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Thermodynamic calculation of M_s in ZrO_2–CeO_2–Y_2O_3 system

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Abstract

The difference of Gibbs free energy between tetragonal and monoclinic phases in ZrO_2–CeO_2–Y_2O_3 as a function of composition and temperature is thermodynamically calculated from the three related binary systems. In 8 mol% CeO_2–0.5 mol% Y_2O_3–ZrO_2, the equilibrium temperature between tetragonal and monoclinic phases, T_0, is obtained as 832.5 K and the M_s temperature of this alloy with a mean grain size of 0.90 μm is calculated as 249.9 K using the approach derived by Hsu et al. [*J. Mater. Sci.*, 18(1983)3206; 20(1985)23; *Acta Metall.*, 37(1989)3091; *Acta Metall. Mater.*, 39(1991)1045; *Mater. Trans. JIM*, 37(1996)1284], which is in good agreement with the experimental one of 253 K.

Keywords: CeO_2; Martensitic transformation; Thermodynamics; Y_2O_3; ZrO_2

1. Introduction

ZrO_2 doped with MgO, Y_2O_3, CeO_2 and other rare-earth oxides has attracted great attention due to its superior mechanical properties resulting from the tetragonal to monoclinic (t→m) transformation, such as fracture toughness approaching to 10 $MPa{\cdot}m^{1/2}$ [6] and flexural strength as high as 2GPa.[7] However, the fracture toughness in Y_2O_3-stabilized tetragonal ZrO_2 polycrystal (Y-TZP) is greatly degraded by low-temperature annealing in humid atmosphere and hot aqueous solution.[8,9] It is reported that the thermal stability of Y-TZP is improved by CeO_2 dopants.[10] On the other hand, partial substitution by Y_2O_3 in Ce-TZP results in reduced grain size and tends to stabilize the tetragonal structure.[11] It is then expected that various kinds of ternary zirconia-based ceramics could be fabricated and studied extensively. To achieve perspective performance of TZP, the calculation of martensitic transformation start temperature (M_s) for t→m transformation is of importance.

The change in total Gibbs free energy associated with the athermal martensitic transformation t→m can be expressed as[1–5]

$$\Delta G^{t\rightarrow m} = V(\Delta G_{ch} + \Delta G_{str}) + S\Delta G_{sur} \tag{1}$$

where subscripts ch, str, and sur refer to the chemical free energy, the strain energy including both shear and dilatational energy, and the surface energy including the surface free energy, twinning energy and micro-cracking energy, respectively. V refers to the volume and S, the area associated with the transformation. The equilibrium temperature between the t→m transformation, T_0, is the temperature at which $\Delta G_{ch} = 0$, and the M_s is defined as the temperature at which $\Delta G^{t\rightarrow m} = 0$.[1–5]

The chemical energy difference between two phases (ΔG_{ch}) of a multi-element system can be calculated from the related binary systems by means of thermodynamic models. The other required parameters in the right hand side of Eq. (1) can be derived through estimation either from some available data or by experiments. Thus the M_s temperature can be calculated according Eq. (1). The present work attempts to calculate the Gibbs free energies for tetragonal and monoclinic phases in ternary ZrO_2–CeO_2–Y_2O_3 system then to deduce the M_s of tetragonal to monoclinic(t→m) transformation through estimating the barriers of transformation in 8 mol% CeO_2–0.5 mol% Y_2O_3–ZrO_2 TZP.

2. Experimental procedure and results

Superfine powders with composition of 8 mol% CeO_2–0.50 mol% Y_2O_3–ZrO_2 were prepared by the coprecipitation method[12] and sintered at 1500 °C for 2 h. The specimens were machined to a size of 2×2×12

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mm for dilatation tests and 3×4×40 mm for three point bending tests at high temperature. The dilatation test was conducted using a LK-02 dilatometer. By drawing a tangent on the dilatometry curve M_s and A_f, the reverse transformation finish temperatures, were determined as −20 °C (253 K) and 658 °C respectively.

