Thermodynamic Optimization of ZrO₂-Containing Systems in the CaO-MgO-SiO₂-Al₂O₃-ZrO₂ System

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ABSTRACT

Predictions of thermodynamic properties and phase equilibria in multicomponent systems are important to understand complex chemical reactions in high temperature processes. The CALPHAD (CALculation of PHAse Diagram) approach of thermodynamic calculations, nowadays, is considered one of the most efficient ways to understand complex chemical reactions and phase relations in multicomponent systems. Therefore, the development of adequate thermodynamic models and databases for materials of interest is essential. The goal of this study is to develop a new thermodynamic database for the ZrO₂-containing unary, binary, and ternary systems in the CaO-MgO-Al₂O₃-SiO₂-ZrO₂ system, which is of great importance to understand the corrosion of ZrO₂-based refractories in various pyrometallurgical industries. Due to the paucity of experimental data, experiments were conducted to verify the phase relations in the ZrO₂-Al₂O₃ and ZrO₂-CaO-SiO₂ systems at 1873 K. Experimental results showed that the tetragonal zirconia solid solution can take up to 0.2 wt. % of Al₂O₃ at 1873 K. Moreover numerous liquidii were determined in the ZrO₂-CaO-SiO₂ system at 1873 K. All the thermodynamic property data and phase diagram data of the ZrO₂-containing subsystems in the CaO-MgO-Al₂O₃-SiO₂-ZrO₂ system were critically evaluated and optimized in this study. The Gibbs energy of liquid oxide was described using the Modified Quasichemical Model (MQM) considering the short-range ordering of the molten oxide.

The thermodynamic models of solid solutions were selected in consideration of real structural data. The prediction of high-order (>3) systems based on the optimizations of binary and ternary systems (\leq 3) shows good agreement with the experimental data available from the literature.

RÉSUMÉ

Prédire les propriétés thermodynamiques et les équilibres de phases des systèmes à composants multiples est important pour comprendre les réactions chimiques complexes des processus à haute température. La méthode de calcul thermodynamique CALPHAD (CALculation of PHAse Diagram) est, de nos jours, considérée comme l'un des moyens les plus efficaces pour comprendre les réactions chimiques complexes et les relations de phase des systèmes multi-composants. Ainsi, le développement de modèles thermodynamiques adéquats et de bases de données pour divers matériaux d'intérêt est essentiel. Le but de cette étude est de développer une nouvelle base de données thermodynamiques pour les systèmes unaire, binaires et ternaires contenant du ZrO₂ dans le système CaO-MgO-Al₂O₃-SiO₂-ZrO₂ qui est d'une grande importance pour comprendre la corrosion des réfractaires à base de ZrO₂ pour diverses industries pyrométallurgiques. En raison de la rareté des données expérimentales, des expériences ont été menées pour vérifier les relations de phase des systèmes ZrO₂-Al₂O₃ et ZrO₂-CaO-SiO₂ à 1873 K. Les résultats expérimentaux ont montré que la solution solide tétragonale d'oxyde de zirconium peut contenir jusqu'à 0,2 % en poids de Al₂O₃. De plus, plusieurs liquidii du système ZrO₂-SiO₂-CaO furent déterminés à 1873 K. Toutes les données des propriétés thermodynamiques et des diagrammes de phase des soussystèmes contenant du ZrO₂ dans le système CaO-MgO-Al₂O₃-SiO₂-ZrO₂ ont été évaluées de façon critique et optimisées dans cette étude. L'énergie de Gibbs du liquide a été décrite en utilisant le Modèle Quasichimique Modifié (MQM) en tenant compte de l'ordre à courte portée du liquide.

Les modèles thermodynamiques de solutions solides ont été choisis en tenant compte des données réelles et structurelles. La prédiction de systèmes à ordre élevé (> 3) basé sur les optimisations des systèmes binaires et ternaires (\leq 3) montre un bon accord avec les données expérimentales disponibles dans la littérature.

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LIST OF SYMBOLS AND ABBREVIATIONS

Experimental method	Phase
AC: adiabatic calorimetry	A: Al ₂ O ₃
CA: chemical analysis	AS ₂ : Al ₂ Si ₂ O ₇
CC: combustion calorimetry	C: CaO
CFM: cone fusion method	CA: CaAl ₂ O ₄
DC: drop calorimetry	CA ₂ : CaAl ₄ O ₇
DIL: dilatometry	CA ₆ : CaAl ₁₂ O ₁₉
DSC: drop solution calorimetry	C ₃ A: Ca ₃ Al ₂ O ₆
DTA: differential thermal analysis	CM ₂ A ₈ : CaMg ₂ Al ₁₆ O ₂₇
emf: electromotive force	C2M2A14: Ca2Mg2Al28O46
EDS: energy-dispersive X-ray spectroscopy	C ₃ MA ₄ : Ca ₃ MgAl ₄ O ₁₀
EPMA: electron probe micro-analysis	CMS ₂ : CaMgSi ₂ O ₆
HTND: high temperature neutron diffraction	C2MS2: Ca2MgSi2O7
HTSC: high temperature solution calorimetry	C ₃ MS ₂ : Ca ₃ MgSi ₂ O ₈
HTXRD: high temperature X-ray diffraction	CS: CaSiO ₃
RS: raman spectroscopy	C ₂ S: Ca ₂ SiO ₄
SAD: selected area electron diffraction	C ₃ S: Ca ₃ SiO ₅
SR: specular reflection	C ₃ S ₂ : Ca ₃ Si ₂ O ₇
TA: thermal analysis	CZ: CaZrO ₃
TE: thermal expansion	CZ4: CaZr4O9
TEM: transmission electron microscopy	C ₆ Z ₁₉ : Ca ₆ Z ₁₉ O ₄₄
QM: quenching method	$C_{13}Z_2A_6: Ca_{13}Zr_2Al_{12}O_{35}$
	C_2ZS_4 : $Ca_2ZrSi_4O_{12}$

C₃ZS₂: Ca₃ZrSi₂O₉

M: MgO

 $M_{39}A_{11}Zr_{14}$: $Mg_{39}Al_{22}Zr_{14}O_{100}$

MS: MgSiO₃

M₂S: Mg₂SiO₄

S: SiO₂

Z: ZrO₂

ZS: ZrSiO₄

Thermodynamic symbols

- n_i : the number of *i* component
- n_{ij} : the number of *i*-*j* pairs
- X_i : mole fraction of *i* component
- *X_{ij}* : pair fraction of *i*-*j* pairs
- Y_i : equivalent fraction of *i* component
- Z_i : coordination number of *i* component

R: gas constant

- ΔG_i^{O} : Gibbs energy of pure compound
- G^m : Gibbs energy of solution

 ΔG^E : excess Gibbs energy

- g_i^0 : chemical potential of *i* component
- Δg_{AB}^{ij} : solution model parameter in the A-B binary system
- ΔH_i^{O} : enthalpy of pure compound
- ΔH°_{f} : enthalpy of formation

- ΔS_i^{O} : entropy of pure compound
- ΔS^{conf} : configurational entropy of solution
- $\boldsymbol{\omega}$: enthalpy of solution
- $\boldsymbol{\eta}$: non-configurational entropy of solution

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Chapter 1. Introduction

ZrO₂-containing ceramics are well known for low thermal conductivity and high fracture toughness as compared to most other ceramic materials. Hence, it is often the material of choice in various high temperature industrial applications such as thermal barrier coatings for jet engine turbines [06Wan] and refractories in pyrometallurgical applications [09Suk]. Moreover, owing to their high ionic conductivity, ZrO₂-containing ceramics are also used as oxygen sensors and electrolyte in solid oxide fuel cells. The thermodynamic properties of ZrO₂-containing systems are important to understand complicated chemical reactions during fabrication and operation of such materials. For example, predictions of probable reactions under thermochemical conditions can determine the life span of composite materials. However, the chemical processes involved are often very intricate to understand, especially for multicomponent systems, due to the complexity of the phase equilibria. Predictions of such phase equilibria can be achieved by adequate thermodynamic modeling of unary, binary, and ternary systems. In this study, the CALPHAD (CALculation of PHAse Diagram) technique [13Kro] was used to obtain a consistent description of both phase diagrams and thermodynamic properties of the systems of interest. Numerous efforts were made in the past to model thermodynamically zirconia-bearing systems. Unfortunately, the quality of the data used has been always an issue due to the high melting temperature and several polymorphic transitions involved with ZrO₂. Moreover, finding a proper thermodynamic model for zirconia solid solutions was also an issue due to the lack of structural data.

The aim of this study is to develop a new thermodynamic database for the ZrO₂-bearing unary, binary, and ternary systems of the CaO-MgO-Al₂O₃-SiO₂-ZrO₂ system. These systems are of great importance to understand the chemical reactions occurring at the interface of slag and zirconia refractories in steelmaking processes, and to fabricate zirconia-based refractories which are often

a form of stabilized or partially stabilized zirconia together with CaO or MgO. All thermodynamic properties and phase diagram data available in the literature, including numerous data published recently, were critically reviewed. Optimization was performed to obtain a consistent set of model equations of the Gibbs energies for all phases as functions of temperature and compositions. Especially, reevaluation of the thermodynamic properties of ZrO₂ unary was performed using new thermodynamic data from the literature. To resolve some discrepancies in the experimental data found in literature and the lack of solubility data of Al₂O₃ in the ZrO₂ solid solution, new phase diagram experiments were also conducted. The accuracy of the new thermodynamic database was evaluated by comparing the experimental data of high-order (>3) systems found in the literature with the calculation results obtained by interpolation from the bounding binary and ternary systems.

Chapter 2. Thermodynamic models and critical evaluation and optimization of systems

2.1 Procedure of critical evaluation and optimization

The goal of thermodynamic optimization is to build a database consistent with thermodynamic principles. To perform a thermodynamic optimization, all available thermodynamic and phase diagram data found in the literature need to be collected first. Usually, literature experimental data are different from one another by more than the reported error limits. Therefore, the quality of collected data needs to be critically evaluated by considering the experimental errors associated to the experimental techniques, sample preparation procedures, and analytical methods employed. Discrepancies in the experimental data can also be resolved from thermodynamic principles. For example, the empirical data of a thermodynamic property such as the activity can be used to evaluate phase diagram measurements because both data are interconnected through the Gibbs energy. In this manner, we can find an experimental data set which is self-consistent. The process of evaluation and optimization is as follow:

- 1) Define the system of interest.
- 2) Collect all available information from the literature.
 - a. Thermodynamic data: phase data, calorimetric data (heat capacity, heat content, enthalpy of formation, mixing enthalpy of solution, and enthalpy of phase transformation), chemical potential data (Gibbs energy of formation, and activities via emf measurements), etc.
 - b. Structural data: cation or anion distributions in sublattices.
 - c. Physical property data: magnetism.

- d. Data from high-order (>3) systems: high-order systems which can be extrapolated to low-order (≤3) systems of interest.
- 3) Choose an appropriate thermodynamic model based on the structure of each phase: structural data are imperative to construct an accurate database for multicomponent systems because the entropy of solution must be properly taken into account in the model to get more reasonable predictions for high-order solution properties from the model parameters of low-order systems.
- 4) Perform critical evaluation of experimental data
- 5) Optimize the model parameters of the system: optimization of the model parameters of each phase is performed based on reliable sets of data evaluated in the previous step. One of the key points of the optimization process is to reduce the number of temperature-dependent model parameters. However, the introduction of temperature-dependent model parameters must be done based on empirical evidences. The optimization of model parameters continue until back-calculations reproduce the experimental data within experimental error limits or as close as possible.
- 6) Back-calculate all the thermodynamic data and phase diagrams of interest.

2.2 Thermodynamic models

In order to describe the entropy of a solution properly, the thermodynamic model must be based on the structure of the solution (and more specifically, on its short-range ordering). In this way, thermodynamic properties of complex solid or liquid solutions can be described with only a small number of model parameters.

2.2.1 Pure elements, compounds, and gas species

The Gibbs energy of a pure component is expressed as:

$$\Delta G_i^{0}(T) = \Delta H_i^{0}(T) - T \Delta S_i^{0}(T)$$

where $\Delta G_i^{0}(T)$, $\Delta H_i^{0}(T)$ and $\Delta S_i^{0}(T)$ are the Gibbs energy, enthalpy and entropy of a compound *i* which take elements at 298 K as references, respectively, and *T* is the absolute temperature.

2.2.2 Liquid solutions

The Gibbs energy of binary liquid solution which takes into account interactions of atoms is generally written as:

$$G^m = n_A g_A^0 + n_B g_B^0 - T \Delta S^{conf} + \Delta G^E$$

where G^m is the Gibbs energy of a solution, n_i is the number of moles of a component i, ΔS^{conf} is the configurational entropy of solution, and G^E is the excess Gibbs energy composed of mixing enthalpy and non-configurational entropy that come from atomic interactions. The excess Gibbs energy; ΔG^E , is often expressed as a polynomial:

$$\Delta G^{E} = \sum_{i,j} \Delta g^{ij}_{AB} n^{i}_{A} n^{j}_{B} / (n_{A} + n_{B})^{i+j}$$

where the excess interaction parameters Δg_{AB}^{ij} (= $a + bT + cT^2 + \cdots$) are dependent on temperature. The expressions of ΔS^{conf} and ΔG^E differ according to the model employed. For example in the Modified Quasichemical Model [00Pel], ΔS^{conf} is dependent of ΔG^E because the changes of atomic configurations that results from the interactions between components is taken into account, whereas in the Bragg-Williams Random Mixing Model, ΔS^{conf} is independent of ΔG^E . The differences in the configurational entropy of solution are crucial for a liquid solution. The Bragg-Williams Random Mixing Model requires many and large arbitrary excess model parameters especially for solutions which have strong short-range ordering behavior; this is due to a wrong configurational entropy in the model formula. As a result, poor predictions are obtained for high-order systems. It is thus important to choose a model which reflects the structure of the solution.

