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Thermodynamic calculations of *t* to *m* martenstic transformation of ZrO_2–CaO binary system

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Abstract

The phase transformation of different polymorphs in zirconia is very important for the processing and mechanical properties of zirconia ceramics. This paper adopts thermodynamic model which is suitable for ceramic system to calculate the Gibbs free energy change of tetragonal and monoclinic phases in ZrO_2–CaO binary system. The difference of the Gibbs free energy between tetragonal and monoclinic phases in ZrO_2–CaO as a function of composition and temperature, namely $t \rightarrow m$ phase transformation driving force, is thermodynamically calculated from the binary systems. Furthermore, in 8.0 mol% CaO–ZrO_2, the equilibrium temperature between tetragonal and monoclinic phases, T_0, was obtained as 1270.3 K, and martensitic transformation starting temperature (M_s) for $t \rightarrow m$ transformation of this ceramic with a mean grain size of 2.0 mm was calculated as 805.9 K, which is good agreement with experiment one of 793 K with 12.9 K residual.

Keywords: D. ZrO_2; Thermodynamics; Martensitic transformation; The Gibbs free energy change; CaO

1. Introduction

Zirconia, unlike many other ceramics, undergoes a martensitic phase transformation with the change of temperature. It exhibits three polymorphs depending on temperature. As the temperature increase, monoclinic turns into tetragonal phase when temperature is up to 1240 °C. Further increase in temperature (up to 2380 °C) leads to conversion of the tetragonal phase into cubic phase again, and it is a reversible process [1–4]. Pure zirconia can only be monoclinic at room temperature. It is possible to stabilize the ZrO_2 in the tetragonal and/or cubic forms at room temperature with the addition of MgO [5–7], Y_2O_3 [8,9], CaO [10], CeO_2 [11] and even a combination of them [12,13]. If only part of the t-ZrO_2 and/or c-ZrO_2 were/was metastable to room temperature, partially stabilized zirconia (PSZ) is formed. The phase transformation of different polymorphs in zirconia is very important for the processing and mechanical properties of zirconia ceramics. Therefore, the related thermodynamic calculation about phase transformation of zirconia is useful to research on the zirconia-based ceramics.

In the past decade, the research on thermodynamics of $t \rightarrow m$ martensitic transformation in ceramics containing ZrO_2 was focuses on interpreting ‘‘size effect’’, namely, there exists a linear relationship between the countdown of *t* phase average grain size and martensitic transformation starting temperature (M_s) (the greater size of parent phase, the higher M_s temperatures). Hsu et al. has calculated the M_s of iron [14–16] and of copper [17,18] alloy successfully, explained the size effects of ZrO_2 ceramics [19]. Zhang [20] and Jiang et al. [21] had done some research on some zirconia system calculation of thermodynamic parameters. Based on the basis of the work, this paper collects relative thermodynamic parameters, and has calculated $t \rightarrow m$ phase transformation driving force, the equilibrium temperature between the $t \rightarrow m$ transformation

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(T_0) and martensitic transformation starting temperature (M_s) for $t \rightarrow m$ transformation of the ZrO_2–CaO binary systems.

The change in total the Gibbs free energy associated with the athermal martensitic transformation ($t \rightarrow m$) is the total of the chemical the free energy, shear energy, dilatational energy and the surface energy [20]. The dilatation strain energy and surface energy are only related to the Young's modulus and the mean grain size respectively. Therefore, how to estimate the shear strain energy is the key to predict the relative martensitic transformation thermodynamics parameters of the zirconia-based ceramics. However, it is inconvenient to measure the yield strength of the parent phase at high temperature, and the residual is introduced inevitably. Due to less high yield strength data on the specific components ceramics reported by the documents, the perfect prediction of M_s would not be made until the critical stress obtained or the parent phase strength empirical formula of different grain size summarized by experiment. Therefore, there is lots of work to do on the martensitic transformation thermodynamics research.

