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THERMODYNAMIC ASSESSMENT OF THE ZrO_2-TiO_2 QUASIBINARY SYSTEM

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Abstract

A thermodynamic description of the ZrO_2-TiO_2 quasibinary system is obtained based on a critical evaluation of limited experimental data from literature. Non-stoichoimetric compound $ZrTiO_4$ is described as $(Ti, Zr)_1O_2$, while $ZrTi_2O_6$ is treated as a stoichiometric phase. Comparison shows that the calculated phase diagram agrees reasonably with the experimental one.

Keywords: thermodynamics, ZrO_2, TiO_2, phase diagram

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1. Introduction

Zirconium titanate solid solutions are of interest due to their useful dielectric properties in the microwave frequency regime [1]. The ZrO_2-TiO_2 phase diagram has been measured by many investigators [2-11]. However, the reported data show some discrepancies. The purpose of the present work is to critically evaluate the experimental phase diagram in the ZrO_2-TiO_2 system and to provide an optimal set of thermodynamic parameters for this system.

2. Evaluation of experimental data

2.1. Mutual solubility between ZrO_2 and TiO_2

Using X-ray lattice parameter and disappearing phase method, Michael J. Bannister determined accurately the solubility of TiO_2 in tetragonal ZrO_2 at 1300°C, 1400°C, 1500°C [12], supported the solubility of ≤20mol% TiO_2 reported by most workers [5-9] [13-14,16], rather than the much higher values of earlier studies [10-11], while the solubility of ZrO_2 in TiO_2 was reported to be less than 10 mol%ZrO_2 [10].

2.2. Compounds

The high-temperature α-PbO_2-type $ZrTiO_4$ [16, 6] and the low-temperature crystalline compound $ZrTi_2O_6$ were not reported until 1954 [10]. Frank [10] revealed the existence of $ZrTiO_4$ confirmed by later investigators. X-ray diffraction measurements were made to determine the boundaries of the $ZrTiO_4$ solid solution in equilibrium with ZrO_2 and TiO_2 [12]. The electrical conductivity measurement [17], XRD, neutron powder diffraction and single-crystal precession camera techniques were used to characterize the structure of the various $ZrTiO_4$ solid solutions. For melting point of the compound $ZrTiO_4$, most of studies [5,17] agreed that $ZrTiO_4$ melted incongruently at 1760±20°C and cannot be grown directly from a melt of its own composition. $ZrTi_2O_6$ is the stable low-temperature crystalline phase, which is treated as a stoichiometric in this work.

2.3. Liquidus line

Liquidus line in the ZrO_2-TiO_2 system was measured by Noguchi et al. [5] The reported liquidus temperatures showed reasonable agreements within the estimated experimental errors. Consequently, these liquidus temperatures are used in the present modeling.

3. Thermodynamic model

The Gibbs energy function ${}^0G_I^{\&} = G_I^{\&}(T) - H_I^{SER}$ for the pure end-member oxides I in & phase is expressed by an equation of the form:

$${}^0G\ (T) = A + BT + CT\ln T + DT^2 + ET^3 + FT^{-1} + HT^7 + IT^{-9} \qquad (1)$$

where H_I^{SER} is the molar enthalpy of the stable element reference (SER) at 298.15 K and T is the absolute temperature. The Gibbs energies of ZrO_2 are taken from results assessed by Du et al. [18], while the Gibbs energy of stable structure TiO_2 is taken from SGTE [1994]. The Gibbs energies for the metastable forms of TiO_2 assumed to be ${}^0G_{TiO2}^{MSS} - {}^0G_{TiO2}^{TSS}$ = 15000 J/(mol of formula) and ${}^0G_{TiO2}^{CSS} - {}^0G_{TiO2}^{TSS}$ =30000 J/(mol of formula)

Tss, Mss and Css are treated with substitutive solid solution model, and the Gibbs energies are expressed by:

$$G_M^S - H^{SER} = x\,{}^0G_{TiO2}^S + (1-x)\,{}^0G_{ZrO2}^S + RT[x\ln x + (1-x)\ln(1-x)] + {}^{ex}G \qquad (2)$$

in which H^{SER} is the abbreviation of $xH_{TiO2}^{SER} + (1-x)H_{ZrO2}^{SER}$ and x is the mole fraction of TiO_2. ${}^{ex}G$ is the excess Gibbs energy in the form of Redlich-Kister polynomial:

$${}^{ex}G = x(1-x)[L^0 + L^1(1-2x)] \qquad (3)$$

in which L^* are the parameters needed to be optimized and linearly dependent on temperature.

