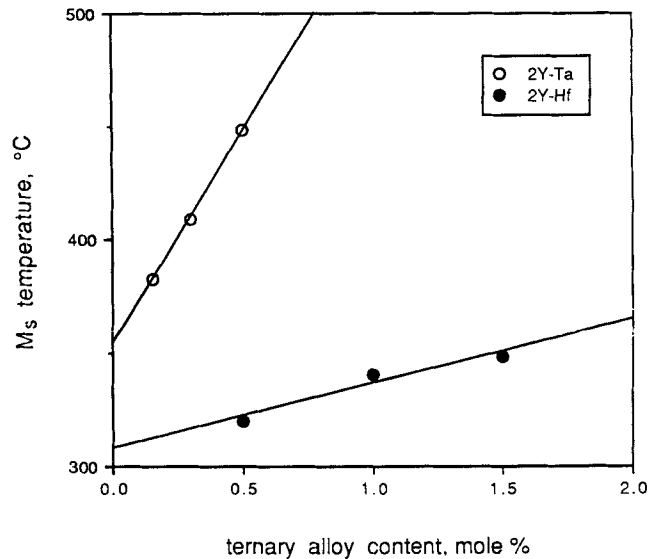


Fig. 2. Comparison of Ta₂O₅ and HfO₂ alloying effects on $t \rightarrow m$ transformation temperature of 2 mol% Y-TZP. Specimens were prepared to have grain sizes of about 1.0 μm by sintering at 1500°C for different times.

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 ZrO₂-Y₂O₃-Ta₂O₅ and -HfO₂ 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 Ta₂O₅ is added to both 2 and 3 mol% Y-TZP, HfO₂ is added to 2 mol% Y-TZP, and Nb₂O₅ is added to 3 mol% Y-TZP. The toughness value of the specimen of 2 mol% Y-TZP with ≥ 0.5 mol% Ta₂O₅ could not be obtained since most of the t -ZrO₂ phase transformed to m -ZrO₂ 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 ZrO₂-Y₂O₃-Ta₂O₅ was determined to be about 0.5 μm for all alloy additions.²⁰ The density of the specimens was $\geq 97\%$ of the theoretical density. No m -ZrO₂ phase was detected in the as-sintered specimens, except in the sample with 1.5 mol% Ta₂O₅ which contained about 8% m -ZrO₂. The fracture toughness increases from 5 to about

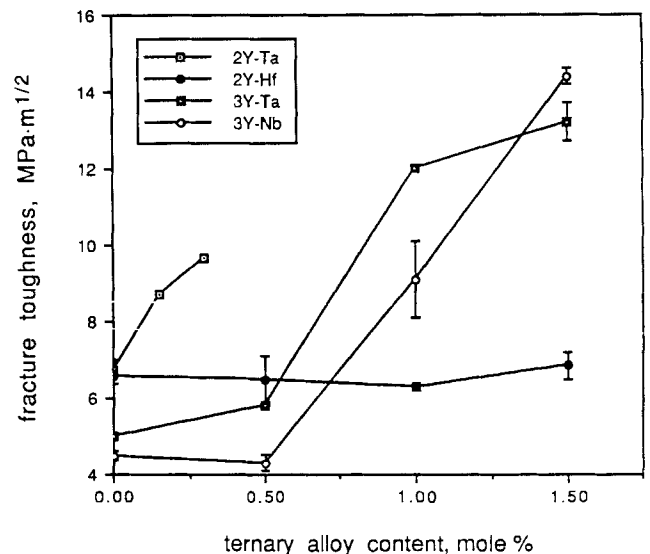


Fig. 3. Ta₂O₅, Nb₂O₅, and HfO₂ alloying effects on fracture toughness of 2 and 3 mol% Y-TZP prepared by sintering at 1500°C for 1 h.