2.2.2.1 Melt structure

Two kinds of oxide components can be considered in an oxide melt: network formers and network breakers. Network formers such as SiO₂ and B₂O₃ are joined together through bridging oxygen (O^0) to make chains or rings whereas network breakers such as Ca²⁺ and Mg²⁺ have a tendency to break these bridged oxygen to form non-bridging oxygen (O^-) or produce free oxygen ions (O^{2-}) . In a SiO₂ melt for example, this depolymerization brings about various types of anionic clusters such as, Si₂O₅²⁻, Si₂O₆⁴⁻, Si₂O₇²⁻ and SiO₄⁴⁻. The degree of the depolymerization, which is often expressed as the ratio between the number of non-bridging oxygen to the number of bridging oxygen, has a strong effect on the physical properties of melts such as the viscosity, thermal conductivity, etc. The Modified Quasichemical Model well describes this short-range ordering by considering the formation of pair bonds.

2.2.2.2 Present model: Modified Quasichemical Model

The Modified Quasichemical Model was developed by Pelton and Blander (1 1986) [86Pel] to describe the behavior of melts which have short-range ordering. The basic concepts for a binary system are discussed here, but the details can be found in Pelton et al. [00Pel] and Pelton and Chartrand [01Pel].

In the Modified Quasichemical Model in pair approximation, the pair exchange reactions of a binary system A and B are written as:

$$(A - A) + (B - B) = 2(A - B) : \Delta g_{AB}$$

where (i - j) represents a type of pair (the number of pairs is notated as n_{ij}), and the Gibbs energy of reaction is $\Delta g_{AB} = \boldsymbol{\omega} - \boldsymbol{\eta} T$. Since the liquid is composed of three types of pairs; (A-A), (B-B), and (A-B) in the binary system, pair fractions (X_{ij}) are calculated from the number of atoms or molecules (n_i) by introducing a coordination number (Z_i) for each component. The mass balances, pair fractions, mole fractions, and equivalent fractions are defined as follows:

Mass balances:

$$Z_A n_A = 2n_{AA} + n_{AB}$$
, $Z_B n_B = 2n_{BB} + n_{AB}$

Pair fractions:

$$X_{ij} = n_{ij}/(n_{AB} + n_{AA} + n_{BB})$$

Mole fractions:

$$X_A = n_A / (n_A + n_B) = 1 - X_B$$

Equivalent fractions:

$$Y_A = Z_A n_A / (Z_A n_A + Z_B n_B) = 1 - Y_B = X_{AA} + X_{AB} / 2$$

In this model, the configurational entropy of mixing is approximated by assuming random distribution of (A-A), (B-B), and (A-B) pairs in one dimension.

$$\Delta S^{config} = -R(n_A \ln X_A + n_B \ln X_B + n_{AA} \ln \left(\frac{X_{AA}}{Y_A^2}\right) + n_{BB} \ln \left(\frac{X_{BB}}{Y_B^2}\right) + n_{AB} \ln \left(\frac{X_{AB}}{2Y_A Y_B}\right))$$

The excess Gibbs energy (ΔG^E) is assumed to be directly related to the number of (A-B) pairs:

$$\Delta G^E = n_{AB} \, \Delta g_{AB}$$

Hence, the Gibbs energy of the solution is expressed as:

$$G^{m} = n_{A}g_{A}^{0} + n_{B}g_{B}^{0} - T\Delta S^{conf} + n_{AB}\Delta g_{AB}$$

The equilibrium distribution of pairs can be calculated by setting

$$(\frac{\partial G^m}{\partial n_{AB}})_{n_A, n_B} = 0$$

at constant n_A and n_B . When Δg_{AB} goes to zero, the Gibbs energy of the solution converges to an ideal solution with $X_{AA}=Y_A^2$, $X_{BB}=Y_B^2$, and $X_{AB}=2Y_A$. When Δg_{AB} is positive, (A-A) and (B-B) pairs are predominant. When Δg_{AB} is strongly negative, ΔS^{conf} presents a minimum at $Y_A=Y_B=1/2$ with a m-shaped curve. These properties indicate that the Modified Quasichemical Model can well describe both positive and negative deviations from ideality. The model has been widely used to describe oxide melts successfully [86Pel].

2.2.3 Solid solutions

In this study, only zirconia-bearing solid solutions (the zirconia Cubic solid solution (Css), the zirconia Tetragonal solid solution (Tss), the zirconia Monoclinic solid solution (Mss), the Lime solid solution (Lss) and the Periclase solid solution (Pss)) were modeled considering actual solution structures. It should be noted that Lss and Pss are rock-salt structure with a miscibility

gap. The solution models which do not contain zirconia such as spinel, mullite, and pyroxene solid solutions, were taken from previous studies [93Eri, 05Jun].

2.2.3.1 Crystal structure of zirconia-bearing solid solutions

Recently, Bogdanov et al. [11Bog] investigated the atomic and superatomic structure of zirconiabearing solid solutions by small-angle neutron scattering (SANS). According to their study, Ca²⁺ substitutes for Zr⁴⁺ by inducing vacancies in the oxygen sublattice. Based on their experimental data, Ca-Zr solid solutions can be modeled by considering two different structures;

- (1) [Ca²⁺, Zr⁴⁺][O²⁻ Va]₂: assuming that the vacancies (Va) are formed and randomly distributed in the anionic (oxygen) sites.
- (2) [Ca²⁺, Zr⁴⁺][O²⁻]₂: assuming that the vacancies (Va) are formed in the oxygen sites but are preferentially located next to Ca²⁺.

However, it turned out that the first model induces too much configurational entropy which results in a maximum on the liquidus and some difficulties in reproducing the activity data, whereas the second model was able to reproduce both the phase diagram data and the activity data of the solid solutions simultaneously. The temperature dependence of the CaO activity data effectively constrains the Gibbs energy of the ZrO_2 solid solution, especially its entropy. The first model induces a large entropy of mixing due to the random distribution of the Va and O²⁻ in the anion sublattice; as a result, the activity data cannot be reproduced. On the other hand, the second model assumes preferential sites for the Va in the anionic sites next to Ca cation which allows to better reproduce the experimental activity data. This indirect thermodynamic result indicates that vacancies may not be randomly distributed in the oxygen sites but preferentially located near Ca²⁺. The same assumption was made by Bogdanov et al. [11Bog] to explain a peak in their small angle scattering data and to calculate correctly density-density pairs. In two separate studies [05Che, 13Pav] on the MnO-ZrO₂ and MgO-ZrO₂ systems, Css was described by assuming random distribution of vacancies over oxygen sites; unfortunately, no specific reason was given for using this two sublattice model. In this study the second model, where vacancies are preferentially located near the network breaker, was selected to model the ZrO₂-bearing solid solutions present in the CaO-ZrO₂ system. The Gibbs energy of the $[Ca^{2+}, Zr^{4+}][O^{2-}]_2$ solution can be either described by the Compound Energy Formalism with Redlish-Kister polynomial expansion, or the Bragg Williams Random Mixing Model with any polynomial expansion.

2.2.3.2 The Bragg-Williams Random Mixing model

The Bragg-Williams Random Mixing model assumes that the configurational entropy remains ideal between A and B atoms. The Gibbs energy of the solution can be expressed as:

$$G^m = n_A g_A^0 + n_B g_B^0 - T \Delta S^{conf} + \Delta G^E$$

where ΔS^{conf} is equal to that of the ideal solution, i.e. $-R(n_A ln X_A + n_B ln X_B)$, while the excess Gibbs energy, ΔG^E , is expressed as a polynomial:

$$\Delta G^E = \sum_{i,j} \Delta g^{ij}_{AB} n^i_A n^j_B / (n_A + n_B)^{i+j}$$

The excess interaction parameter Δg_{AB}^{ij} (= $a + bT + cT^2 + \cdots$) is temperature dependent. When only the Δg_{AB}^{11} interaction parameter is used, the model converges to a regular solution model. The non-configurational entropy is non-zero when the excess interaction parameter Δg_{AB}^{ij} is a function of temperature. The Compound Energy Formalism uses the Redlich-Kister polynomial for ΔG^E , which can be converted to the general polynomial expression above.

Chapter 3. Key phase diagram experiments in the ZrO₂-CaO-SiO₂ and ZrO₂-Al₂O₃ systems

3.1 Key phase diagram experiments

Due to the lack of experimental data and discrepancies between reported phase diagram data in the literature, key experiments were conducted at 1873 K in the ZrO₂-Al₂O₃ and ZrO₂-CaO-SiO₂ systems. Prior to the experiments, phase diagram calculations were performed using the preliminary thermodynamic database constructed from all the data available in the literature. The key experimental points which can most efficiently constrain the Gibbs energies of each system were selected based on preliminary calculations. The equilibria of samples were confirmed by varying the duration of experiments, and analyzing the composition and phases by electron probe micro-analysis (EPMA) and X-ray diffraction (XRD). The final optimization of the systems was then performed by taking into account of the new key experimental results.

3.2 Experimental procedure

Reagent grade ZrO₂ (99.978 wt%), CaCO₃ (99.95 wt%), Al₂O₃ (99.99 wt%), and SiO₂ (99.995 wt%) powders from Alfa Aesar (USA) were used to prepare the starting materials. CaCO₃ was first calcined at 873 K to obtain CaO using a ST-1700C box furnace (Sentro Tech, USA; inner dimensions: 10 cm x 10 cm x 20 cm) equipped with Pt₃₀Rh-Pt₆Rh (type B-thermocouple) for 24 hours. Due to the hygroscopic nature of CaO, the quantity prepared was stored in a desiccator. The reagent materials were carefully measured and mechanically mixed in appropriate proportions by using an agate mortar filled with isopropanol for a 30 min.

Experiments were performed in a DelTech® vertical tube furnace (Figure 1) equipped with a dense alumina tube. Temperatures were measured using Pt₃₀Rh-Pt₆Rh (type B) thermocouples in air. The

height of the hot zone was found to be 3 cm at 1873 K. About 20 mg of starting materials were encapsulated in sealed Pt crucibles (4 mm OD x 3.873 mm ID x 10 mm length) to avoid any material loss by evaporation during the experiments. The encapsulated samples were loaded in an alumina boat and suspended in the hot zone with a Pt wire. At the end of the runs, the samples were quenched in water. The duration of the experiments was determined based on the homogeneity of the composition of the quenched samples. Test runs were performed for 20 hours, 3 days, and 14 days and an equilibration time of 14 days was found to be sufficient to reach equilibrium.

After quenching, each sample was cast in epoxy. Phase identification and composition analysis were conducted by EPMA (JEOL 8900 probe at McGill University) using an accelerating voltage of 15 kV and a beam current of 20 nA. The beam diameter was varied between 3 to 10 μ m, depending on the phase sizes. Counting times were of 20 s on peaks and 10 s on backgrounds, and data were reduced with the ZAF corrections using synthetic alumina (Al) and natural diopside (Ca, Si) and zircon (Zr) standards. XRD (Co-K α radiation, λ =1.79 Å) was also employed for phase identification if required. Analytical results are listed in Table 1. Experimental results are discussed for each system below.

Chapter 4. Thermodynamic optimization results and discussion

4.1 Pure ZrO₂

Literature review

Zirconia is known to have three different polymorphs: the monoclinic (α) phase at low temperature, the tetragonal (β) phase at intermediate temperature, and the cubic (γ) phase at high temperature. The existence of the cubic γ phase was an issue for a while. Smith and Cline [62Smi] detected it using high temperature X-ray diffraction (HTXRD) but Weber [62Web] suggested that it was due to the sample contamination. The existence of the cubic structure was later confirmed by Wolten [63Wol] and Navrotsky et al. [05Nav] using HTXRD and differential thermal analysis (DTA) and is now accepted by other authors [75Ack, 04Che, 04Wan]. Details of transition temperatures between the three polymorphs are summarized in Table 2.

The polymorphic transition from α - to β -ZrO₂ was investigated by many researchers [50Cou, 63Wol, 66Kir, 68Ruh, 75Ald, 77Ruh, 79Che, 84Ruh, 85Ada, 85Per, 86Ban, 87She, 90Dur, 90Fre, 95And, 95Yas, 97Kas, 99Hay, 01Jer, 03Sim, 06Mor]. Most of these studies agree that the transition temperature is located between 1440 and 1478 K. Moreover, numerous studies [50Cou, 66Kir, 79Che, 06Mor] found a discontinuity in the heat capacity at the transition point. The polymorphic transition at high temperature was investigated by Smith and Cline [62Smi] and Wolten [63Wol], both using HTXRD, and recently by Navrotsky et al. [05Nav], using DTA. Despite the high temperatures involved, the transition temperature data (which lie between 2553 and 2584 K) are in good agreement with each other.

The melting point of zirconia was determined by different types of experiments summarized in

Table 2 [25Hen, 32Cla, 66Nog, 70Lat]. Most reports found the melting temperature located between 2950 and 2960 K, but Noguchi et al. [66Nog] reported a rather high temperature: 2995 K.

The thermodynamic properties of ZrO_2 are summarized in Table 3. The enthalpy of formation of monoclinic zirconia (α -ZrO₂) was measured by many researchers [30Sie, 34Neu, 38Rot, 54Hum, 64Hub, 67Kor] using combustion calorimetry. The most recent determinations (Humphrey [54Hum] (-1094.1 kJ/mol), Huber et al. [64Hub] (-1100.8 kJ/mol), and Kornilov et al. [67Kor] (-1100.6 kJ/mol)) are in excellent agreement with each other. The preference was given to the data of Huber et al. [64Hub] (-1100.8 kJ/mol) because their measurement were performed using high purity zirconia (99.97 %), whereas other studies did not indicate the purity of their materials or showed data discrepancies with each other.

The enthalpy of transition between α - and β -ZrO₂ was determined by numerous authors [50Cou, 65Tsa, 66Kir, 79Che, 95Yas, 01Jer, 03Sur, 06Mor]. All these enthalpies vary between 4.362 and 5.941 kJ/mol with the exception of Kirillin et al. [66Kir] (7.718 kJ/mol) and Chekovskoi et al. [79Che] (8.297 kJ/mol), which are much higher. The enthalpy of 5.941 kJ/mol, determined by Coughlin and King [50Cou], was used in the review of Ackerman et al. [75Ack]. Recent studies by Yashima [95Yas] and Moriya and Navrotsky [06Mor], who employed high purity zirconia (99.9 wt. %), produced results (5.870 and 5.430 kJ/mol, respectively) which are similar to Coughlin and King [50Cou]. Therefore, the present optimization also favored a transition enthalpy of about -5.4 kJ/mol.

