Phase Relations in the ZrO₂-MgO-FeO_x System: Experimental Data and Assessment of Thermodynamic Parameters

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Submitted: 3 February 2021 / in revised form: 23 February 2021 / Accepted: 23 February 2021 / Published online: 2 April 2021
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Abstract Thermodynamic parameters were assessed for the MgO–FeO_x system and combined with already available descriptions of ZrO₂–FeO_x and ZrO₂–MgO systems to calculate preliminary phase diagrams for planning experimental investigations. Samples of selected compositions were heat treated at 1523, 1673 and 1873 K and characterized using x-ray and scanning electron microscopy combined with energy dispersive x-ray spectroscopy (SEM/EDX). Experiments indicated extension of cubic ZrO₂ solid solution into the ternary system at 1873 K (75 mol.% ZrO₂, 10 mol.% FeO_x and 15 mol.% MgO) and limited solubility of 4 mol.% ZrO₂ in spinel phase. Based on the obtained results thermodynamic parameters of C–ZrO₂ and spinel phase were optimized.

Keywords heat capacity · phase diagram · phase equilibria · thermodynamic database · ZrO₂-based system

1 Introduction

The composite materials find extensive industrial applications. An example of a high-tech innovative composite materials is the TRIP-Matrix-Composite (TMC), which is based on high-alloyed austenitic TRIP-steel and reinforcing ceramic particles of zirconia partially stabilized by MgO (Mg-PSZ).^[1] Under compressive loading,

metastable austenite of the steel matrix transforms into martensite increasing strength. Besides this, the ceramic particles of Mg-PSZ undergo a stress-induced transformation from tetragonal into monoclinic structure resulting in an additional increase of strength.^[2] The particular composite materials exhibit excellent mechanical properties such as ductility, plasticity, damage resistance and extraordinary high values of specific energy absorption in compression.^[3] Therefore, TMC have a wide range of possible technological applications especially in automotive production in the context of the weight reduction of automobile chassis contributing to an exhaust emissions decrease.

However, a development of such complex composite materials requires a wide range of investigations in the field of applied science, as well as fundamental materials science. Both components of TMC, namely the steel matrix and ceramic particles should be well studied separately first. Then, compatibility of components and possible interfacial reactions should be considered in order to estimate and to optimize their interactions within the composite material. Thereby, knowledge of phase equilibria and the underlying thermodynamics play a crucial role.

Thus, the development of TMC requires a multicomponent thermodynamic description, which would include all alloying elements of the matrix, as well as components of ceramics such as ZrO₂ and MgO as well as oxides appearing due to steel oxidation and impurities. Consequently, both types of materials had to be investigated, not only the steel matrix but also ceramic components. An extensive thermodynamic database for the steel including Fe, Mn, Cr, Ni, Ti, Mo, W, V, Si, C and N was developed by Franke and Seifert using the CALPHAD method.^[4] In order to be able to simulate interfacial reactions of ceramic particles with the steel matrix, a ceramic database had to be

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implemented into the database for the steel-based materials. Thereby, it was necessary to include zirconium, magnesium and oxygen into the available thermodynamic description. First of all, the Fe-Mg-Zr-O system is of major interest because it links the metal systems to the ceramics. Experimental data for the oxide part of the system are not available so far. Therefore, the aim of this work is experimental study and thermodynamic modelling of the ZrO₂-MgO-FeO_x system. Merging thermodynamic description of oxide system with Fe-Mg-Zr system based on binary extrapolation will make it possible to calculate reactions at the ceramic—steel interface.

2 Literature Survey for the Fe-Mg-Zr-O System

Thermodynamic modelling of the Fe-Mg-Zr-O system is essential for the understanding of possible interfacial reactions between steel and ceramic materials. As mentioned above, the Fe-Mg-Zr-O system is a key sub-system for the development of the TRIP-Matrix-Composite.