14 MPa · m^{1/2} as the Ta₂O₅ or Nb₂O₅ 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*-ZrO₂ due to the alloying shown in Fig. 1. The influence of Nb₂O₅ alloying is similar to that due to Ta₂O₅ but the effect of HfO₂ alloying is not noticeable as compared with that of Ta₂O₅ alloying. The trends of Ta₂O₅ and HfO₂ 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, Ta₂O₅ and Nb₂O₅ are strong destabilizers which enhance the transformability of Y-TZP, as compared with HfO₂. Figure 4 shows the Ta₂O₅ alloying effect on the bending strength and *m*-ZrO₂ fraction on the polished surface of 3 mol% Y-TZP. The bending strength slightly increases with the addition of Ta₂O₅ up to 1.0 mol% and decreases with further addition of Ta₂O₅. This decrease in the bending strength of the samples with 1.5 mol% Ta₂O₅ is due to the presence of a large amount of *m*-ZrO₂ 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% Ta₂O₅ due to the increased amount of *m*-ZrO₂ phase.²⁰ The alloying effect on the transformability has been demonstrated by measuring the *m*-ZrO₂ phase fraction on the fracture surface of the bend test specimens, where the increasing trend of *m*-ZrO₂ fraction after the fracture as a function of Ta₂O₅ 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% Ta₂O₅ or Nb₂O₅ after indentation with the maximum load of 490 N employed in the present study.

The effects of Ta₂O₅, Nb₂O₅, and HfO₂ 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*-ZrO₂ 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 Y₂O₃, Yb₂O₃, Gd₂O₃,²¹ and CeO₂^{22,23} to stabilize *t*-ZrO₂ is found to decrease the tetragonal distortion as summarized in Fig. 6. This is the exactly opposite effect of the alloying of Ta₂O₅, Nb₂O₅, and HfO₂ which enhances the

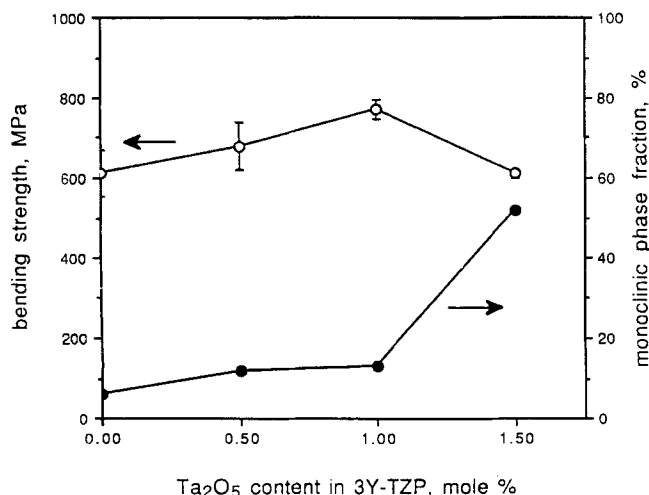


Fig. 4. Influence of Ta₂O₅ alloying on four-point bending strength and *m*-ZrO₂ phase content on polished surface of 3 mol% Y-TZP prepared by sintering at 1500°C for 1 h.

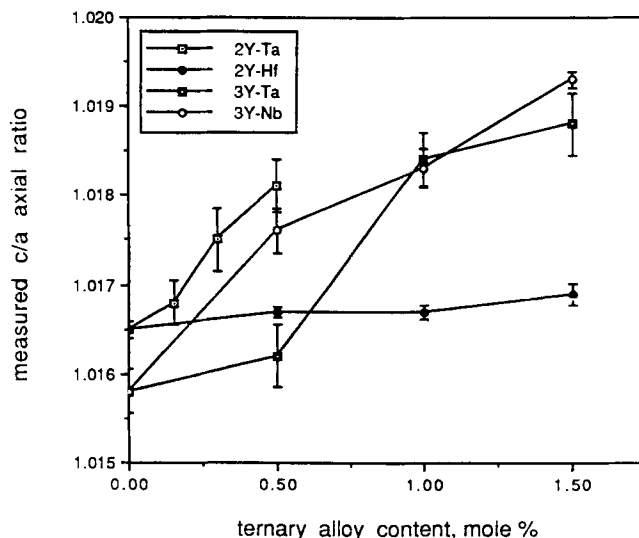


Fig. 5. Ta₂O₅, Nb₂O₅, and HfO₂ alloying effects on *c/a* axial ratio of 2 and 3 mol% Y-TZP.