Two-sublattice ionic solution model is used to account for the liquid phase in order to be consistent with the model used for the oxide database including titanate . The liquid is modeled with two sublattices $(Zr^{+4},Ti^{+4})_2(O^{-2})_4$, one for cations and another for anions. The Gibbs energy

per mole of formula unit is:

$$^{0}G_{M}^{L} = y_{Ti}{}^{0}G_{TiO2}^{L} + y_{Zr}{}^{0}G_{ZrO2}^{L} + RT[y_{Ti}\ln y_{Ti} + y_{Zr}\ln y_{Zr}] + y_{Ti}y_{Zr}[{}^{0}L_{Zr,Ti:O}^{L} + (y_{Ti} - y_{Zr})^{1}L_{Zr,Ti:O}^{L}] \quad (4)$$

The compound $ZrTi_2O_6$ is molded as a stoichiometric phase and its Gibbs energy is expressed by using Neumann-Kopp rule [19]:

$$^{0}G_{ZrO2:TiO2}^{ZrTi2O6} - {}^{0}G_{ZrO2}^{TSS} - 2{}^{0}G_{TiO2}^{TSS} = A + BT \quad (5)$$

where A and B are enthalpy and entropy of formation, respectively.

The compound $ZrTiO_4$ has a limited solution region. As a consequence, it is treated as a non-stoichiometric phase. According to the crystal structure [6,16], $ZrTiO_4$ should be molded as $(Ti, Zr)_1O_2$, since there is only one crystallographic position for the metal atoms, which is shared by Ti and Zr. Its Gibbs energy is described as:

$$^{0}G_{M}^{ZrTiO4} = y_{Ti}{}^{0}G_{TiO2}^{\alpha-PbO2} + y_{Zr}{}^{0}G_{ZrO2}^{\alpha-PbO2} + RT[y_{Ti}\ln y_{Ti} + y_{Zr}\ln y_{Zr}] + y_{Ti}y_{Zr}[{}^{0}L_{Zr,Ti:O}^{ZrTiO4} + (y_{Ti} - y_{Zr})^{1}L_{Zr,Ti:O}^{ZrTiO4}] \quad (6)$$

$^{0}G_{TiO2}^{\alpha-PbO2}$ and $^{0}G_{ZrO2}^{\alpha-PbO2}$ are the Gibbs energies of TiO_2 and ZrO_2 at a-PbO2 structures respectively. Due to the lack of experimental thermodynamic data, the assumptions $^{0}G_{ZrO2}^{PbO2} - {}^{0}G_{ZrO2}^{TSS} = 15000J/mol$ of formula and $^{0}G_{ZrO2}^{PbO2} - {}^{0}G_{ZrO2}^{TSS} = 15000J/mol$ of formula are adopted in the modeling.

4. Optimization and Results

The model parameters are evaluated using the PARROT program [20], which works by minimizing the square sum of the differences between experimental and computed values. In the assessment procedure, each piece of experimental information is given a certain weight. The weight is changed systematically during the assessment until most of the experimental data are accounted for within the experimental certainty.

A successful optimization depends on the thermodynamic models, the choice of the parameters and the start values for these parameters. Our optimization procedure is as follows:

In a preliminary modeling, $ZrTiO_4$ is simplified as a stoichiometric phase in order to get a good set of starting values for parameters. Since there are no thermodynamic data, the optimization is difficult. In this

system only the solubility of the end-member solid solution and liquidus temperatures are reported. The optimization begins with the Tss and $ZrTiO_4$ phases. Then using the liquidus data, incongruent melting point and relevant invariant reactions, the Gibbs energies of the other phases are assessed one by one. For $ZrTi_2O_6$, it is impossible to adjust the coefficients A and B in Eq(5) independently since all data concerning this compound are only in the narrow temperature range. Consequently, the coefficients A and B are subject to the constraint A/B=-3400 [21]. Both Mss and Css solid solution have only a very limited range, it is enough to describe them using only one parameter for each of them.

Based on the above preliminary modeling, $ZrTiO_4$ is considered as a no-stoichiometric phase. The parameters of Tss, $ZrTiO_4$ and liquid are optimized simultaneously.

Finally, all experimental information is taken into account in one optimization procedure. The thermodynamic parameters obtained in the present work are listed in Table 1.