Recently, Navrotsky et al. [05Nav] provided the first experimental data regarding the enthalpy of transition between β - and γ -ZrO₂. Although the reported data were rather scattered, their value (3.4 ± 2.1 kJ/mol at 2584 K) is in fair agreement with the estimated transition enthalpy (5.56 kJ/mol at

2650K) of the β - to γ -ZrO₂ transition reported by Ackerman et al. [75Ack] (within error limits). No experiment has been carried out for the enthalpy of fusion.

The heat capacity of zirconia at low temperature (< 298.15 K) was measured by Kelley [44Kel] and Tojo et al. [99Toj] using adiabatic calorimetry (Table 4) and by Nevitt et al. [90Nev] using a heat pulse method. As shown in Figure 2a, all these studies are in good agreement and appear consistent with the heat capacity data collected above 298.15 K [50Cou, 66Kir, 79Che, 06Mor]. By extrapolating and integrating their low temperature heat capacity data, Kelley [44Kel] and Tojo et al. [99Toj] obtained an entropy of formation at 298.15 K of 49.79 and 50.33 J/mol·K, respectively. More weight was put on the entropy determined by Tojo et al. [99Toj] because they measured the heat capacity over a larger temperature range than Kelley [44Kel]. The entropy of transition between α - and β -ZrO₂ was calculated from the enthalpy of transition and the transition temperature. All these values are listed in Table 4.

Most of the high temperature heat capacity data of α - and β -ZrO₂ were derived from the heat content data measured by drop calorimetry [50Cou, 66Kir, 79Che]. Recently, careful measurements of the heat capacity and the heat content data were performed by means of two different techniques [06Mor]: DSC and transposed temperature drop calorimetry (TTDC). The heat capacity of the γ -ZrO₂ phase has not been investigated. Heat content data originally measured by Coughlin and King [50Cou], Kirillin et al. [66Kir], Chekovskoi et al. [79Che], and Moriya and Navrotsky [06Mor] are depicted in Figure 2b. Notte that the low temperature (< 298.15K) C_p data of α -ZrO₂ by Kelley [44Kel] and Tojo et al. [99Toj], which were determined by adiabatic calorimetry, are consistent with the C_p data (> 298.15 K) reported by Coughlin and King [50Cou], and Moriya and Navrotsky [06Mor]. The data obtained by Krillin et al. [66Kir] and Chekovskoi et al. [79Che] deviate slightly from the other data especially near the α - β transition region. In the case of the C_p of β -ZrO₂, the discrepancies observed between the experimental data are large. Interestingly, the most recent data by Moriya and Navrotsky [06Nav] show that the C_p of α - and β -ZrO₂ are nearly the same. Considering the data reported by Moriya and Navrotsky [06Nav] the most reliable, it was assumed that all three solid ZrO₂ polymorphs have the same C_p function in this study.

Thermodynamic modeling

According to the thermodynamic modeling of the Zr-O system by Arroyave et al. [02Arr], a small solubility of Zr is present in the cubic ZrO₂ phase. However, it gives nearly no difference in the thermodynamic properties at high temperatures (3000 K) under oxidizing conditions. Even at Fe saturation for steelmaking applications, the solubility of Zr is very limited. Therefore, the solubility of Zr in ZrO₂ at high temperatures is ignored in this study.

Recently, the thermodynamic properties of the β -ZrO₂, including the β - to γ -ZrO₂ transition enthalpy, were investigated by Navrotsky et al. [05Nav] and Moriya and Navrotsky [06Mor]. These new experimental data show discrepancies with the previous optimization by Pelton et al. [91Pel]; for this reason, a revision of the ZrO₂ unary system was performed.

In this study, ΔH_{298}° was taken from Huber et al. [64Hub] because their measurements were performed using high purity zirconia (99.97 %) and ΔS_{298}° was taken from Tojo et al. [99Toj] who measured the low temperature heat capacity over a large temperature range (15 to 298 K). The transition temperatures of solid ZrO₂ were taken from Moriya and Navrotsky [06Mor]. The heat capacities of α - and β -ZrO₂ were obtained by smoothing all the experimental data available regardless of the phase transformation and expressed as one function, because the discontinuity from the phase transformation has marginal effects on the thermodynamic properties. This method allowed us to predict the heat capacity of γ - ZrO₂ as well by extrapolating the function to high temperatures. The optimization results are shown in Figure 2 along with experimental data. The heat content calculated using the optimized heat capacity function from this study also well reproduces the heat content experimental data as shown in Figure 2b. The optimized enthalpy of transition between α - and β -ZrO₂ is in good agreement with many experimental data. In the case of the transition enthalpy between β - and γ -ZrO₂, the optimized value is 6.0 kJ/mol, which is slightly higher than the only experimental datum; 3.4 ± 2.1 kJ/mol, by Navrotsky et al. [05Nav]. The optimized transition enthalpy value (6.0 kJ/mol) is in good agreement with the phase diagram data between β - and γ -ZrO₂ solid solutions in the CaO-ZrO₂ binary system. The melting temperature of ZrO₂ as well as its ΔH_{fus}° and ΔS_{fus}° were taken from the thermochemical data compilation of Barin [89Bar].

4.2 ZrO₂-CaO system

Literature review

Our optimized ZrO₂-CaO phase diagram is shown in Figure 3 along with all experimental data. The invariant reactions are summarized in Table 5. Previously, two thermodynamic assessments [92Du, 09Wan] were carried out for of this system. The ZrO₂-CaO system has three stoichiometric compounds: CaZrO₃, CaZr₄O₉ and Ca₆Zr₁₉O₄₄. Their structures are summarized in Table 6. The existence of CaZr₄O₉ and Ca₆Zr₁₉O₄₄ is controversial; many research groups investigated them [52Duw, 63Tie, 63Fer, 65Bar, 68Gar, 72Piz, 73Mic, 76Hud, 77Stu, 82Hel, 87Dur, 91Dic, 93Yin] but no general consensus was made about their presence in the ZrO₂-CaO system. Therefore, CaZr₄O₉ and Ca₆Zr₁₉O₄₄ were not taken into account in the previous work [91Pel]. According to

Michel [73Mic], CaZr₄O₉ and Ca₆Zr₁₉O₄₄, designated as ϕ_1 and ϕ_2 , are stable from 1323 to 1623 K and below 1323 K, respectively. Hellman and Stubican [82Hel] thoroughly characterized the compounds in terms of composition and structure. After 38 days of prolonged heating, he found that both have a low temperature stability limit of 1373 K and an upper decomposition limit of 1508 and 1628 K, respectively. Later experimental studies [83Mar, 91Dic] support the general results reported by Hellman and Stubican [82Hel]. Therefore, these two compounds were also taken into account in this study.

The liquidus of the ZrO₂-CaO binary system was determined in numerous investigations [28War, 29Ruf, 47Cur, 67Nog, 69Tra, 77Stu]. Early experimental data [28War, 29Ruf, 47Cur, 67Nog] show discrepancies but the data from the most recent studies [69Tra, 77Stu] are in fair agreement with each other. The anomaly in the liquidus at 7 mol % CaO reported by Noguchi et al. [67Nog, 68Nog] is not generally accepted in the literature; such an anomaly is thermodynamically little plausible. Thus, the most recent studies [69Tra, 77Stu] (which show no liquidus anomaly) are considered more credible than earlier studies [28War, 29Ruf, 47Cur, 67Nog].

Numerous studies [53Die, 55Nad, 57Coc, 63Tie, 67Nog, 73Mic, 77Stu, 87Dur, 93Yin] were conducted to measure the lower stability limit of the cubic ZrO₂ solid solution (Css) by means of X-ray diffraction (XRD) and most of the data are in a good agreement. The solubility limit of CaO in cubic ZrO₂ was measured by many authors [29Ruf, 52Duw, 55Nad, 67Nog, 69Tra]. The tetragonal ZrO₂ solid solution (Tss) was investigated by four different authors [65Bar, 77Stu, 83Hel, 87Dur]. The experimental phase boundary data of Tss are fairly consistent with each other except for the data reported by Duran et al. [87Dur]. The existence of the monoclinic ZrO₂ solid solution (Mss) was reported by Jacob and Waseda [94Jac]. They tentatively suggested a maximum solubility of CaO in monoclinic ZrO₂ of 3 mol% at 1200 K and 2 mol% at 900 K. However, it was

mentioned in their report that the solubility limit is not accurate due to difficulties in obtaining equilibrium at low temperature. The limited solubility of ZrO₂ in CaO (Lss) was reported by Noguchi et al. [67Nog] and Traverse and Foex [69Tra].

The transition temperature between orthorhombic CaZrO₃ (o-CaZrO₃) and cubic CaZrO₃ (*c*-CaZrO₃) was reported by several authors [69Tra, 85Han, 89And]. Although all studies employed XRD analysis, the reported transition temperature varies from 1873 to 2273 K.

The enthalpy of formation of CaZrO₃ was investigated by several researchers [64Lvo, 71Kor, 86Bro, 88Mur]. Lvova and Feodosev [64Lvo] and Korneev et al. [71Kor] measured the enthalpy of formation by combustion calorimetry, whereas Brown and Bennington [86Bro], and Muromachi and Navrotsky [88Mur] used HF solution calorimetry and high temperature solution calorimetry, respectively. Since Ca-containing phases tend to precipitate CaF₂ when reacting with HF, HF solution calorimetry is more sensitive to sample purity than other techniques. Therefore, data reported by Brown and Bennington [86Bro] deviate from all other data. Yin et al. [96Yin] measured the enthalpy of formation of Ca₆Zr₁₉O₄₄ by solution calorimetry. However, optimization results based on their enthalpy of formation of Ca₆Zr₁₉O₄₄ are incompatible with the phase equilibrium data measured by Hellman and Stubican [82Hel]. This inconsistency was also pointed out by Wang et al. [09Wan]. As the phase equilibrium data are considered more reliable, the thermodynamic data measured by Yin et al. [96Yin] were not taken into account in this optimization.

The heat capacity and heat content data of CaZrO₃ are reported in Figure 4. King and Weller [60Kin] measured the heat capacity of CaZrO₃ between 51 and 298 K. By interpolating the heat capacity data to 0 K and by integrating them with respect to temperature, an entropy of formation

was calculated. The entropy of formation in this study was optimized by taking this value and adjusting it within the error limit indicated in the report of King and Weller [60Kin]. The heat content of CaZrO₃ was measured by many researchers [65Mez, 82Gve, 89Sah, 96Hun]. The heat content are in a fair agreement each other. In particular, Saha et al. [89Sah] determined the heat capacity of CaZrO₃ using DSC.

The activity of CaO in ZrO₂ solid solutions was measured using the electromotive force (emf) by Pizzini and Morlotti [72Piz], Levitski et al. [77Lev] and Tanabe and Nagata [96Tan]. From the emf data, they also derived the Gibbs energy of CaZrO₃. In general, their experimental results are in fair agreement with our calculated value.

Thermodynamic modeling

The optimized Gibbs energies of the stoichiometric compounds and the model parameters of the solids and liquid solutions are listed in Table 7 to 10. The thermodynamic data of CaO were taken from the previous optimization of Wu et al. [93Wu] whereas those of ZrO₂ and CaZrO₃ were re-optimized.

The enthalpy of formation of CaZrO₃ was optimized based on the data measured by Lvova and Feodosev [64Lvo], the entropy of formation was taken from King and Weller [60Kin], and the heat capacity at high temperature was optimized using heat content and heat capacity data [82Gve, 89Sah, 96Hun]. The transition temperature between o- and c-CaZrO₃ was taken from Hanon [85Han]. Heat capacity and heat content calculations from the previous optimization of Pelton et al. [91Pel] and this study are shown in Figure 4. The calculation results of both optimizations are in good agreement, except for the heat capacity value at 298 K. The Gibbs energy of formation of CaZrO₃ was evaluated using emf measurements [77Lev, 96Tan, 94Jac, 01Rog] but the temperature

ranges of the experiments and the reference states varies from one another. Comparisons of the experimental data with the present calculations are summarized in Table 8. Since the reference states of ZrO₂ are not specified in the report of Levitski et al. [77Lev], their experimental data could not be compared. Our calculated Gibbs energy of formation is in good agreement with the recent experiment data of Jacob and Waseda [94Jac] and Rog and Potoczek-Dudek [01Rog].

The compounds $CaZr_4O_9$ and $Ca_6Zr_{19}O_{44}$ were modeled based on their stability ranges reported by Hellmann and Stubican [82Hel]. However, it is thermodynamically impossible to have the same decomposition temperature for $CaZr_4O_9$ and $Ca_6Zr_{19}O_{44}$. Therefore, the decomposition temperature of $Ca_6Zr_{19}O_{44}$ was decreased by 50 K from the original experimental temperature of 1373 K. The Gibbs energies of $CaZr_4O_9$ and $Ca_6Zr_{19}O_{44}$ can be obtained by following equations:

$$G_{CaZr4O9}$$
 (J/mol) = G_{CaO} + $4G_{ZrO2(m)}$ - 36.93T

$$G_{Ca6Zr19O44} (J/mol) = 6G_{CaO} + 19G_{ZrO2(m)} - 47120 - 177.79T$$

Our calculated CaO activities are depicted in Figure 5 along with experimental data. Most experimental results are well reproduced apart from the results at 0.2 mol fraction from Pizzini and Morlotti [72Piz]. According to their experimental data, it seems that there is no phase change at 0.2 mole fraction of CaO between 1200 and 1400 K. In the equilibrium phase diagram depicted in Figure 3, a phase transition from 'Mss-ZrO₂ + CaZrO₃' to 'CaZr₄O₉' can be seen in this temperature range. As Hellman and Stubican [82Hel] demonstrated, the formation of CaZr₄O₉ is very slow, which suggests that the emf measurements of Pizzini and Morlotti [72Piz] were conducted under metastable conditions without CaZr₄O₉. The dotted line in the activity diagram of Figure 5(c) shows such metastable calculations.

The liquid solution was optimized using the MQM. Most liquidus and eutectic reactions are well reproduced.

4.3 ZrO₂-MgO system

Literature review

Four stoichiometric solid phases, $MgZr_6O_{13}$ [87Sim, 84Ros], $MgZr_3O_7$ [53Die], $Mg_2Zr_3O_8$ [53Die], and $Mg_2Zr_5O_{12}$ [83Far, 87Sim] were suggested to exist in the ZrO₂-MgO binary system. However, all these compounds are usually believed to be metastable; therefore, none of them were considered in this study.