transformability of Y-TZP. Thus the destabilizer and the stabilizer for the *t*-ZrO₂ might be differentiated depending on its role in the changes of the tetragonality of the resulting solid solution. Again, the effects of Ta₂O₅ and Nb₂O₅ alloying on the tetragonality are distinguished from the effect of HfO₂. In particular, the influences of Ta₂O₅ and HfO₂ 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 ZrO₂-Y₂O₃-Ta₂O₅ 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*-ZrO₂ 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'*-ZrO₂, which is known as nontransformable *t'*-ZrO₂.^{10,24} The *c/a* ratio of *t'*-ZrO₂ in the system Y₂O₃-ZrO₂ is closer to unity than that of transformable *t*-ZrO₂ with the same concentration of Y₂O₃ in the range from 10.9 to 13.0 mol% YO_{1.5},²⁵ where the tetragonality of the transformable *t*-ZrO₂ is already small. The even smaller tetragonality of *t'*-ZrO₂ is likely responsible for its nontransformability. Another indication is in the system Y₂O₃-CeO₂-ZrO₂, where the substitution of Y₂O₃ for CeO₂ causes a decrease in the fracture toughness and an increase of the phase stability of Ce-TZP.²⁶ This Y₂O₃ alloying effect is predictable since the decrease in the tetragonality due to Y₂O₃ is more pronounced than that due to CeO₂, as shown in Fig. 6. The alloying effect of Y₂O₃ and CeO₂ on tetragonality is consistent with that on the *m* → *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 CeO₂.²⁷ Evidently, *t*-ZrO₂ solid solutions become unstable as their tetragonality increases toward 1.020 (Fig. 6), which corresponds to the *b/a* axial ratio of *m*-ZrO₂ at room temperature.²⁸ On the other hand, they become stable as the tetragonality decreases toward unity, which corresponds to *c*-ZrO₂. This relationship allows the classification of oxides into either a stabilizer (decreasing tetragonality) or a destabilizer (increasing tetragonality) for the *t*-ZrO₂ phase at room temperature.

Table I. Comparison of Measured and Calculated Lattice Parameters of *t*-ZrO₂ Solid Solutions

Composition (mol%)			<i>a</i> (nm)		Δa (%)*	<i>c</i> (nm)		Δc (%)*
ZrO ₂	Y ₂ O ₃	Ta ₂ O ₅	Measd	Calcd		Measd	Calcd	
ZrO ₂	Y ₂ O ₃	Ta ₂ O ₅						
98.0	2	0.0	0.50971	0.50982	-0.02	0.51812	0.51785	0.05
97.85	2	0.15	0.50966	0.50979	-0.03	0.51820	0.51798	0.04
97.7	2	0.3	0.50961	0.50975	-0.03	0.51851	0.51811	0.08
97.5	2	0.5	0.50930	0.50971	-0.08	0.51854	0.51828	0.05
97.0	3	0.0	0.50984	0.51041	-0.11	0.51792	0.51735	0.11
96.5	3	0.5	0.51024	0.51030	-0.01	0.51849	0.51778	0.14
96.0	3	1.0	0.50984	0.51019	-0.07	0.51924	0.51819	0.20
95.5	3	1.5	0.50989	0.51007	-0.04	0.51949	0.51861	0.17
ZrO ₂	Y ₂ O ₃	Nb ₂ O ₅						
96.5	3	0.5	0.50962	0.51030	-0.13	0.51857	0.51778	0.15
96.0	3	1.0	0.50968	0.51019	-0.10	0.51903	0.51819	0.16
95.5	3	1.5	0.50967	0.51007	-0.08	0.51950	0.51861	0.17
ZrO ₂	Y ₂ O ₃	HfO ₂						
97.5	2	0.5	0.50957	0.50981	-0.05	0.51810	0.51784	0.05
97.0	2	1.0	0.50960	0.50980	-0.04	0.51809	0.51783	0.05
96.5	2	1.5	0.50951	0.50978	-0.05	0.51813	0.51782	0.06