The present work attempts to calculate the difference of the Gibbs free energy between tetragonal and monoclinic phases, the equilibrium temperature between the $t \rightarrow m$ transformation (T_0) and martensitic transformation starting temperature (M_s) for $t \rightarrow m$ transformation of the ZrO_2–CaO binary systems.

2. Calculation of the Gibbs free energy change and T_0

In order to evaluate thermodynamic properties in ZrO_2–CaO system, the expressions of the Gibbs free energy change as functions of temperature for tetragonal and monoclinic phases should be derived firstly.

Using the approach of calculating iron-based and copper-based alloy derived by Hsu et al., the Gibbs free energy change in system of ZrO_2 ceramic $t \rightarrow m$ martensitic transformation is shown as follow [5,7–9,20]:

$$\frac{\Delta G^{t\rightarrow m}}{V} = \Delta G_{\mathrm{ch}} + \Delta G_{\mathrm{dil}} + \Delta G_{\mathrm{sh}} + \left(\frac{S}{V}\right)\Delta G_{\mathrm{sur}} \tag{1}$$

where subscripts ch, dil, sh and sur refer to the chemical free energy per volume, the dilatational energy per volume, shear energy per volume, and the surface energy including the surface free energy, twinning energy and micro-cracking energy, respectively, V refers to the volume, and S is the area associated with the transformation.

The equilibrium temperature between the $t \rightarrow m$ transformation (T_0), is the temperature at which $\Delta G_{\mathrm{ch}} = 0$, and the M_s is defined as the temperature at which $\Delta G^{t\rightarrow m} = 0$ [22–26]. The two-phase chemical free energy difference (ΔG_{ch}) of a binary system can be obtained by relative thermodynamic data and models. The required various parameters of the right Eq. (1) can be estimated through relevant data or measured by experiment. Therefore, M_s can be calculated by Eq. (1).

Table 1
Summary of the lattice stability parameters (J/(mol of cation), T in K)[a] [27,28].

${}^0G^{\text{l-ZrO}_2} = 0.00$	${}^0G^{\text{l}-\text{CaO}} = 0.00$
${}^0G^{\text{c-ZrO}_2} = -\ 87986.6 + 29.496T$	${}^0G^{\text{c-CaO}} = -\ 17464 + 27.446T$
${}^0G^{\text{t-ZrO}_2} = -\ 93954.8 + 31.755T$	${}^0G^{\text{t-CaO}} = 27724 + 27.446T$
${}^0G^{\text{m-ZrO}_2} = -\ 99978.8 + 35.898T$	${}^0G^{\text{m-CaO}} = -\ 50936 + 31.714T$

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

For a binary system, the Gibbs free energy of one mole simple substitutional phase B is expressed by the equation as follows [20]:

$$G_m^B(x,T) = \sum_{i=1}^{2} x_i^o G_i^B(T) + RT\sum_{i=1}^{2} x_i \ln x_i + x_1x_2\sum_{j=0}^{1} K_{(J+3)}(x_1 - x_2)^j \tag{2}$$

The first term is the mechanical mixture of the pure components, the second term is an ideal solution, and the third (last) term is the excess Gibbs energy function. The parameter K_{3+j} ($j = 0$, 1) is the interaction coefficient, which may be dependent on temperature, and x_i is referred to mole fraction of each component, R is referred to the molar gas constant. The lattice stability parameters and the Redlich–Kister coefficient of the 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. When T_{ss} and M_{ss} in the binary systems are all regular solutions, the Gibbs free energy for a binary system has the form as follows:

$$G^{v}(T) = \sum_{i=1}^{2} x_i^o G_i^B(T) + RT\sum_{i=1}^{2} x_i \ln x_i + x_1x_2K_3^{12} \tag{3}$$

By calculating, the difference of the Gibbs free energy between t and m phases in x mol% CaO–ZrO_2 can be obtained as follows using the parameters listed in Tables 1 and 2:

The Gibbs free energy of t phase in x mol% CaO–ZrO_2:

$$G(T) = -93954.8 + 8357.8x + 113321x^2 - 19.0289xT + 31.755T + 14.7199x^2T + RT\sum_{i=1}^{2} x_i \ln x_i \tag{4}$$

Table 2
Summary of the thermodynamic parameters for the binary systems[b] [29].