The phase diagram of the ZrO₂-MgO system is shown in Figure 6 along with experimental data. The liquidus of the binary ZrO₂-MgO system was investigated by numerous authors [30War, 33Ebe, 39Zhi, 47Cur, 68Nog, 87Sim]. The earliest data by Wartenberg and Werth [30War] are at odd with all other experimental data. Therefore, their data were not considered in this study. Most liquidus data other than the ones reported by Noguchi and Mizuno [68Nog] are in fair agreement. As for the liquidus of the ZrO₂-CaO system, Noguchi and Mizuno [68Nog] reported a local minimum on the liquidus of the ZrO₂-MgO system at about 0.1 mole fraction of MgO, which is thermodynamically improbable [910ka]. The eutectic reaction occurs at about 0.5 mole fraction of MgO.

Cubic (Css), tetragonal (Tss), and monoclinic (Mss) ZrO₂ solid solutions were observed together with periclase solid solution (Pss). The Css phase boundaries were determined by many research groups [29Ruf, 47Cur, 52Duw, 61Coc, 62Hin, 65Vie, 67Gra, 68Nog, 70Col, 81Sco, 87Sim, 88Ech, 88Stu, 91Dur, 93Yin, 13Pav]. With exception of the early studies [61Coc, 62Hin, 65Vie], most eutectoid data [67Gra, 70Col, 87Sim, 93Yin] are consistent with each other. In Figure 6, only the most recent data together with the experimental data of Viechnichi and Stubican [65Vie] for high temperature Css are shown. According to Viechnichi and Stubican [65Vie], the high temperature experimental data of the Css phase boundary are less accurate due to slow quenching. Sim and Stubican [87Sim] thoroughly characterized the Css phase boundary by diverse methods such as lattice parameter measurements, high temperature in situ XRD, and DTA. Duran et al. [91Dur] also performed an extensive research on the Css phase boundary. Although the eutectoid compositions reported by Sim and Stubican [87Sim] and Duran et al. [91Dur] are slightly different, the general topology of the solid solution is the same. However, as pointed out by Viechnichi and Stubican [65Vie], the experimental phase boundary above 2000 K is narrower even with very rapid quenching.

The solubility of MgO in tetragonal zirconia has also been investigated by many researchers [52Duw, 59Kau, 65Vie, 67Gra, 87Sim, 88Ech, 91Dur]. As shown in Figure 6, noticeable solubility of MgO in tetragonal ZrO₂ was reported by Duwez et al. [52Duw] and Sim and Stubican [87Sim]. However, the work of Kauer et al. [59Kau] together with the most recent studies [67Gra, 87Sim, 88Ech] suggest that the solubility of MgO reaches less than 1 mol %. The large solubility measured by Duwez et al. [52Duw] seems to be less reliable compared to most recent experimental data; it was thus ignored in the current study.

Sim and Stubican [87Sim] and Duran et al. [91Dur] measured a eutectoid temperature of 1679 K for the tetragonal solid solution (Tss) by means of DTA. The Tss eutectoid is located in a relatively low temperature region and the accuracy of this point is little reliable due to the sluggishness of the phase transformation in the ZrO₂ solid solution. As both experimental studies employed the same technique and samples with similar purity, it is hard to determine which data set is more

reliable. For the monoclinic ZrO_2 , no accurate solubility data were reported in the literature. According to Echigoya et al. [88Ech], no trace of MgO in monoclinic ZrO_2 was detected by EDS in their experiments. Therefore, we assumed no solubility of MgO in monoclinic ZrO_2 .

Henriksen [79Hen] found that MgO can take up to 0.075 mol % of ZrO₂ at 1885 °C in its structure. According to Scott [81Sco], the solubility of ZrO₂ in MgO at 1873 K is small enough to be ignored. As a result, we considered the solubility of ZrO₂ in MgO to be close to zero.

The only available thermodynamic property data for the binary ZrO₂-MgO system is the enthalpy of formation of the cubic ZrO₂ solid solution determined by Yin et al. [96Yin]. The Css sample was prepared by quenching from 1843K after holding for 50 hours. The heat of formation of the solid solution was measured by drop solution calorimetry with a (Li, Na)BO₂ solvent at 1100 K.

Thermodynamic modeling

The optimized phase diagram at the ZrO₂-MgO system is shown in Figure 6. All optimized thermodynamic model parameters are listed in Table 9 and 10. As can be seen in the diagram, the most reliable experimental data mentioned above were well reproduced. The invariant reactions are listed in Table 11. The enthalpy of mixing of the cubic ZrO₂ solution measured by Yin et al. [96Yin] is compared with our calculations in Figure 7. As can be seen, the present calculations reproduce the experimental data within experimental error limits.

One of the noticeable difference from the previous work by Pelton et al. [91Pel] is the solidus of the cubic ZrO₂ solution. Pelton et al. intentionally added a negative temperature dependent parameter to increase the stability of the cubic solution at high temperatures to reproduce the liquidus data of Noguchi and Mizuno [68Nog]. Unfortunately, no solidus data were available for

the cubic solid solution. Therefore, new experimental data on the Css solubility at high temperatures is necessary for a better understanding of the system. The calculated MgO liquidus in Figure 6 is different from the experimental data. This difference originates from the melting temperature of MgO. Recently, Pavlychkov et al. [13Pav] reported a new assessment of the ZrO₂-MgO binary system. To model the solid solutions in ZrO₂-rich region, they used the compound energy formalism (CEF) with the sublattice structure [Zr⁴⁺ Mg²⁺] [O²⁻ Va]. Because the mixing entropy of the two-sublattice model is greater than that of the liquid, there was a maximum in their liquidus, which is inconsistent with the experimental data available.

4.4 ZrO₂-SiO₂ system

Literature review

The phase diagram of the ZrO₂-SiO₂ system is depicted in Figure 8 along with the experimental data available in the literature. Liquid immiscibility in the ZrO₂-SiO₂ system was first observed by Barlett [31Bar]. Toropov and Galakhov [56Tor] investigated the miscibility gap and found that it lies between 58.7 and 77.0 mol % SiO₂ at 2523 K with a consolute point at 69.8 mol % SiO₂ and 2703 K. The presence of immiscibility in the ZrO₂-SiO₂-FeO ternary system was reported by Jones et al. [67Jon] and the existence of liquid immiscibility in the ZrO₂-SiO₂ system is thus now accepted as a fact.

The liquidus in the ZrO₂-SiO₂ system was only investigated by Zhirnova [34Zhi], Toropov and Galakhov [56Tor], and Kamaev [05^aKam]. Zhirnova [34Zhi] reported a liquidus with two eutectic points and no miscibility gap. Moreover, ZrSiO₄ (zircon) was considered to be stable up to the liquidus, which is inconsistent with later experimental results [53Cur, 67But, 76Ans, 05^aKam, 08Kai] showing that zircon decomposes to ZrO₂ and SiO₂ above either about 1823 or 1949 K.

According to numerous works [53Cur, 56Tor, 67But, 05^aKam], only one eutectic reaction do exists and it is $L \rightarrow ZrO_2 + SiO_2$.

Despite the fact that no experimental solubility of SiO₂ in ZrO₂ was reported in the literature, the phase diagrams of numerous research groups [34Zhi, 49Gel, 53Cur, 56Tor] show some SiO₂ solution in solid ZrO₂. The solubility varies between 6 and 18 mol % SiO₂, which is rather large. Lang et al. [65Lan] conducted a rigorous investigation on the solubility of SiO₂ in solid ZrO₂ by means of HTXRD and according to them, the solubility of ZrSiO₄ in ZrO₂ does not exceed 0.3 wt%.

There is a controversy over the melting or dissociation temperature of ZrSiO₄. Early studies by Washburn and Libman [20Was] and Zhirnova [34Zhi] reported that zircon melts congruently at 2823 and 2703 K, respectively. However, many studies [31Bar, 45Gel, 33Hei, 53Cur, 57Coc, 67But, 76Ans, 05^aKam, 08Kai] reported that zircon decomposes to ZrO₂ and SiO₂ before it melts. These experimental decomposition temperatures are tabulated in Table 12. Anseau et al. [76Ans] carried out quenching experiments with high purity ZrSiO₄ and found that zircon decomposes slowly at 1798 K. Recent studies conducted by Kamaev et al. [05^aKam] using DTA and Kaiser et al. [08Kai] using HTXRD reported that the decomposition temperature is about 1948 K, which is in agreement with the previous result of Butterman and Foster [67But]. In this study, the decomposition temperature of ZrSiO₄ is considered to be 1948 K.

Coughlin and King [50Cou] measured the heat content of zircon between 400 and 1800 K by drop calorimetry. Kelley [41Kel] measured the heat capacity at low temperature from 52 to 294 K using adiabatic calorimetry and calculated its entropy by extrapolating below 52 K. Recently, the enthalpy of formation of zircon was measured by Ellison and Navrotsky [92Ell] using high

temperature solution calorimetry. The available data can well constrain the Gibbs energy of ZrSiO₄.

Thermodynamic modeling

Our optimized phase diagram of the ZrO_2 -SiO₂ system is presented in Figure 8. The main difference between the present study and the one by Pelton et al. [91Pel] is the decomposition temperature of $ZrSiO_4$. Both assessments cannot reproduce the liquidus of ZrO_2 in the SiO₂-rich region. In fact, it is impossible to reproduce the liquidus of Kamaev et al. [05^aKam] with the liquid-liquid miscibility gap. As liquid SiO₂ is very viscous and has sluggish dissolution kinetics, Kamaev et al. most probably underestimated the liquidus of ZrO_2 in their DTA measurement.

According to our literature review, the low temperature heat capacity and heat content data of zircon (Figure 9) were well optimized in the previous work of Pelton et al. [91Pel]. However, a recent experimental determination of the enthalpy of formation of ZrSiO₄ by Ellison and Navrotzky [92Ell] indicates that the value optimized by Pelton et al. [91Pel] is 5 kJ/mol too high. As a result, their decomposition temperature was smaller than 1948 K. In this study, the dissociation temperature of ZrSiO₄ is well calculated if the thermodynamic properties of ZrSiO₄ from the literature are simply used. This indicates that the thermodynamic and phase diagram data are consistent with each other. The optimized invariant reaction points of the ZrO₂-SiO₂ system are compared with experimental data in Table 12. To reproduce the liquid-liquid miscibility gap in SiO₂-rich region, four temperature-independent parameters were required with the MQM.

4.5 ZrO₂-Al₂O₃ system

Literature review

Numerous studies [28War, 53Die, 61Suz, 65Kra, 68Cev, 70Sch, 81Fis, 87Vol] established that

there is no intermediate compound in the ZrO_2 -Al₂O₃ system. However, no consensus exists yet about the presence of solid solution in ZrO_2 and Al₂O₃. Suzuki et al. [61Suz] observed no mutual solubility between ZrO_2 and Al₂O₃ in the lattice parameters of quenched samples using XRD. On the other hand, Nishiyama and Okamoto [64Nis] and Rutman [85Rut] reported tentatively that tetragonal ZrO_2 (Tss) may contain up to 0.12 mol % of Al₂O₃ at 1223 ± 50 K. However, the data are not considered accurate, due to the XRD detection limits [06Sar]. Recently, Jerebtsov et al. [00Jer] confirmed the existence of both ZrO_2 (Tss) and Al₂O₃ (corundum solid solution) using DTA and X-ray fluorescence (XRF). According to them, zirconia solid solution contains 0.84 mol % Al₂O₃ at 1358 K and may contains up to 1.08 mol % Al₂O₃ at the eutectic temperature. However, no details about the experimental technique and analytical methods used are given in their paper.

Many researchers [61Suz, 68Cev, 70Alp, 70Sch, 81Fis, 00Jer, 05^bKam, 06Uda] have determined the eutectic reaction; it varies between 0.5 and 0.7 mol fraction of Al₂O₃ and 1973 and 2183 K. However, the most recent studies [70Alp, 70Sch, 81Fis, 00Jer, 05^bKam] are in a good agreement with each other and locate the eutectic reaction at about 0.63 ± 0.01 mol fraction of Al₂O₃ and 2153 ± 20 K.

The existence of a liquid-liquid miscibility gap in the ZrO₂-Al₂O₃ binary system has been reported by several researchers [64Alp, 05^bKam, 06Uda]. Kamaev et al. [05^bKam] observed some phase separation using DTA, SEM and XRD. Udalov et al. [06Uda] later confirmed the existence of liquid immiscibility using XRD. However, all these studies do not agree about the location and the temperature of the miscibility gap. Furthermore, it is not clear why liquid immiscibility is experimentally observed in this system. Thermodynamically, it is little plausible to observe liquid immiscibility with such liquidus data. Therefore, liquid immiscibility is not taken into account in this study as shown in the ZrO₂-Al₂O₃ phase diagram of Figure 10.

Key phase diagram experimental results

The solubility of Al₂O₃ in the zirconia solid solution is still an issue. Previously, Pelton et al. [91Pel] optimized Tss based on the study of Alper et al. [64Alp] which reported that there is up to 7 wt% of alumina in Tss. However, the most recent measurements [00Jer] performed by XRF disagree with the data reported by Alper et al. [64Alp]. Key experiments were thus conducted to confirm or not the solubility of Al₂O₃ in Tss. Since zirconia has a higher melting point (2950 K) than alumina (2327 K), the starting material employed was prepared with a composition of 80 wt% Al₂O₃; this maximized our chances to reach equilibrium. Two samples were then fired at 1873 K for 3 and 14 days, respectively. A back scattered electron image of the sample annealed for 14 days at 1873 K is depicted in Figure 11. EPMA analysis of the samples quenched after 3 and 14 days at 1873 K had virtually the same composition (which suggest that equilibrium was reached) with a content of 0.2 wt% Al₂O₃ in zirconia. On the other hand, the solubility of ZrO₂ in solid Al₂O₃ was below the detection limit of the EPMA. The present experimental results were incorporated in our optimization of the ZrO₂-Al₂O₃ system. The largest difference between our study and the previous work of Pelton et al. [91Pel] is the solubility limit of Al₂O₃ in ZrO₂. Our current optimization results are in fair agreement with the experimental results reported by Murakami et al. [00Mur] in higher-order system; the ZrO₂-CaO-Al₂O₃ ternary system.