The mean grain size of the tetragonal phase was measured as 0.90 μm by scanning electron micrographs and the density of the specimen was measured as 5.844 g/cm^3 by the method of Archimedes principle.

The three point bending test was conducted by using a Shimadzu AG-100 kNA universal testing machine at 750, 900, 1050 °C above A_f temperature to avoid the occurrence of stress induced martensite, then to extrapolate the yield strength σ_y of the tetragonal phase near the martensitic starting temperature (M_s), as shown in Fig. 1. The yield strength of the parent phase (t phase) for three point bending test at M_s, σ_y (M_s) was directly obtained as 338.5 MPa. The yield strength σ_b (M_s) for compression would be estimated by multiplying σ_y (M_s) by a factor of 6.9 [13] for zirconia as 2335.65 MPa.

3. Calculation of Gibbs free energy

In order to evaluate thermodynamic properties in ZrO_2–CeO_2–Y_2O_3 system, the expressions of Gibbs free energy as functions of temperature for tetragonal and monoclinic phases should be derived first. However, none of thermodynamic data related has been reported in this ternary system so far except for a phase diagram in the temperature range of 1400–1700 °C.[14] One of the reasons comes from the sluggish reaction kinetics for experimental determinations of phase equilibria in oxide system especially in the relatively low temperature range we are interested in. Therefore the function of Gibbs free energy for this system should be extrapolated from thermodynamic data of the three binaries, CeO_2–Y_2O_3, Y_2O_3–ZrO_2 and CeO_2–ZrO_2.

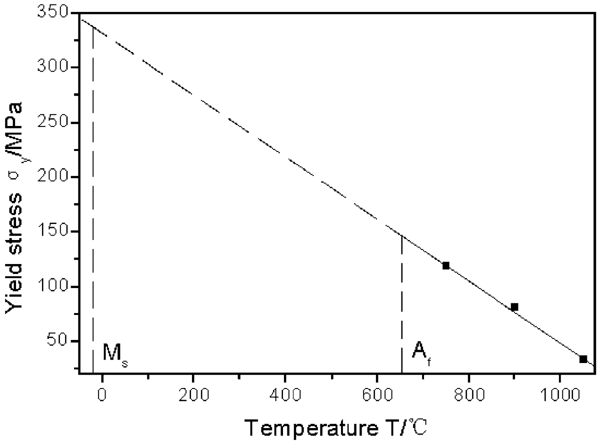

Fig. 1. The yield strength for three point bending test vs temperature in 8 mol% CeO_2–0.50 mol% Y_2O_3–ZrO_2.

For a binary system, the Gibbs free energy of one mole simple substitutional phase B is expressed by the equation as follows:

$$G_m^B(x,T) = \sum_{i=1}^{2} x_i \, {}^\circ G_i^B(T) + RT\sum_{i=1}^{2} x_i \ln x_i + x_1 x_2 \sum_{j=0}^{1} K_{(j+3)}(x_1 - x_2)^j \tag{2}$$

where the first term corresponds to the mechanical mixture of the pure components, the second term to an ideal solution, and the third(last) term to the excess Gibbs energy function. The parameter K_{3+j} ($j=0,1$) is the interaction parameter, which may be temperature dependent. The lattice stability parameters and the Redlich–Kister coefficient of the three binary systems used in the calculation are listed in Tables 1 and 2. As indicated in Table 2, all of K_4 in tetragonal solid solution (T_{ss}) and monoclinic solid solution (M_{ss}) are equal to zero indicating that the solutions are regular.