*Table 1. Thermodynamic description of the ZrO_2-TiO_2 system.**

G^{CSS}_{ZrO2} -1125234.1+496.72262T-80Tln(T) (298.13 ≤ T ≤ 2983)
-1151298.9+568.29043T-87.864Tln(T)+4.87454*$10^{33}T^{-9}$ (T≤6000)

G^{TSS}_{ZrO2} -1124404.1+495.89773T-80.2998Tln(T)+0.00108741T^2 (298.13≤T ≤2983)
-1161302.3+571.87337T-87.864Tln(T)+8.71*$10^{33}T^{-9}$ (T≤6000)

G^{MSS}_{ZrO2} -1125386.9+411.83491T-67.5063Tln(T)-0.00491334T^2+635630T^{-1} (298.13≤T≤2983)
-1139046.7+564.80249T-87.864Tln(T)-5.46242*$10^{33}T^{-9}$ (T≤6000)

G^{HSS}_{ZrO2} -71457+28.188*T+G^{L}_{ZrO2} (298.13 ≤ T ≤ 6000)

G^{TSS}_{TiO2} -966837.628+381.983614T-63.19571TlnT-.005910235T^2+3.25307833*$10^{-11}T^3$
+517357T^{-1} (298.13 ≤ T≤ 2983)
-1018565.34+675.854122T-100Tln(T) (T≤5000)

G^{L}_{ZrO2} -1040369.9+382.69045T-67.5063Tln(T)-.00491334T^2+635630T^{-1}+2.9780*$10^{-22}T^7$
(298.13 ≤ T 2983)
-1060705.8+538.008T-87.864Tln(T) (T≤ 6000)

Table 1. (Continued)

G^{L}_{TiO2} G^{TSS}_{TiO2} +68000-31.1212815T (298.13 ≤ T ≤ 5000)

CSS: (TiO_2, ZrO_2)

$${}^{0}G^{CSS}_{ZrO2} - 2H^{SER}_{O} - H^{SER}_{Zr} = G^{CSS}_{ZrO2} \quad (298.13 \le T \le 6000)$$

$${}^{0}G^{CSS}_{TiO2} - 2H^{SER}_{O} - H^{SER}_{Ti} = G^{TSS}_{TiO2} + 30000 \quad (298.13 \le T \le 5000)$$

TSS: (TiO_2, ZrO_2)

$${}^{0}G^{TSS}_{ZrO2} - 2H^{SER}_{O} - H^{SER}_{Zr} = G^{TSS}_{ZrO2} \quad (298.13 \le T \le 6000)$$

$${}^{0}G^{TSS}_{TiO2} - 2H^{SER}_{O} - H^{SER}_{Ti} = G^{TSS}_{TiO2} \quad (298.13 \le T \le 5000)$$

$${}^{0}L^{Tss}_{TiO2,ZrO2} = 7802.19 + 9.834T, \; {}^{1}L^{TSS}_{TiO2,ZrO2} = 3659.4634$$

MSS: (TiO_2, ZrO_2)

$${}^{0}G^{MSS}_{ZrO2} - 2H^{SER}_{O} - H^{SER}_{Zr} = G^{MSS}_{ZrO2} \quad (298.13 \le T \le 6000)$$

$${}^{0}G^{MSS}_{TiO2} - 2H^{SER}_{O} - H^{SER}_{Ti} = G^{TSS}_{TiO2} + 15000 \quad (298.13 \le T \le 5000)$$

$${}^{0}L^{MSS}_{TiO2,ZrO2} = -3301.847 + 16.6737T$$

IONIC_LIQ: $(Zr^{+4}, Ti^{+4})_2(O^{-2})_4$

$${}^{0}G^{IONIC\_LIQ}_{Zr+4:O-2} - 4H^{SER}_{O} - 2H^{SER}_{Zr} = 2G^{L}_{ZrO2} \quad (298.13 \le T \le 6000)$$

$${}^{0}G^{IONIC\_LIQ}_{Ti+4:O-2} - 4H^{SER}_{O} - 2H^{SER}_{Ti} = 2G^{L}_{TiO2} \quad (298.13 \le T \le 5000)$$

$${}^{0}L^{IONIC\_LIQ}_{Ti+4,Zr+4:O-2} = 144935 - 99.995T,$$

$${}^{1}L^{IONIC\_LIQ}_{Ti+4,Zr+4:O-2} = -68579.7 + 39.215T$$

$ZrTiO_4$: $(Zr^{+4},Ti^{+4})_1(O^{-2})_2$

$${}^{0}G^{PbO2}_{TiO2} - 2H^{SER}_{O} - H^{SER}_{Ti} = G^{TSS}_{TiO2} + 15000 \quad (298.13 \le T \le 5000)$$

$${}^{0}G^{PbO2}_{ZrO2} - 2H^{SER}_{O} - H^{SER}_{Zr} = G^{TSS}_{ZrO2} + 15000 \quad (298.13 \le T \le 6000)$$

$${}^{0}L^{ZrTiO4}_{Ti+4,Zr+4:O-2} = -61179.37 + 11.519T$$

$ZrTi_2O_6$: (ZRO_2: TIO_2)

$${}^{0}G^{ZrTi2O6}_{ZrO2:TiO2} - 6H^{SER}_{O} - 2H^{SER}_{Ti} - H^{SER}_{Zr} = G^{TSS}_{ZrO2} + 2G^{TSS}_{TiO2} - 66349 + 38.867T$$

* In J/(mol-formula); Temperature (T) in Kelvin.