4.6 ZrO₂-CaO-MgO system

Literature review

A limited number of experimental data are available in the literature for this system. Longo and
Podda [78Lon] investigated the subsolidus phase relations; unfortunately, no experimental data are tabulated or depicted in their report and as a consequence their experimental results could not be considered. Hellmann and Stubican [83Hel] and Yin and Argent [93Yin] attempted to characterize the homogeneity range of cubic ZrO₂ solid solution in the ZrO₂-CaO-MgO system using XRD from 1573 to 1773 K but experimental results at these two temperatures do not agree with each other. According to Yin and Argent [93Yin], Hellmann and Stubican [83Hel] made a wrong assumption when calculating the phase boundary compositions from their XRD patterns. The correct calculation method is elaborated in the paper of Yin and Argent [93Yin] and we considered these results.

The eutectic point in the CaZrO₃-MgO section was determined by Aza et al. [74Aza]. However, no actual experimental point other than the calculated phase diagram of the CaZrO₃-MgO system is available in their paper. Apparently, their CaZrO₃-MgO section was drawn by interpolating the experiment results they obtained in the quaternary ZrO₂-MgO-CaO-SiO₂ system. Yin et al. [96Yin] measured the enthalpy of mixing of the cubic ZrO₂ solid solution in the ZrO₂-CaO-MgO system by means of a high temperature drop solution calorimetry with a (Li, Na)BO₂ solvent. Serena et al. [05Ser] thoroughly characterized the phase relations in the MgO·CaO-ZrO₂ section at relatively high temperatures, i.e. 1873, 1973, and 2023 K. To ensure equilibrium, the samples were hold at each temperature for 16 h and then reground and reheated for another 16 h at the corresponding temperatures until no variation was observed by XRD in the phase assemblages. Samples were analyzed by EPMA, EDS, and XRD.

Thermodynamic modeling

Thermodynamic modeling of the ZrO₂-CaO-MgO system was previously performed by Du et al.

[92Du] and Serena et al. [05Ser]. Figure 12 shows liquidus projections of the ZrO₂-CaO-MgO system calculated from the present optimization. The Gibbs energies of the ZrO₂ solid solutions and the liquid phase were predicted in the ZrO₂-CaO-MgO system from the parameters of the bounding binary systems using the Toop interpolation technique by assuming ZrO_2 as an asymmetric component. It can be seen in Figure 13 that the predicted homogeneity ranges of the ZrO₂ solid solutions are in fair agreement with the recent data of Yin and Argent [93Yin], Yin et al. [96Yin], and Serena et al. [05Ser] but not with the data reported by Hellmann and Stubican [83Hel]. Our calculated isoplethal section of the MgO·CaO-ZrO₂ is shown in Figure 14a. One small ternary parameter was necessary to reproduce the liquidus of this section. Our calculated results are in good agreement with the experimental data of Yin and Argent [93Yin] and Serena et al. [05Ser] whereas the calculated results from the previous optimization of Pelton et al. [91Pel] show large discrepancies especially in the ZrO₂-rich region. The eutectic point reported by Aza et al. [74Aza] is also in fair agreement with our calculated results, as indicated in Figure 14b. The enthalpy of solution measured by Yin et al. [96Yin] is compared with the calculated value from the current optimization and the one of Pelton et al. [91Pel] in Figure 15. The present optimization can reproduce the experimental data within the experimental error limits.

4.7 ZrO₂-CaO-SiO₂ system

Literature review

Qureshi and Brett [68^aQue, 68^bQue] investigated the phase relationships in the ZrO₂-CaO-SiO₂ system. Phase equilibria were established by holding the samples at temperatures up to 2023 K for up to 18 h. Regrinding and reheating of pre-fired samples was also carried out to ensure that equilibrium was reached. Air-quenched samples were analyzed by EPMA and XRD. According

to their experiments, only one ternary compound (Ca₃ZrSi₂O₉) exists in this ternary system. They also presented the phase diagrams of twelve isopleths. Aza et al. [93Aza] reexamined the CaO·SiO₂-ZrO₂ system using the quenching method in liquid nitrogen. The experiments were conducted with high purity materials (99.5 to 99.99 wt%) and samples were fired at target temperatures for up to 24 h with intermediate grindings to reach equilibrium. The quenched samples were analyzed by SEM/EDS and XRD. According to them, no ternary compound exists in the ZrO₂-CaO-SiO₂ system, which is in disagreement with the earlier study of Qureshi and Brett [68^aQue, 68^bQue]. Lopato et al. [95Lop] investigated the phase relations in the Ca₂SiO₄-CaZrO₃ section using HTXRD and DTA; the temperatures of the phase boundaries differ by about 50 K between the two techniques.

In total, three ternary compounds, CaZrSi₂O₇, Ca₂Si₄ZrO₁₂, and Ca₃Si₂ZrO₉, were reported in the literature for the CaO·SiO₂-ZrO₂ system. The CaZrSi₂O₇ phase was observed by Ansell et al. [80Ans]. However, it was identified as metastable by Morgan et al. [87Mor]. Morgan et al. [87Mor] synthesized the ternary compounds by blending SiO₂, cabosil, ZrO₂ in isopropanol solution, and drying the samples at 393 K. After milling and firing the samples from 1273 to 1773 K, XRD was taken for the powder of samples. According to their report, CaZrSi₂O₇ is not stable in the ambient pressure, and Ca₂Si₄ZrO₁₂, and Ca₃Si₂ZrO₉ were identified as orthorhombic and monoclinic respectively. This is in accordance with previous reports by Kordyuk and Gul'ko [62Kor], and Al-Hermezi et al. [86Al-Her].

Jacob and Waseda [94Jac] calculated the formation Gibbs energy of $Ca_2ZrSi_4O_{12}$ by means of emf. Since $Ca_2ZrSi_4O_{12}$ is stable with $ZrSiO_4$ and SiO_2 at the temperature range 973 to 1273 K, the formation Gibbs energy of $Ca_2ZrSi_4O_{12}$ from the oxides can calculated by measuring the difference of CaO chemical potential. The emf cell used for the experiment is designated below.

$$2CaO + 3SiO_2 + ZrSiO_4 \rightarrow Ca_2ZrSi_4O_{12}$$

Optical grade single crystal of CaF₂ was used for electrolyte. The experiments were conducted under high oxygen partial pressure at the targeted temperature. Rog et al. [05Rog] also conducted emf experiment for Ca₂ZrSi₄O₁₂ under the similar condition using different electrolyte (Ca- β ''alumina). Both experimental results are in a good agreement within the experimental error range. The formation energy of Ca₃ZrSi₂O₉ was also reported on their paper by Rog et al. [05Rog] using the following emf cell.

However, their emf cell assemblage is thermodynamically unstable. According to the phase diagram, the three phase assemblage; " $Ca_3ZrSi_2O_9 + CaZrO_3 + Ca_2SiO_4$ " cannot be in equilibrium. Therefore, only the thermodynamic data of $Ca_2ZrSi_4O_{12}$ is taken from Rog et al. [05Rog].

Experimental results and thermodynamic modeling

Figure 16 shows liquidus projections of the CaO-SiO₂-ZrO₂ system calculated from the present optimization. The Gibbs energy of Ca₂ZrSi₄O₁₂ was optimized based on experimental emf data [94Jac, 05Rog]. The heat capacity of the compound was approximated by the Neumann Kopp rule of indicated constituents; ZrSiO₄, CaO and SiO₂. Enthalpy and entropy of formation were adjusted to reproduce the emf results: ΔH_f = -196.95 kJ/mol and ΔS = -2.08 J/mol·K. As mentioned above, the cell configuration of Ca₃Si₂ZrO₉ by Rog et al. [05Rog] was incorrect. Hence, the Gibbs energy

data of Ca₃Si₂ZrO₉ is completely wrong. When the reported Gibbs energy is used as it is, Ca₃Si₂ZrO₉ appears to be too stable in the ternary system at 1573 K. This result contradicts with the data reported by Jacob and Waseda [94Jac]. Therefore, the Gibbs energy of Ca₃Si₂ZrO₉ was optimized based on the phase equilibria data. The heat capacity as well as entropy were estimated by Neumann Kopp approximation of ZrO₂ (m), SiO₂ (Tridymite-h) and CaO. Enthalpy of formation was adjusted to reproduce the phase equilibria at 1573 K reported by Jacob and Waseda [94Jac]; it is -252.128 kJ/mol. The optimized Bibbs energies of formation of Ca₂ZrSi₄O₁₂ and Ca₃Si₂ZrO₉ are compared with empirical data in Figure 17.

Qureshi and Brett [68ªQue, 68^bQue] reported many phase diagrams of isoplethal sections in the ZrO₂-CaO-SiO₂ ternary system. However, in the study [68^bQue] for low basicity region (low CaO/SiO₂), they could not find Ca₂ZrSi₄O₁₂. This is contradictory with later studies [62Kor, 86Al-Her, 94Jac, 05Rog]. Hence, the results of Qureshi and Brett [68^bQue] for low basicity region is rather doubtful. This is most probably due to insufficient equilibrium time at high SiO₂ region. To determine the accurate phase diagram, several key experiments were conducted to find liquid boundaries by varying equilibrium time at 1873 K. Analysis of each equilibrated sample by EPMA indicated that it takes more than three days to reach equilibria, which was much longer than the equilibration time employed in the previous studies [68^aQue, 68^bQue, 93Aza]. The isothermal phase diagram at 1873 K is calculated in Figure 18 along with present key experimental results. As can be seen, most experiments of phase equilibria and their compositions are well reproduced in the optimized phase diagram. All the isoplethal sections of the CaO-SiO₂-ZrO₂ system studied by Qureshi and Brett [68ªQue, 68^bQue] are also computed in Figure 19. Most of the experimental data by Qureshi and Brett [68^aQue] in molar CaO/SiO₂ \geq 1 are well reproduced. However, the liquidus temperatures reported by them in molar CaO/SiO₂ \leq 1 are much lower than the present experimental results as shown in Figure 19. The present optimization can accurately reproduce the present key experimental data. It is believed that the inaccurate phase diagram information in low basicity region is successfully resolved in this study.

4.8 ZrO₂-CaO-Al₂O₃ system

Literature review

The existence of ternary compounds in the ZrO₂-CaO-Al₂O₃ system was studied by Berezhnoi and Kordyuk [63Ber], and Espinosa de los Monteros and White [73Esp]. Both reports agree that only one ternary compound exists in this ternary system. However, they disagree on the compositions of the compound, even though they both investigated the system by means of quenching method and XRD analysis. Ca₇Al₆ZrO₁₈ was reported as a ternary compound by Berezhnoi and Kordyuk [63Ber], whereas Espinosa de los Monteros and White [73Esp] reported Ca₁₃Al₁₂Zr₂O₃₅ (C₁₃A₆Z₂) stoichiometry. The recent study conducted by Murakami et al. [00Mur] confirmed the existence of Ca₁₃Al₁₂Zr₂O₃₅ (C₁₃A₆Z₂) by using the same experimental technique. Thus, only the stoichiometric compound Ca₁₃Al₁₂Zr₂O₃₅ (C₁₃A₆Z₂) was considered in this study. No experimental data has been reported for the thermodynamic properties of this compound.

The phase diagram of the ZrO₂-CaO-Al₂O₃ system was investigated by several authors [63Ber, 81Ban, 85Lid, 86Mur, 96Sak, 00Mur]. Liddle and Brett [85Lid] studied the isopleIthal section of the system CaAl₂O₄ (CA)-CaZrO₃ (CZ) by means of classical quenching method with XRD and EMPA analysis. According to their experiment, the eutectic temperature of L \rightarrow CA+CZ is 1798 K, which is in fair agreement with the early study (1823 ± 10 K) by Berezhnoi and Kordyuk [63Ber]. The slope of liquidus of CZ by Liddle and Brett [85Lid] is steeper than that proposed by Berezhnoi and Kordyuk [63Ber]. Sakai and Suito [96Sak] investigated isothermal section of the

 ZrO_2 -CaO-Al₂O₃ system at 1873 K. Their study focused on characterizing liquidus of CaO, Al₂O₃ and ZrO_2 (crucibles made of CaO, Al₂O₃ and ZrO_2 were used to contain the liquid meld) by using quenching method with XRD and EDS analysis. However, Murakami et al. [00Mur] put considerable doubt on the experimental results studied by Sakai and Suito [96Sak]. They suggested that there is possibility that reaction product might be formed between the crucibles. Moreover, liquid and the equilibrium solid phase could be different from crucible materials. Therefore, Murakami et al. [00Mur] conducted equilibration experiments using Pt crucible at 1773 and 1873 K followed by XRD and EPMA analysis. Their experimental results over the phase boundary of ZrO_2 solid solution indicates that the solubility of Al₂O₃ in ZrO_2 is limited. This results support the recent experimental data reported by Jerebtsov et al. [00Jer] and the present key experimental data in the binary ZrO_2 -Al₂O₃ system.

Bannister [81Ban] reported subsolidus phase equilibria in the ZrO₂-CaO-Al₂O₃ system at 1973 K for the development of an oxygen sensor using stabilized ZrO₂ by means of quenching method with XRD phase analysis. Muromura and Hinatsu [86Mur] studied the subsolidus phase equilibria at 1653 K. But XRD analysis indicated that the same samples contained four phases in equilibrium, which may result from insufficient equilibration time or slow quenching.

Thermodynamic modeling

Figure 20 shows the calculated liquidus projection of the ZrO_2 -CaO-Al₂O₃ ternary system from this study. For the liquid phase, Toop type interpolation technique was used to predict the Gibbs energy of ternary solution from their binary parameters, assuming ZrO_2 as an asymmetric component. Two ternary parameters were added to better reproduce all liquidus in the system. Only one ternary compound (C₁₃A₆Z₂) is considered in this work. Since no experimental data has been reported for the thermodynamic properties of this compound, heat capacity and entropy of the compound were estimated by the Neumann-Kopp approximation from CaO(lime), Al₂O₃(corundum), and ZrO₂(monoclinic). Enthalpy of formation (ΔH°_{f}) of this compound was adjusted to reproduce its melting point (1813 ± 10 K) reported by Espinosa de los Monteros and White [73Esp]. The optimized enthalpy of formation from elements is ΔH°_{f} = 523.2 kJ/mol. The Gibbs energies of solid ZrO₂ solutions were predicted from binary parameters without any ternary model parameter.