Direct extrapolating from the related binaries on the basis of geometry method has been extensively accepted to evaluate the thermodynamic properties of a ternary system.[16,18] However, on applying these models a matter of ternary interaction parameters emerges.[18] Fortunately, the Hoch–Arpshofen model[19,20] is suitable for such extrapolation in ceramics[21] without using a ternary interaction parameter. When T_{ss} and M_{ss} in the three binary systems are all regular solutions, the Gibbs free energy for a ternary system has the form as follows:

$$G^\nu(T) = \sum_{i=1}^{3} x_i \, {}^\circ G_i^\nu(T) + RT\sum_{i=1}^{3} x_i \ln x_i + x_1 x_2 K_3^{12} + x_1 x_3 K_3^{13} + x_2 x_3 K_3^{23} \tag{3}$$

where K_3^{12}, K_3^{13}, K_3^{23} are K_3 in the three binaries respectively. Eq. (3) has the same form as Muggianu's equation used for the calculation of the ZrO_2–CeO_2–Y_2O_3 phase diagram by Li et al.,[17] but differs from the other geometry method in weight factor.

By extrapolating, the difference of Gibbs free energy between t and m phases in x mol% CeO_2–y mol% $YO_{1.5}$–ZrO_2 can be obtained as follows using the parameters listed in Tables 1 and 2:

$$\begin{aligned}\Delta G_{ch}^{t\rightarrow m} = {} & -6024.0 + 4.143T + x(-9536.42 + 6.787515T) \\ & + y(-5478.7 + 97.43551T) + x2(91780.42 + 238.20385T) \\ & - y2(32422.7 - 98.12601T) + xy(124203.12 + 300.07784T)\end{aligned} \tag{4}$$

When x or y is equal to zero, the above equation degrades to a form for a binary system.

We can deduce the T_0 temperature in binary or ternary system as a function of composition by setting the above equation equal to zero. Fig. 2 shows the relationship between T_0 and mole fraction of solute in ZrO_2–CeO_2 and ZrO_2–Y_2O_3 in which the two curves are in fact the lines of the t–m phase equilibrium in the two phase diagrams[14,22] because of the same expression of Gibbs free energy and input. It is apparent that T_0 in the two binaries decreases with the mole fraction of CeO_2 and $YO_{1.5}$. However, the two curves do not have the same descending trend. It appears that $YO_{1.5}$ is more effective to lower T_0 than CeO_2 with solute content less than 5%, but the case inverses when the solute content increases continuously since the T_0 curve of ZrO_2–CeO_2 has a steeper slope than that of ZrO_2–Y_2O_3.

Fig. 3 shows the relationship between T_0 temperature and the mole fraction of $YO_{1.5}$ in three ternary ZrO_2–CeO_2–Y_2O_3 alloys of different compositions. It is evident that the three curves are in the same style. Moreover, a small amount of $YO_{1.5}$ as the third addition will decrease T_0 temperature of the system significantly but the effect weakens with the increase in content of $YO_{1.5}$ or CeO_2. The quantity of the T_0 temperature decreased for every increasing per mol% CeO_2 almost holds invariant with the fixed $YO_{1.5}$ content. It implies that CeO_2 and $YO_{1.5}$ play their role independently as stabilizers in zirconia-containing ceramics and there does not exist any strong interaction between their effects on lowering the T_0 temperature of the system.

For 8 mol% CeO_2–0.5 mol% Y_2O_3–ZrO_2, the difference of chemical free energy between tetragonal and monoclinic solid solutions can be obtained by substituting the appropriate values into Eq. (4) for t→m transformation as follows:

$$\Delta G_{\mathrm{ch}}^{\mathrm{t}\rightarrow\mathrm{m}} = -6155.417 + 7.394T \tag{5}$$

Setting $\Delta G_{\mathrm{ch}}^{\mathrm{t}\rightarrow\mathrm{m}} = 0$, we obtain that T_0 of this system is equal to 832.5 K.