Thermodynamic descriptions of all binary sub-systems of the Fe-Mg-Zr-O system are available.^[5–10] Based on the available critical evaluation for the ternary Fe-Mg-Zr sub-system, an extrapolation from binaries would give reliable results due to the absence of ternary phases and significant ternary interactions.^[11]

According to available literature, the Fe-Mg-O system is well studied. There are many experimental data on phase relations, as well as on thermodynamic properties. A proper critical evaluation of all available experimental data and thermodynamic modelling of the Fe-Mg-O system have been presented by Jung et al.^[12] However, the authors have accepted thermodynamic models (quasi-chemical model for liquid and associate model for magnesio-wustite phase) which are incompatible with the thermodynamic description of the current work. The last thermodynamic description of the Fe-Mg-O system has been presented by Dilner et al.^[13] Thermodynamic models of phases used in Ref^[13] are the same as in the present work, but several parameters are different from the accepted parameters for the spinel phase assessed by Zienert and Fabrichnaya.^[14] Therefore, thermodynamic parameters of the Fe-Mg-O system need to be re-assessed in order to obtain a self-consistent thermodynamic description.

Data on the phase relations in the Mg-Zr-O system were limited by binary systems and quasi-binary system ZrO₂-MgO. Concerning oxide sub-systems of the ternary Mg-Zr-O system, a detailed review of available experimental data and first thermodynamic modelling of the MgO-ZrO₂ system was performed by Du and Jin.^[15] Later on, an optimization of the MgO-ZrO₂ system was done by Yin and Argent^[16] using their own data obtained using solution

calorimetry for enthalpies of formation of the cubic ZrO₂ based solid solutions with different content of MgO. Critical evaluation of the MgO-ZrO₂ system was made by Serena et al.^[17] as a part of an assessment of the system CaO-MgO-ZrO₂. The last experimental investigation and thermodynamic modelling of the MgO-ZrO₂ system has been performed by Pavlyuchkov et al.,^[18] where the thermodynamic description was improved by using the compound energy formalism^[19] for modelling of ZrO₂ based solid solutions.

Experimental data for the Fe-Zr-O system were quite scarce due to difficulties in experimental studies of such systems.^[20] Since Fe can have several oxidation states, phase equilibria in this system depends on oxygen partial pressures and a requirement to control the partial pressure of oxygen during experiments becomes crucial for any experimental investigations of phase relations in this system. Substantial experimental difficulty is a possible reaction of samples with a crucible material.^[20] For the first time, a thermodynamic database of the Fe-Zr-O system was derived by Huang.^[21] The obtained thermodynamic description was based on binary descriptions only. Moreover, presented calculations of the oxide part of the system were not fitted to reproduce experimental data of available literature.^[22, 23] The first thermodynamic assessment of the ternary area of the Fe-Zr-O system was performed by Fabrichnaya and Pavlyuchkov^[24] to reproduce all available experimental data. However, this work^[24] was focused mostly on the oxide system of FeO-Fe₂O₃-ZrO₂. A preliminary description of Fe-Zr system^[25] was introduced to calculate interaction between T-ZrO₂ and metallic liquid.

The most recent systematic experimental study of binary Fe-Zr system was performed by Stein et al.^[26] In their work, Stein et al. succeeded in eliminating several contradictions and ambiguities. Regarding thermodynamic properties, detailed review of experimentally measured and calculated values is presented in work of Saenko et al.^[8] Lück and Wang^[27] performed the experimental measurements of the heat capacity for C15-ZrFe₂ phase in the range of temperatures between 313 K and 653 K. Thermodynamic properties for the intermetallic phases were experimentally measured and calculated using ab-initio methods in the work of Mukhamedov et al.^[28] The most recent thermodynamic assessment was performed by Saenko et al.^[8] The available thermodynamic data, as well as phase diagram data presented by Stein et al.^[26] were considered in the optimization and are well reproduced in calculations. Thus, the last thermodynamic description of Saenko et al.^[8] was implemented in the current optimization of the Fe-Zr-O system.

All stable phases in the Fe-Mg-Zr-O system and their crystal structures are listed in Table 1.