The ZrO_2–CaO system				
Phase	Reference state		${}^0L$ (J/(mol of cation))	${}^1L$ (J/(mol of cation))
	ZrO_2	CaO		
Liquid	l-ZrO_2	l-CaO	$-169081 + 27.694T$	–
C_{ss}	c-ZrO_2	c-CaO	$-113013 - 6.5908T$	$-8703.35 + 4.1054T$
T_{ss}	t-ZrO_2	t-CaO	$-113321 - 14.7199T$	–
M_{ss}	m-ZrO_2	m-CaO	-42891.7	–
CaO_{ss}	p-ZrO_2	p-CaO	0.0	–

Abbreviations: l, liquid; C_{ss}, T_{ss}, and M_{ss}, cubic, tetragonal and monoclinic ZrO_2 solid solutions, respectively; CaO_{ss}, periclase CaO solid solution, respectively.

[b] Temperature (T) in kelvin.

The Gibbs free energy of m phase in x mol% CaO–ZrO$_2$:

$$G(T) = -99978.8 + 6151.1x + 42891.7x^2 - 4.184xT + 35.898T + RT\sum_{i=1}^{2} x_i \ln x_i \tag{5}$$

Using Eq. (5) minus Eq. (4), the difference of Gibbs free energy between t and m phases in x mol% CaO–ZrO$_2$ could be obtained:

$$\Delta G_{\text{ch}}^{t\rightarrow m} = -6024.0 + 4.143T + x(-2206.7 + 14.8449T) - x^2(70429.3 + 14.7199T) \tag{6}$$

It was deduce that the T_0 temperature in binary system as a function of composition by setting the above Eq. (6) equal to zero. For 8.0 mol% CaO–ZrO$_2$, the difference of chemical free energy between tetragonal and monoclinic solid solutions could be obtained by substituting the appropriate values into Eq. (6) for $t \rightarrow m$ transformation as follows:

$$\Delta G_{\text{ch}}^{t\rightarrow m} = -6651.284 + 5.236T \tag{7}$$

Eq. (7) was also the $t \rightarrow m$ phase transformation driving force. Setting $\Delta G_{\text{ch}}^{t\rightarrow m} = 0$, it was obtained that T_0 of this system was equal to 1270.3 K.

2.1. Thermodynamic calculation of the M_s temperature

It is expected that various kinds of zirconia-based ceramics could be fabricated and studied extensively. To achieve perspective performance of PSZ, the calculation of the equilibrium temperature between the $t \rightarrow m$ transformation (T_0) and martensitic transformation starting temperature (M_s) for $t \rightarrow m$ transformation is of importance.

Assuming that when the new phase (m) just grows out in tetragonal solid solution of 8.0 mol% CaO–ZrO$_2$, it is lenticular with a disk radius of r, a sphere radius of R and a thickness of 2 h, and the parent (t phase) is a spherical crystal with a diameter of d at the M_s temperature. The schematic diagram of martensitic morphology is shown in Fig. 1 [20].