4. Thermodynamic calculation of the M_s temperature

Assuming that when the new phase (m) just grows out in tetragonal solid solution of 8 mol% CeO_2–0.5 mol% Y_2O_3–ZrO_2, it is lenticular with a disk radius of r, a sphere radius of R and a thickness of $2h$, and the parent (t phase) is a spherical crystal with a diameter of d at the M_s temperature, then the free energy change per unit transformed volume for t→m martensitic transformation can be written as:

Table 1
Summary of the lattice stability parameters (J/mol of cation, T in K)[a] [15,16]

$^{\circ}G^{\mathrm{l-ZrO_2}} = 0.00$	$^{\circ}G^{\mathrm{l-CeO_2}} = 0.00$	$^{\circ}G^{\mathrm{l-YO_{1.5}}} = 0.00$
$^{\circ}G^{\mathrm{c-ZrO_2}} = -87986.6 + 29.496T$	$^{\circ}G^{\mathrm{c-CeO_2}} = -195800.00 + 70.018T$	$^{\circ}G^{\mathrm{h-YO_{1.5}}} = -56735.0 + 20.9200T$
$^{\circ}G^{\mathrm{t-ZrO_2}} = -93954.8 + 31.755T$	$^{\circ}G^{\mathrm{t-CeO_2}} = -87917.50 + 39.783T$	$^{\circ}G^{\mathrm{t-YO_{1.5}}} = -35617.5 + 26.4625T$
$^{\circ}G^{\mathrm{m-ZrO_2}} = -99978.8 + 35.898T$	$^{\circ}G^{\mathrm{m-CeO_2}} = -11697.50 + 288.915T$	$^{\circ}G^{\mathrm{m-YO_{1.5}}} = -14697.5 + 29.9120T$

[a] l, c, t, m, are liquid, cubic, tetragonal and monoclinic ZrO_2, respectively. h is hexagonal $YO_{1.5}$.

Table 2
Solution parameters of three binary systems (T in K)[a]

Phase	Reference state		K_3 [J/(mol of cation)]	K_4 [J/(mol of cation)]	Reference
	ZrO_2	$YO_{1.5}$			
ZrO_2–$YO_{1.5}$ system					
Liquid	Liquid	Liquid	$-183750.8+72.39814T$	$-48733.3+9.47562T$	15
Css	c-ZrO_2	c-$YO_{1.5}$	$-12059.5+11.15647T$	$-13783.5-5.37868T$	
Hss	c-ZrO_2	h-$YO_{1.5}$	50419.5	0.0	
Tss	t-ZrO_2	t-$YO_{1.5}$	−25800.2	0.0	
Mss	m-ZrO_2	m-$YO_{1.5}$	$-58222.9+98.12601T$	0.0	
ZrO_2–CeO_2 system					
Liquid	Liquid	Liquid	$-234651.45+58.96182T$	$123981.04-47.84299T$	16
Css	c-ZrO_2	c-CeO_2	$10853.50-54.62258T$	$60175.77-24.91597T$	
Tss	t-ZrO_2	t-CeO_2	−54284.36	0.0	
Mss	m-ZrO_2	m-CeO_2	$-146064.78-238.20385T$	0.0	
$YO_{1.5}$–CeO_2 system					
Css	c-$YO_{1.5}$	c-CeO_2	$11168.97+11.00000T$	$-2852.630+4.78084T$	17
Tss	t-$YO_{1.5}$	t-CeO_2	$240T$	0.0	
Mss	m-$YO_{1.5}$	m-CeO_2	$400T$	0.0	

[a] C_{ss}, T_{ss}, M_{ss} are cubic, tetragonal and monoclinic ZrO_2 solid solution, respectively. H_{ss} is hexagonal solid solution.

$$\Delta G^{t\to m}/V = \Delta G_{ch} + \Delta G_{str} + (S/V)\Delta G_{sur} \quad (6)$$

where V is the transformed volume with a lenticular shape being equal to $(1/6)\pi h(3r^2+h^2)\times 2$, S is the surface area of the transformed phase being equal to $2\pi Rh\times 2$.