Table 1 Crystal structures and corresponding thermodynamic models of all stable phases in the Fe-Mg-Zr-O system

Phase	Crystal system	Space group	Sublattice model
Gas	...	...	(O2)
Ionic liquid	...	...	(Fe+2, Mg+2, Zr+4)1(O–2, Va, FeO3/2)1
BCC	Cubic	$Im\bar{3}m$	(Fe, Mg, Zr)1(O, Va)3
FCC	Cubic	$Fm\bar{3}m$	(Fe, Mg, Zr)1(O, Va)1
HCP	Hexagonal	P63/mmc	(Fe, Mg, Zr)1(O, Va)0.5
C15-Fe2Zr	Cubic	$Fd\bar{3}m$	(Fe, Zr)2(Zr, Fe)1
Hex.-Fe2Zr	Hexagonal	P63/mmc	(Fe)2(Zr, Fe)1
FeZr2	Tetragonal	I4/mcm	(Fe)1(Zr)2
FeZr3	Orthorhombic	Cmcm	(Fe)1(Zr)3
M–ZrO2	Monoclinic	P21/c	(Fe+2, Fe+3, Mg+2, Zr+4)1(O–2, Va)2
T–ZrO2	Tetragonal	P42/nmc	(Fe+2, Fe+3, Mg+2, Zr+4)1(O–2, Va)2
C–ZrO2	Cubic	$Fm\bar{3}m$	(Fe+2, Fe+3, Mg+2, Zr+4)1(O–2, Va)2
FeOx (Halite)	Cubic	$Fm\bar{3}m$	(Fe+2, Fe+3, Mg+2, Va)1(O–2)1
Fe3O4 (Spinel)	Cubic	$Fd\bar{3}m$	(Fe+2, Fe+3, Mg+2)1(Fe+2, Fe+3, Mg+2, Zr+4, Va)2(Fe+2, Mg+2, Va)2(O–2)4
Fe2O3 (Corundum)	Trigonal	$R\bar{3}c$	(Fe+3, Zr+4)2(O–2, Va)1(O–2)3

3 Experimental

3.1 Sample Preparation

For ceramic systems, the co-precipitation method was used for the sample preparation. Chemically pure salts of the desired elements have been used as the initial materials. The zirconium acetate solution in acetic acid $Zr(CH_3COO)_4$ (99.99%, Sigma-Aldrich), magnesium nitrate $Mg(NO_3)_2$ (99.97%, Alfa Aesar) and iron nitrate $Fe(NO_3)_3$ (99.97%, Alfa Aesar) have been used as initial reagents. In the first step, the starting chemicals were diluted and dissolved in distilled water in order to obtain more suitable concentrations for the co-precipitation process (solutions: 1.14 mol/l for the zirconium acetate solution, 0.494 mol/l for the magnesium nitrate, and 0.8 mol/l for iron nitrate). The concentration of the obtained initial solutions was measured by Inductively Coupled Plasma—Optical Emission Spectrometry (ICP-OES). Calculated volumes of the obtained solutions were mixed together in order to get around 2 grams of oxide powder of desired molar ratio. The obtained solution was dropped from a burette at low speed (around 1 ml per minute) into a beaker containing about 500 ml of the aqueous solution of NH_4OH with pH value above 9.0. After evaporation at 333 K during 1–2 h, the obtained substance was dried at 353 K for 2–3 days. Finally, a pyrolysis of the dried powder was performed at 1073 K for 3 h in the air atmosphere. The obtained oxide powder was pressed into cylindrical pellets at 250 MPa and sintered in air atmosphere in Pt crucibles

using a NABERTHERM furnace in order to reach equilibrium state. Annealing duration was chosen depending on sintering temperature.

3.2 Sample Characterisation

In the current investigation, XRD was applied using an URD63 diffractometer (Seifert, FPM, Freiberg, Germany) equipped with a graphite monochromator and $CuK\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The goniometer of the diffractometer was working in Bragg-Brentano geometry. The measured samples in powder form were placed on single crystalline silicon substrate with (510) orientation. In this case, the orientation of the substrate does not show any peak on the XRD pattern in the range of $15\text{--}110^\circ$ of 2θ . The Rietveld refinement was applied for the evaluation of all measured diffraction patterns in order to obtain the volume fractions of present phases as well as lattice parameters. The program Maud^[29] was applied.