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

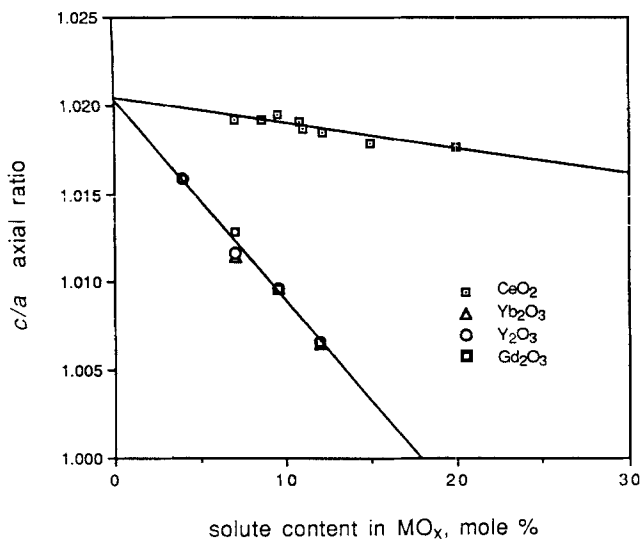


Fig. 6. Compositional dependence of *c/a* axial ratio of *t*-ZrO₂ solid solutions stabilized by various oxides (Refs. 21 to 23).

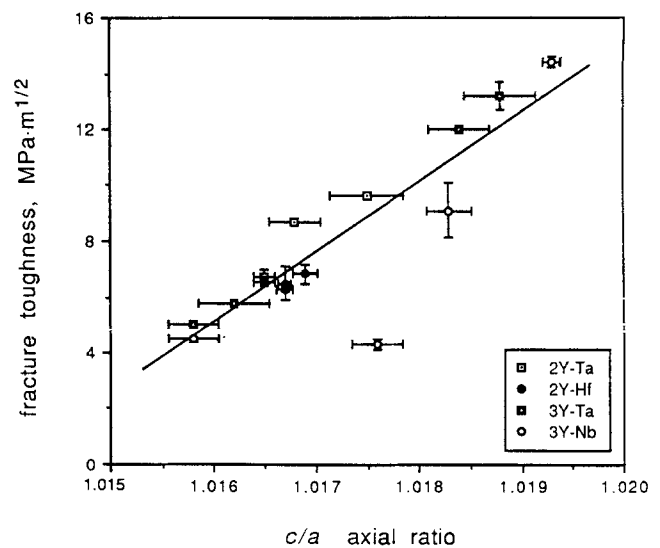


Fig. 8. Fracture toughness as a function of tetragonality.

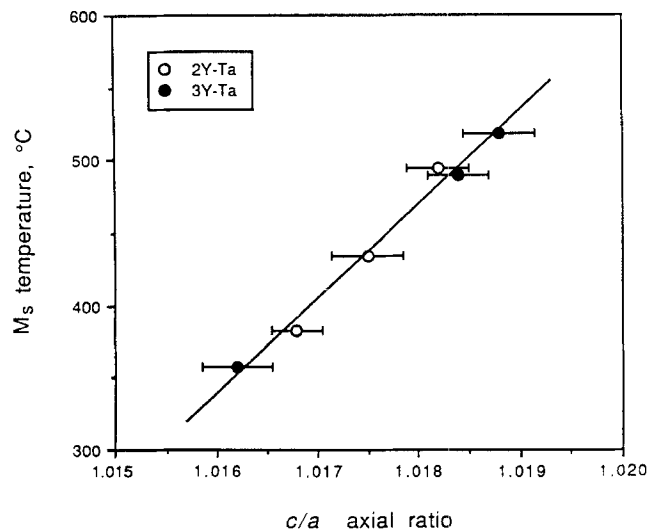


Fig. 7. Relationship between *t* → *m* transformation temperature and *c/a* axial ratio of Y(Ta)-TZP.