The change of the strain energy is composed of the shear strain energy required for the onset of transformation and the dilatational strain energy, i.e.

$$\Delta G_{str} = \Delta U_{shr} + \Delta U_{dil} \quad (7)$$

The shear strain energy ΔU_{shr} has the expression

$$\Delta U_{shr} = (1/2)\tau_c \gamma_T \quad (8)$$

where τ_c is the required critical shear stress at M_s temperature for inducing the t→m transformation, which can be estimated as $(1/2)\sigma_b(M_s)$, considering the Schmid factor as 1/2, γ_T is the transformation strain, which is taken to be 0.157 according to Hannink et al.[23] Thus

$$\Delta U_{shr} = (1/2)\tau_c\gamma_T = (1/2)[(2335.65\ \ (\mathrm{MPa})/2)\times 0.157]$$
$$= 91.674\times 10^6\ \ \mathrm{J/m^3} = 2002.2\ \ \mathrm{J/mol}.$$

The dilatation strain energy is given by

$$\Delta U_{dil} = [E/9(1-\upsilon)](\Delta V/V)^2 \quad (9)$$

where E and ν are the Young's modulus and Poisson's ratio of the material respectively, and $\Delta V/V$ is the relative volume change associated with the transformation t→m. With the modulus value of ZrO_2 measured at 293–1633 K as 168.68–94.15 GPa,[24] we take $E = 168.68$ GPa as the value of Young's modulus near the M_s temperature and $\Delta V/V = 0.0528$ which is calculated by the change of lattice constants of t and m phases.[25,26] Taking $\nu = 0.25$[27] thus the dilatational strain energy can be estimated as 69.67×10^6 J/m^3≈1521.6 J/mol.

The change in surface energy ΔG_{sur} per volume includes the contribution of the increase of the surface area owing to the formation of the new phase and the occurrence of twinning in martensite, which can be expressed as

$$\Delta G_{sur} = (S/V)(\Delta\sigma_a + \Delta\sigma_{tw}) \quad (10)$$

where $\Delta\sigma_a$ is the free energy change per unit area, taken to be 0.36 J/m^2,[28] and $\Delta\sigma_{tw}$ is that of the contribution from the twin boundaries. Evans et al.[29] estimated the $\Delta\sigma_{tw}$ using the following equation

$$\Delta\sigma_{tw} = [(\eta-1)(\eta-1)/6\eta]\Gamma_{tw} \quad (11)$$

where Γ_{tw} is the energy of a twin boundary taken to be 0.43 J/m^2, and η is the number of twins assumed to be 8. Thus $\Delta\sigma_{tw}$ is equal to 0.564 J/m^2.

According to the morphology of martensite as usually observed in zirconia[30] and zirconia containing ceramics[31,32] it is reasonable to assume that $R = d$, $r = d/3$, and so $h \approx d/10$, where d is the mean diameter of the grain size of t phase measured as 0.90 μm in present work. Setting all the parameters into Eq. (10), we obtain

$$\Delta G_{sur} = 35.883\times 10^6\ \ \mathrm{J/m^3} = 783.7\ \ \mathrm{J/mol}.$$

Consequently, the required chemical free energy for compensating the total resistance of the onset of t→m transformation is

$$\begin{aligned}\Delta G_{ch}^{t\to m} &= \Delta U_{shr} + \Delta U_{dil} + (S/V)(\Delta\sigma_a + \Delta\sigma_{tw})\\ &= (2002.2 + 1521.6 + 783.7)\ \ \mathrm{J/mol}\\ &= 4307.5\ \ \mathrm{J/mol}.\end{aligned}$$

Substituting Eq. (5) into Eq. (6) and letting Eq. (6) equal to zero, we can obtain the M_s temperature as 249.9 K (−23.1 °C) in 8 mol% CeO_2–0.5 mol% Y_2O_3–ZrO_2 with the mean grain size of 0.90 μm as indicated in Fig. 4. The difference of Gibbs free energy between t

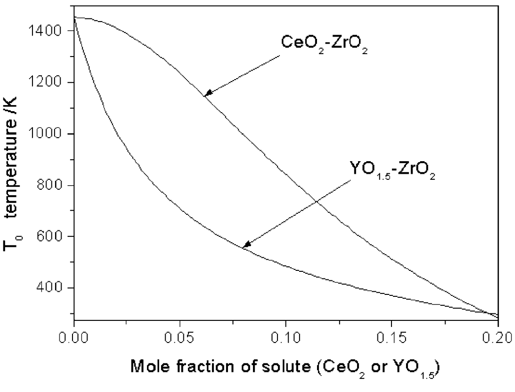

Fig. 2. T_0 vs mole fraction of solute in binary systems.