SEM/EDX allows measuring the chemical composition of the microstructural features. For example, boundaries in phase diagrams, which are often deduced from results of characterization of sample series with different compositions after equilibration at fixed temperatures, can be plotted as composition versus a temperature. Afterwards, these results can be applied for modelling of homogeneity ranges of e.g. solid phases.

The microstructures of the samples were analysed using Scanning Electron Microscope—LEO 1530 Gemini (Zeiss, Germany). The microscope was equipped with a field emission cathode, used at the acceleration voltage of 20 kV

with working distance of 8–10.5 mm. An EDX detector (Bruker AXS Mikroanalysis GmbH) was used to verify chemical compositions of samples, to determine chemical composition of the present phases, which was also used for identification of phases, as well as to estimate composition of liquid in eutectic reactions. The uncertainty of EDX measurements is around 2–4 at.%. For most of samples SEM images were recorded using back scattered electrons (BSE), while secondary electrons were considered only for few samples in order to distinguish phases from pores. Samples were ground and polished to 1 μm .

For imaging in the SEM, samples must be electrically conductive, at least at their surface, and electrically grounded in order to prevent the accumulation of electrostatic charge at the surface at the interaction with the electron beam. Therefore, samples composed of oxides were coated with a graphite layer.

4 Thermodynamic Modelling

Temperature dependence of the Gibbs energy function of a stoichiometric phases or end members of solid solutions at a certain T referred to the enthalpy of its phase at room temperature 298 K are described in the form presented in Eq 1 (all temperatures in this article are given in Kelvin units, energy units are given in Joule per mole).

$$G(T) = \Delta_f H_{298}^0 + \int_{298}^T C_p dT - T \left(S_{298}^0 + \int_{298}^T (C_p/T) dT \right) \quad (\text{Eq 1})$$

where S_{298}^0 is the standard entropy, $\Delta_f H_{298}^0$ is the enthalpy of formation at r.t. and C_p is the heat capacity expressed as:

$$C_p = a + bT + cT^{-2} + dT^2 + eT^{-3} + \dots \quad (\text{Eq 2})$$

The magnetic contribution G_p^{mag} can be taken into account according to Inden–Hillert–Jarl^[30] formalism (Eq 3).

$$G_p^{\text{mag}} = RT \ln(\beta_0 + 1) g(\tau) \quad (\text{Eq 3})$$

where $\tau = T/T^*$, T^* is the critical temperature (the Curie temperature T_C for ferromagnetic materials or the Neel temperature T_N for antiferromagnetic materials), β_0 the average magnetic moment per atom and $g(\tau)$ is a function depending on τ .^[31]

The Gibbs energy $G_{A_a B_b}(T)$ of a stoichiometric phase $A_a B_b$ in case of absence of heat capacity data was modeled using Neumann-Kopp rule as:

$$G_{A_a B_b} = aGHSE_R_A + bGHSE_R_B + \alpha + \beta T \quad (\text{Eq 4})$$

where $GHSE_R_i$ is the Gibbs energy of the pure element i referred to the enthalpy of pure element i at 298 K in its

standard element reference (SER) state, α and β are parameters to be optimized representing enthalpy and minus entropy of formation of phase from components, respectively. Adopting Eq 4, the difference between heat capacity of the compound and a sum of heat capacities of components multiplied by their stoichiometric coefficients is assumed to be zero.

Solid solutions and compounds having a homogeneity range can have two or more different sites in the crystal structure (sublattices) which can be occupied by atoms or ions or more complex species. The composition dependence of the Gibbs energy of such phases can be described by the compound energy formalism developed by Hillert.^[19] In this case, each sublattice is associated with a specific atomic site in the crystal structure. The model of the phase with two sublattices can be presented by the formula $(A,B)_k(C,D)_m$, indicating that A and B species mixed on the first sublattice whereas C and D mixed on the second sublattice. Coefficients k and m are stoichiometric numbers for the first and second sublattice, respectively. The constitution of the phase is described by site fractions Y_i^S (i.e. fraction of the species i occupying each sublattice S). The case when each sublattice is fully occupied by one species corresponds to the end-member compound e.g. $A_k D_m$ or $B_k C_m$. It should be noted that the end-member compounds are related with each other by reciprocal reaction (Eq 5).