Figure 21 and 22 show the calculated isothermal phase diagrams of the CaO-Al₂O₃-ZrO₂ system and the pseudo-binary CaAl₂O₄-CaZrO₃ section along with experimental data by Bannister [81Ban] and Muromura and Hinatsu [86Mur]. Since Tss has diffusionless transformation to Mss, it is impossible to quench Tss. Therefore, all the Mss of the experimental data reported by Muromura and Hinatsu [86Mur] are in fact Tss at the experimental temperature. Two parameters were introduced to liquid to reproduce the liquidus reported by Murakami et al. [00Mur] and Liddle and Brett [85Lid].

4.9 ZrO₂-MgO-SiO₂ system

Literature review

Many attempts have been made for the phase diagram study of the ZrO₂-MgO-SiO₂ system. However, only a few comprehensive studies are available. Beetle et al. [48Bee] reported that there is no ternary compound in this system. Foster [51Fos] and Pandit and Jacob [95Pan] investigated the subsolidus phase equilibria at 1723 and 1700 K respectively using classical quenching method. Their experimental data are in fair agreement with each other. Melting behavior of the ZrO₂-MgO-SiO₂ system was studied by Hossain and Brett [68Hos] by means of classical quenching method with XRD phase analysis. They reported the isopleths of the SiO₂-MgO with 5, 10, 15, 20 wt% ZrO₂. Since Hossain and Brett [68Hos] scrutinized the phase relation of the ZrO₂-MgO-SiO₂ ternary system with high purity materials, their experimental data are considered more reliable than the study by Berezhnoi, and Karyakin [52Ber].

Thermodynamic modeling

The calculated liquidus projection of the ZrO₂-MgO-SiO₂ from this study is presented in Figure 23. Toop interpolation technique was used for the prediction of the Gibbs energy of liquid ZrO₂-MgO-SiO₂ phase with MgO as an asymmetric component. No ternary parameter was necessary. Subsolidus phase equilibria and the isopleths of MgO-SiO₂ with 5 to 20 wt% ZrO₂ [68Hos] are presented in Figure 24 and 25, respectively. As can be seen in Figures 24 and 25, all experimental data are reasonably well reproduced.

4.10 ZrO₂-MgO-Al₂O₃system

Literature review

No ternary compound had been reported until the sub-solidus experiment was conducted by Tassot et al. [86Tas]. They found the ternary phase: $Mg_{5+x}Al_{2.4-x}Zr_{1.7+0.25x}O_{12}$, where $-0.4 \le x \le 0.4$, stable above 1873. The existence of this ternary phase was also confirmed by Pavlyuchkov et al. [14Pav]. They detrmined the stability range of this phase from 1894 to 2114 K by DTA. The composition of the ternary phase was analyzed by EDS. Pavlyuchkov et al. [14Pav] also investigated the phase relations at 1523, 1873, and 2023 K, equilibrating the samples for 10-14 days, 7 days and 6 hours respectively, followed by furnace cooling. Less than 2 wt% of ZrO₂ in spinel (MgAl₂O₄) was detected. Shevchenko et al. [93She] investigated the phase diagram of the ZrO₂-MgAl₂O₄ section

by means of DTA. Their experimental results shows slight discrepancy with those reported by Pavlyuchkov et al. [14Pav].

Thermodynamic modeling

The predicted liquidus projection of the ZrO₂-MgO-Al₂O₃ system is presented in Figure 26. The isothermal phase diagrams and the isopleth of the MgAl₂O₄-ZrO₂ are presented in Figure 27 and 28, respectively, along with experimental data. The Gibbs energy of ternary ZrO₂-MgO-Al₂O₃ liquid system was predicted based on the Toop type approximation from binary parameters with ZrO₂ as an asymmetric component. The optimization was performed based on experimental results reported by Pavlyuchkov et al. [14Pav]. Since good consensus has been achieved on the existence of the ternary compound, the ternary compound $Zr_{14}Al_{22}Mg_{39}O_{100}$ is included on current optimization. The Gibbs energy of ternary compound $Zr_{14}Al_{22}Mg_{39}O_{100}$ was optimized based on the phase equilibria data. Neumann Kopp approximation was used to calculate heat capacity from ZrO_2 (monoclinic), Al_2O_3 (corundum), and MgO (periclase). Then, enthalpy and entropy of the component were adjusted in accordance with the phase diagram data reported by Pavlyuchkov et al. [14Pav]. The optimized ΔH_f = 396.684 kJ/mol and ΔS = 493 J/mol·K. No ternary model parameter was introduced in ZrO₂ solid solutions. As can be seen in Figure 27 and 28, most of experimental data are well reproduced.

Some of the experiment data by Pavlyuchkov et al. [14Pav] show four phases in equilibrium. This indicates that the experiment duration was insufficient to reach equilibrium. Two liquid ternary model parameters were used for the optimization.

4.11 ZrO₂-Al₂O₃-SiO₂system

Literature review

Rea [39Rea] firstly investigated the ZrO₂ -Al₂O₃-SiO₂ system by means of Cone Fusion method. A ternary eutectic point was tentatively suggested as 75 wt% SiO₂, 10 wt% ZrO₂ and 15 wt% Al_2O_3 at 1887 K. However, specific experimental methods and analysis methods were not described in the report. The first phase diagram of the ZrO₂ -Al₂O₃-SiO₂ system was published by Budnikov and Litvakovskii [56Bud]. The authors focused on clarifying melting points of aluminarich composition region by means of classical quenching method and XRD analysis. A ternary eutectic reaction was reported to be located at 53 wt% Al₂O₃, 17 wt% SiO₂, and 30 wt% ZrO₂; 2073 K, which is in fair agreement with a later study conducted by Cevales [75Cev] 50.9 wt% Al₂O₃, 16.3 wt% SiO₂, and 32.8 wt% ZrO₂; 1958 K. Qureshi and Brett [68°Qur] and Greca et al. [92Gre] thoroughly characterized the phase relations of the ZrO₂-SiO₂-Al₂O₃ system by means of quenching method followed by XRD and EPMA phase analysis. Qureshi and Brett [68°Qur] fired their samples up to 2013 K for 1-5 h and quenched by air, whereas Greca et al. [92Gre] quenched their sample with water after holding their samples at high temperatures for 6-24 hours. However, some of the experimental data reported by Greca et al. [92Gre] indicates that their samples was not in equilibrium even after firing the samples for 24 hours. All the invariant points of the ZrO₂ -Al₂O₃-SiO₂ system which have been reported in the literature are tabulated in the Table 13.

Thermodynamic modeling

The Gibbs energy of ternary ZrO_2 - Al_2O_3 - SiO_2 system was calculated based on the Toop type approximation from each binary system with Al_2O_3 as an asymmetric component. Three ternary parameters were added to have better fit for the available experimental data. The calculated liquidus projection of the ZrO₂-Al₂O₃-SiO₂ system are presented in Figure 29 along with invariant reactions reported in the literature [39Rea, 56Bud, 75Cev]. The ternary liquid parameter was optimized based on the experimental data reported by Qureshi and Brett [68°Qur] and Greca et al. [92Gre], as their experimental techniques and analysis methods have better accuracy. Qureshi and Brett [68°Qur] did not tabulated their analysis results, but plotted on phase diagrams. Greca et al. [92Gre], on the other hand, tabulated their analysis results as well as plotting data points in regarding phase diagrams. However, the identified phases of some of the plotted data points are not consistent with the tabulated data. Thus, only credible data points which show the same phase identification in both table and diagram took into consideration for the current optimization. The calculated phase diagrams are depicted in Figure 30 along with the experimental data. All experimental data in wide composition range are well reproduced within experimental error limits.

4.12 High-order (>3) systems

The present thermodynamic database containing all model parameters of unary, binary, and ternary systems can be used to predict the phase diagrams and thermodynamic properties in high-order (>3) systems. Two quaternary systems: the ZrO₂-CaO-MgO-SiO₂ and ZrO₂-CaO-MgO-Al₂O₃ systems have available experimental data to validate the prediction of present database.

4.12.1 ZrO₂-CaO-MgO-SiO₂ system

Phase diagram of the ZrO₂-CaO-MgO-SiO₂ system was firstly suggested by Berezhnoi and Kordyuk [62Ber]. However, as their proposed solid-state compatibility relationships are rather different from later studies [74Aza, 78Sir], their experimental results are not considered in this work. Aza et al. [74Aza] extensively investigated the phase relationships of the quaternary system by means of classical quenching method with XRD, and EPMA phase analysis. They conducted

experiments up to 2623 K. Sircar et al. [78Sir] also reported experimental phase diagram of this quaternary system. However, experimental data could not be compared in this work, because it is very difficult to extract exact experimental data from their diagrams. The predicted phase diagrams are compared in Figure 31 with experimental data from Aza et al. [74Aza]. Except the isopleth of the Ca₂SiO₄-CaZrO₃-25.6 wt% MgO, the predicted phase diagrams are in good agreement with the experimental data. In case of the Ca₂SiO₄-CaZrO₃-25.6 wt% MgO section, the stability of Ca₂SiO₄ is predicted about 100 K higher than experimental results, which is originated from the modeling of the CaO-MgO-SiO₂ system. Overall the predictability of the present database is very high in the wide range of compositions.

4.12.2 ZrO₂-CaO-MgO-Al₂O₃ system

Liddle and Brett [85Lid] investigated the phase diagram of the MgAl₂O₃-CaZrO₃ isopleth using classical quenching method with EPMA and XRD phase analysis. This is the only phase diagram information available in this quaternary system. The predicted phase diagram of the MgAl₂O₃-CaZrO₃ isopleth is presented in Figure 32 along with the experimental data by Liddle and Brett [85Lid]. In general, the phase assemblage and liquidus are well predicted. In the MgAl₂O₄-rich region, experimental data indicates the existence of "L + MgAl₂O₄ + ZrO₂ solid solution", whereas the prediction only shows the "L + MgAl₂O₄". ZrO₂ solid solution might be the result of quenched crystal of ZrO₂ during the quenching of the sample.

Chapter 5. Summary and conclusion

As part of the thermodynamic database development of the ZrO₂-CaO-MgO-Al₂O₃-SiO₂ system, the thermodynamic properties and phase equilibria of the ZrO₂, ZrO₂-CaO, ZrO₂-MgO, ZrO₂-SiO₂, ZrO₂-Al₂O₃, ZrO₂-CaO-MgO, ZrO₂-CaO-SiO₂, ZrO₂-CaO-Al₂O₃, ZrO₂-MgO-SiO₂, ZrO₂-MgO, ZrO₂-CaO-SiO₂, ZrO₂-CaO-Al₂O₃, ZrO₂-Al₂O₃, ZrO₂-Al₂O₃-SiO₂ systems were optimized in this study. Based on all available experimental data, the thermodynamic property of solid and liquid ZrO₂ were newly optimized. The Gibbs energy of liquid solution was described using the Modified Quasichemical Model, and the ZrO₂ solutions of cubic, tetragonal, and monoclinic structure were described using the random mixing model considering the defect structure of ZrO₂ solution. The Gibbs energies of the liquid and solid solutions were properly predicted in ternary and high-order systems using geometric interpolation model with no ternary parameters in ZrO₂ solid solutions; very few ternary parameters in liquid solutions. The prediction of phase diagrams in quaternary systems prove the high accuracy of the present database. The prepared database containing all optimized model parameters can be used for the calculations of phase diagrams and thermodynamic properties.

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	Initial composition (wt. fr.)			Time	Phase	Phase composition (wt. fr.)					
	ZrO ₂	CaO	SiO ₂	Al ₂ O ₃	hours		ZrO ₂	CaO	SiO ₂	Al ₂ O ₃	
						L	0.190 ± 0.003	0.215 ± 0.001	0.595 ± 0.002		
S 1	0.200	0.103	0.698		72	S	0.002	0.001	0.997		
						ZS	0.671 ± 0.007	0.001	0.328 ± 0.001		
						L	0.221 ±0.002	0.250 ± 0.001	0.529 ± 0.002		
S2	0.450	0.151	0.400		72	Ζ	0.998 ± 0.002	0.001	0		
						ZS	0.670 ± 0.005	0	0.330 ± 0.001		
62					20	L	0.204 ± 0.003	0.329 ± 0.003	0.467 ± 0.002		
83	0.301	0.300	0.399		20	Ζ	0.997 ± 0.004	0.003	0.001		
S 4					70	L	0.184 ± 0.01	0.393 ± 0.005	0 422 +0.02		
54	0.300	0.338	0.362	/	12	Ζ	0.996 ± 0.005	0.003	0.423 ± 0.02		
						Ζ	0.902 ± 0.007	0.097 ± 0.002	0.001		
S5	0.200	0.103	0.698		72	C_2S	0.021 ± 0.001	0.631 ± 0.003	0.348 ± 0.001		
						C_3ZS_2	0.296 ± 0.002	0.418 ± 0.002	0.287 ± 0.001		
						L	0.115 ± 0.004	0.510 ± 0.005	0.375 ± 0.004		
S6	0.130	0.520	0.350		336	C_2S	0.022 ± 0.001	0.637 ± 0.002	0.341 ± 0.003		
							C_3ZS_2	0.417 ± 0.001	0.291 ± 0.002	0.292 ± 0.001	

Table1. Experimental results of the ZrO₂-Al₂O₃, ZrO₂-CaO-SiO₂ systems

\$7	0.2	0.8	226	Ζ	0.998 ±0.005	0.002
57	0.2	0.8	550	А	0 ± 0.005	1

	10010 =1 1101		
Phase	Temperature (K)	Technique	Reference
$\alpha \rightarrow \beta$	1478	DC	Coughlin and King [50Cou]
	1328	HTXRD	Wolten [63Wol]
	1420	DC	Kirillin et al. [66Kir]
	1433	DTA	Ruh et al. [68Ruh]
	1273	HTXRD	Aldebert et al. [75Ald]
	1429	DTA	Ruh et al. [77Ruh]
	1423	DC	Chekhovskoi et al. [79Che]
	1425	DTA	Ruh et al[84Ruh]
	1452	DIL	Adams et al. [85Ada]
	1343	RS	Perry et al. [85Per]
	1473	DTA	Bannister and Barnes [86Ban]
	1423	DTA	87Shevchenko et al [87She]
	1473	DTA	Duran et al. [90Dur]
	1450	HTND	Frey et al. [90Fre]
	1446	DTA	Andrievsakaya et al. [95And]
	1477	DSC	Yashima et al. [95Yas]
	1469	DIL	Kasper and Troyanchuk[97Kas]
	1454	DIL	Hayakawa et al. [99Hay]
	1438	DTA	Jerebtsov et al. [01Jer]
	1380	ND	Sim et al. [03Sim]
	1460	DSC, DC	Moriya and Navrotsky[06Mor]
	1480	Optimized	Pelton et al. [91Pel]
	1472	Optimized	This work
$\beta \rightarrow \gamma$	2558	HTXRD	Smith and Cline [62Smi]
	2553	HTXRD	Wolten [63Wol]
	2584	DTA	Navrotsky et al. [05Nav]
	2633	Optimized	Pelton et al. [91Pel]
	2584	Optimized	This work
$\gamma \rightarrow L$	2960	CFM	Henning [25Hen]
	2950	CFM	Clausing [32Cla]
	2995	SR	Noguchi et al. [66Nog]
	2953	TA	Latta et al. [70Lat]
	2950	Optimized	Pelton et al. [91Pel]
	2950	Optimized	This work

Table 2. Transition temperatures of pure ZrO₂

CFM: cone fusion method, DC: drop calorimetry, DSC: differential scanning calorimetry, DTA: differential thermal analysis, DIL: dilatometry, HTND: high temperature neutron diffraction HTXRD: high-temperature X-ray diffraction, RS: Raman spectroscopy, SR: specular reflection, TA: thermal analysis.