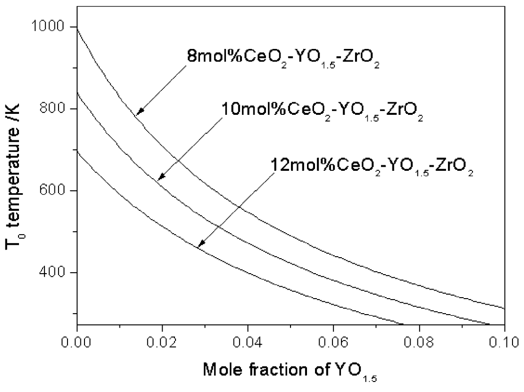

Fig. 3. T_0 vs mole fraction of solute in ternary systems.

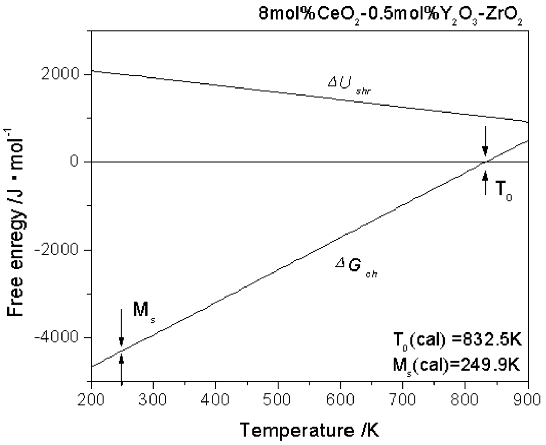

Fig. 4. Free energy as a function of temperature in 8 mol% CeO_2–0.5 mol% Y_2O_3–ZrO_2.

and m phases $\Delta G_{ch}^{t\rightarrow m}$ as a driving force for t→m martensitic transformation increases with the decreasing temperature. The calculated M_s, 249.9 K is in good agreement with the experimental one of 253 K and the difference 3 K is within the error limit of ±12 K evaluated in Ref. 5.

Based on a rather simple expression of the difference of Gibbs free energy, we have successfully calculated the M_s of a ternary alloy by the method derived by Hsu et al.[1–5] It is believed that this method could also be used to predict the M_s of all of the ternary ZrO_2–CeO_2–Y_2O_3 alloys.

The above derivation indicates that the shear strain energy is the biggest barrier for t→m transformation and how to estimate it is the key to predict the M_s of the system for the dilatational strain energy and the surface energy being only related to the Young's modulus and the mean grain size respectively. However, it is inconvenient to measure the yield strength of the parent phase at high temperature, and the extrapolating reduces the reliability of the calculation because of the error inevitably introduced. The prediction is still difficult owing to the scarcity of strength values in literature and the arduousness of the experiments. Therefore, the perfect prediction would not be made until the critical stress inducing martensite could be calculated theoretically after uncovering the mechanism of the t→m transformation or an empirical formula for the strength of tetragonal phase could be derived as a function of composition and mean grain size on the basis of a large number of experimental data.

5. Conclusions

1. The difference of Gibbs free energy between tetragonal and monoclinic phases in ternary ZrO_2–CeO_2–Y_2O_3 system is evaluated as a function of composition and temperature.
2. In 8 mol% CeO_2–0.50 mol% Y_2O_3–ZrO_2, the T_0 temperature is obtained as 832.5 K and the M_s temperature of this alloy with a mean grain size of 0.90 μm are calculated thermodynamically as 249.9 K by the approach derived by Hsu et al., which is in good agreement with the experimental one of 253 K.

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