According to Eq. (1) the chemical energy difference between two phases (ΔG_{ch}) of binary system can be calculated from the related binary systems by means of thermodynamic models. The other required parameters in Eq. (1) can be derived through Eqs. (8)–(10) and 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 binary ZrO$_2$–CaO system then to deduce the M_s of tetragonal to monoclinic ($t \rightarrow m$) transformation through estimating the barriers of transformation in 8.0 mol% CaO–ZrO$_2$ (Ca-PSZ).

$$V = \left(\frac{1}{6}\right)\pi h(3r^2 + h^2) \times 2 \tag{8}$$

$$S = 2\pi Rh \times 2 \tag{9}$$

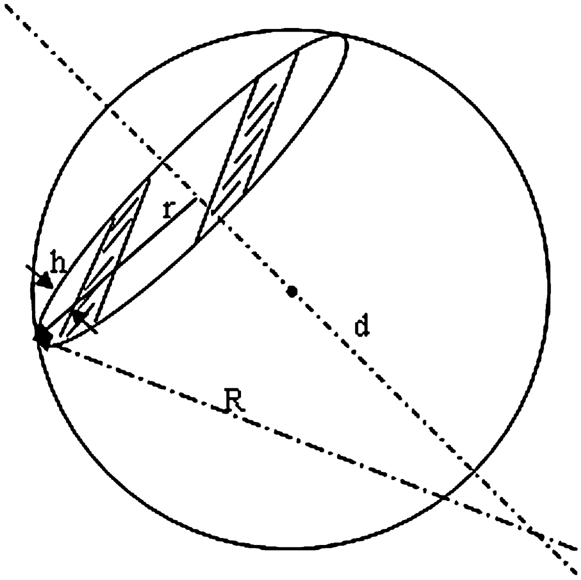

Fig. 1. Schematic diagram of martensitic morphology.

Assuming that when the new phase (m) just grows out in tetragonal solid solution of 8.0 mol% CaO–ZrO$_2$, then the free energy change per unit transformed volume for $t \rightarrow m$ martensitic transformation can be written as Eq. (1).

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.

$$\Delta G_{\text{str}} = \Delta U_{\text{shr}} + \Delta U_{\text{dil}} \tag{10}$$

The shear strain energy ΔU_{shr} has the expression

$$\Delta U_{\text{shr}} = \frac{1}{2}\tau_c\gamma_T \tag{11}$$

where τ_c is the required critical shear stress at M_s temperature for inducing the $t \rightarrow m$ transformation, which can be estimated as $(1/2)\sigma_b(M_\text{S})$, 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. [30].Thus

$$\Delta U_{\text{shr}} = \frac{1}{2}\tau_c\gamma_T = \left(\frac{1}{2}\right)\left[\frac{(650(\text{MPa}))}{2 \times 0.157}\right] = 25.5125 \times 10^6\ \text{J/m}^3 = 557.2\,\text{J/mol}$$

The dilatation strain energy is given by

$$\Delta U_{\text{dit}} = \frac{E}{9(1-v)}\left(\frac{\Delta V}{V}\right)^2 \tag{12}$$

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 $t \rightarrow m$. With the modulus value of ZrO$_2$ measured at 293–1633 K as 168.68–94.15 GPa [31], it was 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 [32,33]. Taking $\nu = 0.2527$ thus the dilatational strain energy could be estimated as 669.67×10^6 J/m^3 $\approx$ 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

$$\Delta G_{\mathrm{sur}} = \left(\frac{S}{V}\right)(\Delta\sigma_a + \Delta\sigma_{\mathrm{tw}}) \tag{13}$$

where $\Delta\sigma_a$ is the free energy change per unit area, taken to be 0.36 J/m^2 [34], and $\Delta\sigma_{\mathrm{tw}}$ is that of the contribution from the twin boundaries. Evans et al. [34] estimated the $\Delta\sigma_{\mathrm{tw}}$ using the following equation

$$\Delta\sigma_{\mathrm{tw}} = \frac{(\eta - 1)(\eta + 1)}{6\eta}\Gamma_{\mathrm{tw}} \tag{14}$$

where Γ_{tw} is the energy of a twin boundary taken to be 0.43 J/m^2, and is the number of twins assumed to be 8. Thus $\Delta\sigma_{\mathrm{tw}}$ was equal to 0.564 J/m^2 [33].