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*-ZrO₂ 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*-ZrO₂ solid solutions at room temperature are expressed as follows:

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

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

where *a* and *c* are in nanometers, Δr_k (in nanometers) is the difference in ionic radius ($r_k - 0.084$) of the *k*th solute cation (r_k) and Zr⁴⁺ (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 *k*th 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

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

where n_k is the number of cations in the k th solute oxide, and M_k is the concentration of the k th solute oxide in mole percent (e.g., n_k is 2 and M_k is 3 for 3 mol% Y₂O₃). The constants in Eqs. (1) and (2) were determined from regression analyses of t -ZrO₂ lattice parameters in the systems Y₂O₃–^{9,10,21,30} Yb₂O₃–^{21,30} Gd₂O₃–^{21,30} and CeO₂–ZrO₂.^{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 -ZrO₂ in the system Y₂O₃–ZrO₂ as a function of the mole percent YO_{1.5} can be represented as

$$a = 0.5086 + 0.00031m_Y \quad (4)$$

$$c = 0.5189 - 0.00026m_Y \quad (5)$$

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 -ZrO₂ in the system Y₂O₃–CeO₂–ZrO₂, proposed by Urabe *et al.*,²⁷ should be

$$a = 0.5086 + 0.00031m_Y + 0.00033m_{Ce} \quad (6)$$

$$c = 0.5189 - 0.00026m_Y + 0.00028m_{Ce} \quad (7)$$

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 0.00052.

The calculated lattice parameters using Eqs. (1) and (2) are compared with the measured values in Table I. Considering the standard error (0.00030 nm) from the regression analyses in Eqs. (1) and (2) and the experimental error in the measurements, which ranges from 0.00001 to 0.00015 nm, the agreement between the calculated and measured lattice parameters is remarkable. Another good agreement can be found in the system MgO–Y₂O₃–ZrO₂,³³ where the measured values for a and c of t -ZrO₂ 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 -ZrO₂ solid solutions as shown in Fig. 9. Comparison of Figs. 9 and 5 shows good qualitative agreement. In Fig. 9 the alloying effects of Ta₂O₅ and Nb₂O₅ on the tetragonality are estimated to be the same since the ionic radii in eightfold coordination

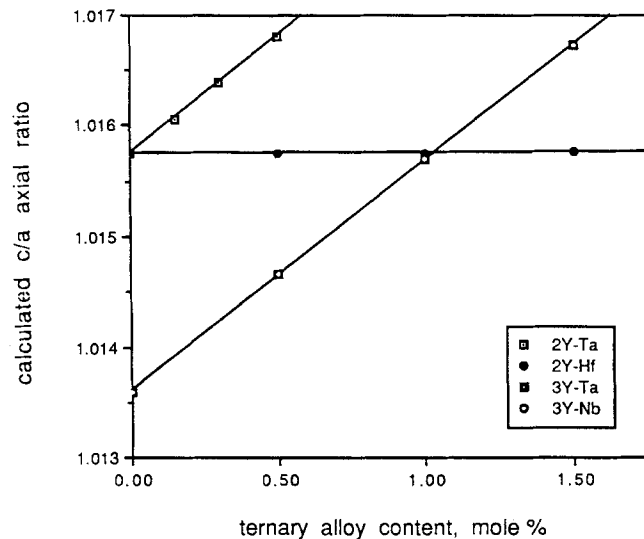


Fig. 9. Calculated c/a axial ratio by using Eqs. (1) and (2) as a function of ternary element content in Y-TZP.

(0.074 nm) and valencies of Ta⁵⁺ and Nb⁵⁺ are identical. The small influence of HfO₂ alloying is clearly due to the same valency and the similar ionic radii of Zr⁴⁺ (0.084 nm) and Hf⁴⁺ (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 -ZrO₂ 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 Ta₂O₅, Nb₂O₅, and HfO₂ to Y₂O₃-stabilized tetragonal ZrO₂ (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 $t \rightarrow m$ 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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