The computed ZrO_2-TiO_2 phase diagram is shown in Fig.1. Fig.2 compares the computed diagram with experimental data [7,12,17]. The calculated invariant reactions are listed in Table 2. In view of the experimental errors, the fit to the experimental data is very satisfactory, except the low-temperature reaction Tss <-> Mss + $ZrTi_2O_6$. Noguchi et al. reported [5] that the reaction temperature is at about 923 K. At so low temperature, kinetics is very sluggish. Consequently, the equilibrium is not reached.

In summary, the ZrO_2-TiO_2 system is assessed in this work by considering all of the experimental data available. It is shown that the experimental information can be satisfactory accounted for by present modeling and the number of the parameters to describe the system is reasonable.

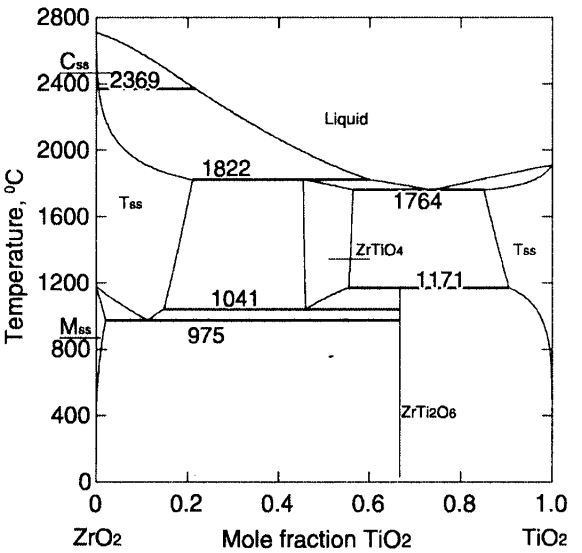

Fig.1 The Calculated ZrO_2-TiO_2 phase diagram

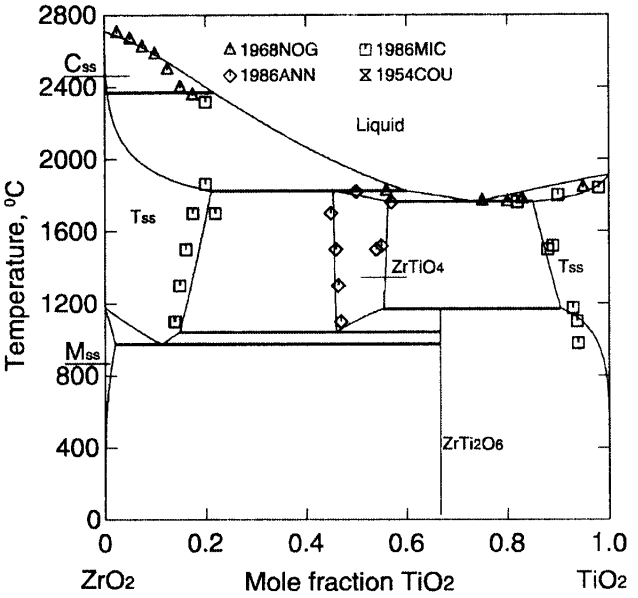

Fig. 2 Comparison between the calculated and experimental phase diagram

Table 2. The Calculated and Experimental invariant Equilibria

Composition (mol% TiO2)			Temperature (C)	Sources
IONIC_LIQ + CSS <->TSS				
12.5			2495	Noguchi et al[5]
21.79			2369	This work
IONIC_LIQ + TSS <-> ZrTiO4				
55	22	50	1820	Mchale et al[14]
60	21.17	45.5	1822	This work
IONIC_LIQ <-> $ZrTiO_4$ + TSS				
80	57	82	1760	Mchale et al[14]
80			1760	Coughanour[10]
80		83.5	1700	Noguchi et al[5]
73.4	56.3	85.0	1760	This work

$ZrTiO_4$ <-> TSS#2 + $ZrTi_2O_6$				
53	93	66.7	1175	Mchale et al[14]
55	94.1	66.7	1171	This work
$ZrTiO_4$ <-> TSS#1 + $ZrTi_2O_6$				
50	14	66.7	1100	Mchale et al[14]
47.5	14.9	66.7	1041	This work
TSS#1 <-> MSS + $ZrTi_2O_6$				
12	10	66.7	650	Noguchi et al[5]
11.4	2.1	66.7	975	This work

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