According to the morphology of martensitic as usually observed in zirconia [35] and zirconia containing ceramics [36,37] it was reasonable to assume that $R = d$, $r = d/3$, and so $h = d/10$, where d is the mean diameter of the grain size of t phase measured as 2.0 mm in present work. Setting all the parameters into Eq. (14), it was obtained

$\Delta G_{\mathrm{sur}} = 16.148 \times 106$ J/mol = 352.7 J/mol

Consequently, the required transformation driving force for inducing $t \rightarrow m$ martensitic transformation was

$$\begin{aligned}\Delta G_{\mathrm{ch}}^{t\rightarrow m} &= \Delta U_{\mathrm{shr}} + \Delta U_{\mathrm{dit}} + \left(\frac{S}{V}\right)(\Delta\sigma_a + \Delta\sigma_{\mathrm{tw}}) \\ &= (557.2 + 1521.6 + 352.7)\,\mathrm{J/mol} = 2431.5\,\mathrm{J/mol}.\end{aligned}$$

Substituting Eq. (7) into Eq. (1) and letting Eq. (1) equal to zero, it was obtained the M_s temperature as 805.9 K (532.9 °C) in 8.0 mol% CaO–ZrO$_2$ with the mean grain size of 2.0 mm as indicated in Fig. 2, which is good agreement with experiment one of 793 K (520 °C) Zhao [38] had been done by the method of thermal expansion in 2000 with 12.9 °C residual. The difference of the Gibbs free energy between t and m phases $\Delta G_{\mathrm{ch}}^{t\rightarrow m}$ as a driving force for $t \rightarrow m$ martensitic transformation increases with the decreasing temperature.

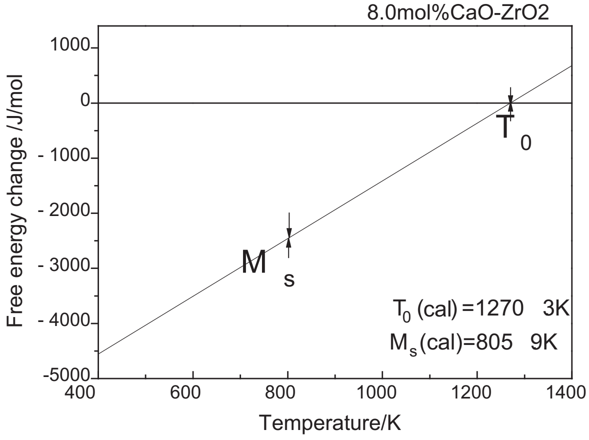

Fig. 2. Free energy change as a function of temperature in 8.0 mol%CaO–ZrO$_2$.

3. Conclusions

Based on the Gibbs free energy change expression and the relative thermodynamic data, T_0, M_s and the difference of the Gibbs free energy between t and m phases in CaO–ZrO$_2$ system could be calculated successfully.

(1) The difference of the Gibbs free energy between tetragonal and monoclinic phases in binary ZrO$_2$–CaO system is evaluated as a function of composition and temperature. And the difference of the Gibbs free energy between t and m phases in x mol% CaO–ZrO$_2$ could be expressed as:

$$\begin{aligned}\Delta G_{\mathrm{ch}}^{t\rightarrow m} &= -6024.0 + 4.143T + x(-2206.7 + 14.8449T) \\ &\quad - x^2(70429.3 + 14.7199T)\end{aligned}$$

(2) In the 8.0 mol% CaO–ZrO$_2$ system ceramics, the required phase transformation driving force for inducing $t \rightarrow m$ martensitic transformation was 2431.5 J/mol.

(3) In 8.0 mol% CaO–ZrO$_2$, the T_0 temperature was obtained as 1270.3 K and the M_s temperature of this binary system with a mean grain size of 2.0 mm are calculated thermodynamically as 805.9 K.

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