				02	
D1	ΔH°_{f}	ΔH°_{fus}	ΔH°_{tr}	T1	Deferreres
Phase	(KJ - IIIOI at 298.13K)	$(solid \rightarrow iquid)$	(1 1 1-1)	Technique	Reference
	Elements as reference	(KJ·mol ⁻¹)	(kJ·mol ⁺)		
α	-1071.5			CC	Sieverts and Gotta [30Sie]
	-1079.4			CC	Neuman et al. [34Neu]
	-1082.8			CC	Roth et al. [38Rot]
	-1094.1			CC	Humphrey [53Hum]
	-1100.8			CC	Huber et al. [64Hub]
	-1100.6			CC	Kornilov et al. [67Kor]
	-1097.4			Optimized	Pelton et al. [91Pel]
	-1100.8			Optimized	This work
$\alpha \rightarrow \beta$			5.941 at 1478 K	DC	Coughlin and King [50Cou]
			5.272 at 1473 K	DC	Tsagareishvili et al. [65Tsa]
			7.718 at 1420 K	DC	Kirillin et al. [66Kir]
			8.297 at 1423 K	DC	Chekhovskoi et al. [79Che]
			5.870 at 1400 K	DSC	Yashima et al. [95Yas]
			5.175 at 1483 K	DTA	Jerebtsov et al. [01Jer]
			4.362 at 1286 K	DSC	Suresh et al. [03Sur]
			5.430 at 1472 K	DSC, DC	Moriya and Navrotsky [06Mor]
			5.953 at 1480 K	Optimized	Pelton et al. [91Pel]
			5.430 at 1472 K	Optimized	This work
$\beta \rightarrow \gamma$			3.4 ± 2.1 at 2584 K	DTA	Navrotsky et al. [05Nav]
			10.585 at 2633 K	Optimized	Pelton et al. [91Pel]
			6.000 at 2584 K	Optimized	This work
$\gamma \rightarrow L$		87.864 at 2950 K		Compilation	Bur. Stand. Cir. 500
•		87.047 at 2950 K		Optimized	Pelton et al. [91Pel]
		87.047 at 2950 K		Optimized	This work

Table 3. Enthalpies of pure ZrO₂

CC: combustion calorimetry, DC: drop calorimetry, DSC: differential scanning calorimetry, DTA: differential thermal analysis

Table 4. Entropies of pure ZrO ₂								
Phase	$S^{\circ}_{298.15}$ (J·mol ⁻¹ ·K ⁻¹)	$\frac{\Delta S^{\circ}_{tr}}{(J \cdot \text{mol}^{-1} \cdot \text{K}^{-1})}$	Technique	Reference				
α	50.330		AC	Kelly [44Kel]				
	49.790		AC	Tojo et al. [99Toj]				
	50.359		Optimized	Pelton et al. [91Pel]				
	49.790		Optimized	This work				
$\alpha \rightarrow \beta$		4.000 at 1487 K	DC	Coughlin and King [50Cou]				
		3.560 at 1475 K	DC	Tsagareishvili et al. [65Tsa]				
		5.840 at 1423 K	DC	Chekhovskoi et al. [79Che]				
		4.070 at 1400 K	DSC	Yashima et al. [95Yas]				
		3.690 ±0.21 at 1472 K	DSC, DC	Moriya and Navrotsky[06Mor]				
		4.021 at 1480 K	Optimized	Pelton et al. [91Pel]				
		3.689 at 1472 K	Optimized	This work				
$\beta \rightarrow \gamma$		1.300 ±0.8 at 2584 K	DTA	Navrotsky et al. [05Nav]				
		4.020 at 2633 K	Optimized	Pelton et al. [91Pel]				
		2.322 at 2950 K	Optimized	This work				
AC: adi	AC: adjubatic calorimetry, DC: drop calorimetry, DSC: differential scanning calorimetry, DTA:							

AC: adiabatic calorimetry, DC: drop calorimetry, DSC: differential scanning calorimetry, DTA: differential thermal analysis.

Type of invariant reaction	Temperature (K)	Composition (mol fr. CaO)	Technique	Reference
$L \rightarrow Css + CaZrO_3$	2573	0.41	QM, XRD	Duwez et al. [52Duw]
-	2533	0.41	HTXRD	Noguchi et al. [67Nog]
	2568	0.41	QM, XRD	Tsagareishvili et al. [69Tra]
	2523	0.4	QM, XRD	Stubican and Ray [77Stu]
	2547	0.371	Optimized	Pelton et al. [91Pel]
	2531	0.382	Optimized	This work
$L \rightarrow Lss + CaZrO_3$	2533	0.69	QM, XRD	Ruff et al. [29Ruf]
	2403	0.7	HTXRD	Noguchi et al. [67Nog]
	2423	0.68	OM. XRD	Tsagareishvili et al. [69Tra]
	2413	0.663	Optimized	Pelton et al. [91Pel]
	2426	0.675	Optimized	This work
$Css \rightarrow Tss + CaZr_4O_9$	1123	0.150	QM, XRD	Stubican and Ray [77Stu]
	1353	0.175	QM, XRD	Duran et al. [87Dur]
	1686	0.162	QM, XRD	Yin and Argent [93Yin]
	1258	0.191	Optimized	Pelton et al. [91Pel]
	1339	0.168	Optimized	This work
$Tss \longrightarrow Mss + Ca_6Zr_{19}O_{44}$	1321	0.07	QM, XRD	Duran et al. [87Dur]
• • • •	1357	0.043	Optimized	Pelton et al. [91Pel]
	1310	0.063	Optimized	This work
$Css + CaZrO_3 \\ \rightarrow CaZr_4O_9$	1530	0.2	Optimized	This work
$Css + CaZr_4O_9 \\ \rightarrow Ca_6Zr_{19}O_{44}$	1622	0.24	Optimized	This work

Table 5. Invariant reaction points of the ZrO₂-CaO system

HTXRD: High temperature X-ray diffraction, QM: quenching method, XRD: X-ray diffraction. Css, Tss, Mss and Lss stand for cubic (γ), tetragonal (β), monoclinic (α) ZrO₂ solid solution and lime (CaO) solid solution respectively.

Phase	Crystal structure	Space group	Technique	Reference
o-CaZrO ₃	Orthorhombic		HTXRD	Hannon [85Han]
c-CaZrO ₃	Cubic		QM, XRD	Tsagareishvili et al. [69Tra]
	Cubic		QM, XRD	Hannon [85Han]
	Cubic		QM, XRD	Andrievskaya et al. [89And]
CaZr ₄ O ₉	Monoclinic		QM, XRD	Stubican and Ray [77Stu]
	Monoclinic	C2/c	QM, XRD, TEM	Hellmann and Stubican [82Hel]
	Monoclinic		QM, XRD	Duran et al. [87Dur]
$Ca_6Zr_{19}O_{44}$	Rhombohedral	R3C	QM, XRD, TEM	Hellmann and Stubican [82Hel]
	Rhombohedral		QM, XRD	Duran et al. [87Dur]
TITLE D D TT 1		<u>.</u>	0.17	

Table 6. Structural data of the compounds present in the ZrO₂-CaO system

HTXRD: High temperature x-ray diffraction, QM: quenching method, TEM: transmission electron microscopy, XRD: X-ray diffraction.

Table 7. Lattice stabilities							
Compound (phase)	⊿H298	S_{298}	C_p				
	$(kJ \cdot mol^{-1})$	$(J \cdot mol^{-1} \cdot K^{-1})$					
ZrO ₂ (m) (298-1472 K)	-1100.7999	49.79	$68.416 + 9.8(10^{-3})T - 1.3452(10^{6})T^{-2} + -1.0882(10^{-6})T^{2}$				
ZrO ₂ (t) (1472-2584 K)	-1095.3699	53.478	$68.416 + 9.8(10^{-3})T - 1.3452(10^{6})T^{-2} + -1.0882(10^{-6})T^{2}$				
ZrO ₂ (c) (2584-2950 K)	-1089.3699	55.800	$68.416 + 9.8(10^{-3})T - 1.3452(10^{6})T^{-2} + -1.0882(10^{-6})T^{2}$				
ZrO ₂ (1) (2950-3500 K)	-1025.0477	54.546	87.864				
CaZrO ₃ (o) (298-2023 K)	-1766.4325	100.08	$115.43 + 1.488(10^{-3})T - 1.812(10^{6})T^{-2} - 1.135(10^{-6})T^{2}$				
CaZrO ₃ (c) (2023-2623 K)	-1766.4275	100.08	$115.43 + 1.488(10^{-3})T - 1.812(10^{6})T^{-2} - 1.135(10^{-6})T^{2}$				
CaZr ₄ O ₉ (r) (1316-1529 K)	-5036.7897	273.84	$C_p(\text{CaO}) + 4C_p(\text{ZrO}_2(\text{m}))$				
Ca ₆ Zr ₁₂ O ₄₄ (m) (1310-1622 K)	-24772.858	1350.3	$6C_p(\text{CaO}) + 12C_p(\text{ZrO}_2(\text{m}))$				
Ca ₂ ZrSi ₄ O ₁₂ (s) (298-1789 K)	-6225.7503	290.140	$2C_p(\text{CaO}) + C_p(\text{ZrSiO}_4) + 3C_p(\text{SiO}_2(q))$				
Ca ₃ ZrSi ₂ O ₉ (s) (298-1879 K)	-5072.5045	254.08	$3C_p(\text{CaO}) + C_p(\text{ZrO}_2(\text{m})) + 2C_p(\text{SiO}_2(\text{q}))$				
Ca ₁₃ Al ₁₂ Zr ₂ O ₃₅ (s) (298-1813 K)	-21035.169	895.24	$13C_p(CaO) + 6C_p(Al_2O_3(c)) + 2C_p(ZrO_2(m))$				
$Mg_{39}Al_{22}Z_{14}O_{100}(s)$	-56905.715	2800.1	$39C_p(MgO) + 11C_p(Al_2O_3(c)) + 14C_p(ZrO_2(m))$				
ZrSiO ₄ (t) (298-1400 K)	-2032.740	84.1	257.680 -0.02555587T-2680.884 T ^(-1/2) 1.0044(10 ⁸)T ⁻³				
(1400-1811 K)			150.624				

		Calculation	Measurement			
	Tomporatura		Jacob and	Tanabe and	Rog and	
Reference	(K)	This work	Waseda	Nagata	Potoczek-Dudek	
	(K)		[94Jac]	[96Tan]	[01Rog]	
	973	-42390	-44695	-	-	
	1023	-42946	-45504	-	-	
7	1073	-43496	-46055	-	-44981	
$ZrO_2(m)$,	1123	-44043	-46864	-	-45541	
CaO	1173	-44586	-47397	-	-45927	
	1223	-45125	-48334	-	-46969	
	1273	-45662	-	-	-47663	
$7\pi0$ (a)	1673	-51270	-	-54610	-	
$Z_{1}O_{2}(c),$	1773	-51722	-	-56380	-	
CaU	1873	-52013	-	-58130	-	

Table 8. Gibbs energy of formation (J·mol⁻¹) of CaZrO₃ from compounds (CaO and ZrO₂)

Where $ZrO_2(m)$ and $ZrO_2(c)$ stand for monoclinic and cubic ZrO_2 each
Tuble 9. Would parameters of solid Solidions (5 mor)						
Structure	System	$\Delta G^{o}{}_{MO}$	ΔG^{o}_{ZrO2}	Δg^{11}		
Cubic	ZrO ₂ -CaO	$1.673 \cdot 10^4$		-7.322·10 ⁴ +8.1588T		
	ZrO ₂ -MgO	$3.7656 \cdot 10^4$		3765.6-9.6232T		
	ZrO ₂ -	$1.6736 \cdot 10^5$				
	Al ₂ O ₃					
Tetragonal	ZrO ₂ -CaO	$1.925 \cdot 10^4$		-3.765·10 ⁴ -1.6736T		
	ZrO ₂ -MgO	$4.01664 \cdot 10^4$		27196		
	ZrO ₂ -	$1.6736 \cdot 10^5$				
	Al ₂ O ₃					
Monoclinic	ZrO ₂ -CaO	$2.301 \cdot 10^4$		$-2.9288 \cdot 10^4$		
Monoxide(lime and	ZrO ₂ -CaO		$8.368 \cdot 10^4$	$-8.368 \cdot 10^4$		
Periclaise)	ZrO ₂ -MgO		$8.368 \cdot 10^4$			

Table 9. Model Darameters of solid solutions (J'mor	Table 9. Model	parameters of solid solutions	(J∙mol⁻¹)
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 $\Delta g^{ex} = \sum_{ij} \Delta g^{ij} X^{i}_{ZrO_2} X^{j}_{MO}, G^{o}_{MO} \text{ of } ZrO_2 \text{ structure} = G^{o}_{MO} + \Delta G^{o}_{MO}, G^{o}_{ZrO_2} \text{ of MO structure} = G^{o}_{ZrO_2} + \Delta G^{o}_{ZrO_2}$

Table 10. Model parameters of liquid solutions (J·mol ⁻¹)					
System	Δg^{ex}				
ZrO ₂ -CaO	$\Delta g_{ZrCa}^{00} = -57739.2, \Delta g_{ZrCa}^{10} = -46024, \Delta g_{ZrCa}^{01} = 16736$				
ZrO ₂ -MgO	$\Delta g^{00}_{ZrMg} = -15899.2$, $\Delta g^{10}_{ZrMg} = -29288$				
ZrO ₂ -SiO ₂	$\Delta g^{00}_{ZrSi} = 27196, \Delta g^{01}_{ZrSi} = -25187.68,$				
	$\Delta g_{ZrSi}^{04} = 17991.2, \Delta g_{ZrSi}^{10} = -12133.6$				
ZrO ₂ -Al ₂ O ₃	$\Delta g_{ZrAl}^{00} = 6276, \Delta g_{ZrAl}^{10} = -14644$				
ZrO ₂ -CaO-MgO	$\Delta g^{101}_{(ZrCa)Mg} = -50208, \Delta g^{001}_{(ZrCa)Mg} = -16736$				
ZrO ₂ -CaO-SiO ₂	$\Delta g^{101}_{(CaZr)Si} = -690360, \Delta g^{001}_{(CaSi)Zr} = 543920,$				
ZrO ₂ -CaO-Al ₂ O ₃	$\Delta g^{011}_{(ZrSi)Ca} = -1129680, \Delta g^{011}_{(CaSi)Zr} = -1966480$				
ZrO ₂ -MgO-SiO ₂	No ternary parameter				
ZrO ₂ -MgO-Al ₂ O ₃	$\Delta g^{001}_{(MgZr)Al} = -41840, \Delta g^{011}_{(MgAl)Zr} = -62760$				
ZrO ₂ -Al ₂ O ₃ -SiO ₂	$\Delta g_{(SiAl)Zr}^{002} = -8363, \Delta g_{(SiAl)Zr}^{001} = -9204.8$				
	$\Delta g_{(AlSi)Zr}^{011} = -56484$				

Table 10. Model parameters of liquid solutions (J·mol⁻¹)

Table 11. Invariant reactions of the ZrO ₂ -MgO system							
Type of	Technique	Temperature	Composition	Reference			
invariant		(K)	(mol fr.)				
reaction							
$L \rightarrow Css + Pss$	XRD	2423	0.5	Ebert and Cohn [33Ebe]			
	XRD	2386	0.55	Noguchi and Mizuno [68Nog]			
	HTXRD	2373	0.5	Sim and Stubican [87Sim]			
$Css \rightarrow Tss +$	Dilatometry	1663	0.165	Cocco and Schromek [61Coc]			
Pss	XRD	1723	0.14	Hinz and Dietzel [62Hin]			
	XRD	1674	0.25	Viechnicki and Stubican [65Vie]			
	XRD	1673	0.137	Colligan [70Col]			
	XRD	1674	0.126	Scott [81Sco]			
	HTXRD	1678	0.131	Sim and Stubican [87Sim]			
	XRD	1673	0.135	Yin and Argent [93Yin]			
	Optimization	1675	0.13	Pelton et al. [91Pel]			
	Optimization	1684	0.131	This work			
$Tss \longrightarrow ZrO_2 +$	Optimization	1459	0.004	This work			
Pss	-						

`able	11.	Invariant	reactions	of the	ZrO ₂ -MgO	svstem
			1	01 11		0,0000000

HTXRD: High temperature x-ray diffraction, XRD: X-ray diffraction

Type of invariant	Technique	Temperature	Composition	Reference
reaction		(K)	(mol fr.)	
$SiO_2 + ZrO_2(t) \rightarrow$	XRD	1723	0.5	Barlett [31Bar]
ZrSiO ₄	TE	1223	0.5	Heindle [33Hei]
	XRD	2050	0.5	Geller and Yavorsky
	XRD	1811	0.5	[45Gel]
	XRD	1993	0.5	Curtis and Sowman
	XRD	1949	0.5	[53Cur]
	XRD, CA	1823	0.5	Cocco and Shromek
	XRD, DTA	1949	0.5	[57Coc]
	HTXRD	1946	0.5	Butterman and Foster
	Optimized	1948	0.5	[67But]
$L \rightarrow ZrO_2(t) + SiO_2$	Optimized	1962	0.99	Anseau et al. [76Ans]
$L_1 \rightarrow L_2 + ZrO_2(t)$	Optimized	2523	0.56	Kamaev et al. [05 ^a Kam]
$L_2 \rightarrow L_1 + ZrO_2(t)$	Optimized	2523	0.82	Kaiser et al. [08Kai]
Consolute reaction	Optimized	2711	0.7	This work
				This work

Table 12. Invariant reaction points of the ZrO₂-SiO₂ system

XRD: X-ray diffraction, CA: chemical analysis, TE: thermal expansion

Type of invariant	Technique	Temperature	Composition (wt fr.)		vt fr.)	Reference
reaction		(K)	ZrO ₂	Al_2O_3	SiO ₂	
$L \rightarrow Al_2O_3(crn) +$	XRD	2073	0.312	0.532	0.156	Budnikov and Litvakovskii[56Bud]
Tss + Mullite	XRD	1958	0.328	0.509	0.163	Cevales[75Cev]
	XRD, EPMA	1978	0.31	0.58	0.11	Greca et al.[92Gre]
	Optimized	2018	0.29	0.48	0.23	This work
$L \rightarrow CZ + SiO_2(crs)$	XRD, EPMA	1823	0.03	0.08	0.89	Qureshi and Brett [68°Qur]
+ Mullite	Optimized	1832	0.022	0.057	0.921	This work
L+Tss \rightarrow ZS +	XRD, EPMA	1918	0.09	0.17	0.74	Qureshi and Brett [68°Qur]
Mullite	Optimized	1876	0.048	0.107	0.845	This work
L+Tss \rightarrow ZS +	XRD, EPMA	1933	0.05	0.05	0.9	Qureshi and Brett [68°Qur]
SiO ₂ (crs)	Optimized	1943	0.011	0.004	0.985	This work

Table 13. Invariant reactions in the ZrO₂ -Al₂O₃-SiO₂ system

XRD: X-ray diffraction, EPMA: Electron Probe Micro Analysis, CZ and ZS stand for CaZrO₃ and ZrSiO₄ each



Figure 1. Schematic diagram of experimental setup with a DelTech® vertical tube furnace







Figure 2. Calculated (a) heat capacity and (b) heat content of pure zirconia along with experimental data.



Figure 3. Calculated phase diagram of the ZrO₂-CaO system along with experimental data.



(a)



Figure 4. Calculated (a) heat capacity and (b) heat content of CaZrO₃ along with experimental data.





(d)

Figure 5. Calculated activity of CaO at (a) 0.05 (b) 0.15 (c) 0.2 (d) 0.4 mol fr. CaO with experimental data from the literature; solid CaO as a reference.



Figure 6. Calculated phase diagram of the ZrO₂-MgO system along with experimental data from the literature.



Figure 7. Calculation of cubic solid solution enthalpy at 298 K with experimental data from the literature; ZrO₂ (monoclinic) and MgO (cubic) as references.



Figure 8. Calculated phase diagram of the ZrO₂-SiO₂ system along with experimental data from the literature.



(a)



Figure 9. Calculated (a) heat capacity, (b) heat content of zircon along with experimental data from the literature.



Figure 10. Calculated phase diagram of the ZrO₂-Al₂O₃ system along with experimental data from the literature.



Figure 11. Back scattered electron image of S7 by EPMA. White particles are found to be zirconia solid solution with $0.2 \text{ wt}\% \text{ Al}_2\text{O}_3$.





Figure 12. Calculated liquidus projection of the ZrO₂-CaO-MgO system by (a) weight fraction and (b) mole fraction.





Figure 13. Calculated isothermal sections of the ZrO₂-CaO-MgO ternary system at (a) 1573, (b) 1693, and (c) 1773 K with experimental data from the literature.



Figure 14. Calculated quasi-binary diagram of (a) the MgO·CaO-ZrO₂ and (b) the CaO·ZrO₂-MgO isoplethal section with experimental data from the literature.



Figure 15. Calculation of cubic solid solution enthalpy at 298 K with experimental data from the literature; ZrO₂ (monoclinic), CaO (cubic), and MgO (cubic) as references.





(b)

Figure 16. Calculated liquidus projection of the ZrO₂-CaO-SiO₂ system by (a) weight fraction and (b) mole fraction.





Figure 17. Calculated Gibbs energy of formation of (a) $Ca_2ZrSi_4O_{12}$ (b) $Ca_3ZrSi_2O_9$ with experimental data from the literature.



Figure 18. Isothermal calculation of the ZrO₂-CaO-SiO₂ system at 1873 K in comparison with the experimental data of this work.







(d)



(e)



(f)



(g)



(h)







(1)



Figure 19. Calculated quasi-binary diagram of (a) the CaSiO₃-ZrO₂, (b) 0.9CaSiO₃·0.1Ca₂SiO₄-ZrO₂, (c) 0.8CaSiO₃·0.2Ca₂SiO₄-ZrO₂, (d) 0.7CaSiO₃·0.3Ca₂SiO₄-ZrO₂, (e) 0.5CaSiO₃·0.5Ca₂SiO₄-ZrO₂, (f) 0.4CaSiO₃·0.6Ca₂SiO₄-ZrO₂, (g) 0.3CaSiO₃·0.7Ca₂SiO₄-ZrO₂, (h) 0.85CaSiO₃·0.15SiO₂-ZrO₂, (i) 0.7CaSiO₃·0.3SiO₂-ZrO₂, (j) 0.65CaSiO₃·0.35SiO₂-ZrO₂, (k) 0.53CaSiO₃·0.47SiO₂-ZrO₂, (l) 0.4CaSiO₃·0.6SiO₂-ZrO₂, (m) 0.1CaSiO₃·0.9SiO₂-ZrO₂, and (n) Ca₂SiO₄-CaZrO₃ isoplethal sections with experimental data from the literature.



(a)



Figure 20. Calculated liquidus projection of the ZrO₂-CaO-Al₂O₃ system by (a) weight fraction and (b) mole fraction.





Figure 21. Isothermal calculation of the ZrO₂-CaO-Al₂O₃ system at (a) 1653, (b) 1773, (c) 1873, and (d) 1973 K in comparison with experimental data in literature.



Figure 22. The CaAl₂O₄-CaZrO₃ isoplethal section calculation in the ZrO₂-CaO-Al₂O₃ system, in comparison with experimental data in literature.





Figure 23. Calculated liquidus projection of the ZrO₂-MgO-SiO₂ system by (a) weight fraction and (b) mole fraction.



Figure 24. Isothermal calculation of the ZrO₂-MgO-SiO₂ system at 1700 K in comparison with experimental data from the literature.





Figure 25. Calculated quasi-binary diagram of the (a) 5 wt %, (b) 10 wt %, (c) 15 wt %, and (d) 20 wt % ZrO₂ isoplethal sections in the ZrO₂-MgO-SiO₂ with experimental data from the literature.



(a)



Figure 26. Calculated liquidus projection of the ZrO₂-MgO-Al₂O₃ system by (a) weight fraction and (b) mole fraction.




(b)



(c)

Figure 27. Isothermal calculation of the ZrO₂-MgO-SiO₂ system at (a) 1523, (b) 1873, and (c) 2023 K in comparison with experimental data from the literature.



Figure 28. The ZrO₂-MgAl₂O₄ isoplethal section calculation in the ZrO₂-MgO-SiO₂ system in comparison with experimental data from the literature.



Figure 29. Calculated liquidus projection of the ZrO₂-Al₂O₃-SiO₂ system by (a) weight fraction and (b) mole fraction.



(a)



(b)



(c)





(e)



(f)



(h)



(j)



(k)





(n)

Figure 30. Calculated quasi-binary diagram of the (a) 0.4SiO₂·0.6Al₂O₃-ZrO₂, (b) $0.5 \text{SiO}_2 \cdot 0.5 \text{Al}_2 \text{O}_3 - \text{ZrO}_2$ $0.6SiO_2 \cdot 0.4Al_2O_3 - ZrO_2$, (c) (d) $0.7 \text{SiO}_2 \cdot 0.3 \text{Al}_2 \text{O}_3 \text{-} \text{ZrO}_2$ (e) $0.8 \text{SiO}_2 \cdot 0.2 \text{Al}_2 \text{O}_3 \text{-} \text{ZrO}_2$ (f) $0.9SiO_2 \cdot 0.1Al_2O_3 - ZrO_2$, (g) $0.95 \text{SiO}_2 \cdot 0.05 \text{Al}_2 \text{O}_3 \text{-} \text{ZrO}_2$ (h) 0.85ZrO₂·0.15SiO₂-0.85Al₂O₃·0.15SiO₂, 0.9ZrO₂·0.1SiO₂-0.9Al₂O₃·0.1SiO₂, (i) (j) 0.8ZrO₂·0.2SiO₂-0.8Al₂O₃·0.2SiO₂, (k) $0.6ZrO_2 \cdot 0.4Al_2O_3 - 0.6SiO_2 \cdot 0.4Al_2O_3$ (1) $0.5ZrO_2 \cdot 0.5Al_2O_3 - 0.5SiO_2 \cdot 0.5Al_2O_3$ (m) $0.45ZrO_2 \cdot 0.55Al_2O_3 - 0.45SiO_2 \cdot 0.55Al_2O_3$, and (n) 0.4ZrO₂ $\cdot 0.6$ Al₂O₃-0.4SiO₂ $\cdot 0.6$ Al₂O₃ isoplethal sections with experimental data from the literature.



(a)



(b)



(c)

Figure 31. Calculated quasi-binary diagram of the (a) 25.6 wt % MgO (b) MgO to CZ/C2S = 1.04 and (c) MgO to CZ/C2S = 5.67 isoplethal sections in the ZrO_2 -CaO-MgO-SiO₂ with experimental data from the literature.



Figure 32. Calculated quasi-binary diagram of the MgAl₂O₄-CaZrO₃ isoplethal section in the ZrO₂-CaO-MgO-Al₂O₃ system with experimental data from the literature.