The Gibbs energy of solution described by the sublattice model with three sublattices is given by

$$\Delta G^{\text{mix}} = \sum_i \sum_j \sum_k Y_i^s Y_j^t Y_k^u G_{ijk} + RT \sum_s \alpha_s \sum_i Y_i^s \ln(Y_i^s) + \Delta G^{\text{Ex}} \quad (\text{Eq 6})$$

where Y_i^s is the mole fraction of constituent i on sublattice s , α_s is the number of sites on sublattice s per mole of formula unit of phase and ΔG^{Ex} is the excess Gibbs energy of mixing expressed as

$$\Delta G^{\text{Ex}} = \left(\sum_t y_j^t \right) \left(\sum_u y_k^u \right) \left(\sum_s y_i^s y_l^s L_{i,l}^s \right) + \left(\sum_s y_i^s \right) \left(\sum_t y_j^t \right) \left(\sum_u y_k^u y_m^u L_{k,m}^u \right) + \left(\sum_s y_i^s \right) \left(\sum_u y_k^u \right) \left(\sum_t y_j^t y_n^t L_{j,n}^t \right) \quad (\text{Eq 7})$$

$$L_{i,l}^s = \sum_n^n L_{i,l}(Y_i^s - Y_l^s)^n \quad (\text{Eq 8})$$

where $L_{i,l}^s$ are binary interaction parameters between species i and l on sublattice s and n is integer number. Higher-

order interaction parameters could also be included giving more complicated excess Gibbs energy terms.

A partially ionic liquid model^[19] was used to describe liquid in multicomponent systems which contains complex charged species. In this work, the liquid was described by two sublattices: the first one is occupied by cations and the second one containing anions, vacancies and neutral species (see Eq 9). The partially ionic liquid model makes it possible to have single liquid description for different kind of liquids namely, metallic liquid with the second sublattice mainly vacant, ionic liquid containing mainly anion species or polymeric liquid containing neutral species.

$$(C_i^{v_i+})_P(A_j^{v_j-}, Va, B_k^0)_Q \quad (\text{Eq 9})$$

where C_i are cations v_i , A_j are anions with correspondent charge v_j , Va is vacancy and B_k are neutral species with covalent character of bonding. The coefficients P and Q are the number of sites on the cation and anion sublattices, respectively, which can be varied with the composition of liquid in terms of electroneutrality.

$$P = \sum_j v_j y_{A_j} + Q y_{Va} \quad (\text{Eq 10})$$

$$Q = \sum_i v_i y_{C_i} \quad (\text{Eq 11})$$

5 Re-assessment of Ternary Systems

5.1 Fe-Zr-O System

The obtained thermodynamic description of the Fe-Zr system was combined with the database for the Fe-Zr-O system developed by Fabrichnaya and Pavlyuchkov^[24]. The thermodynamic model of the spinel phase in the Fe-Zr-O system has been modified based on crystallographic considerations.

In the work of Fabrichnaya and Pavlyuchkov,^[24] the solubility of ZrO₂ in the Fe₃O₄ magnetite phase (spinel structure) was described by the following formula $(\text{Fe}+2, \text{Fe}+3, \text{Zr}+4)\text{T}1(\text{Fe}+2, \text{Fe}+3, \text{Va})\text{O}2(\text{Fe}+2, \text{Va})\text{I}2(\text{O}-2)_4$, since there was no data indicating which of the crystallographic sites is occupied by Zr+4. However, based on crystallographic data for Mg₂TiO₄ and Fe₂TiO₄ it seems more reasonable that the large Zr+4 cation occupies the larger octahedral sites and, therefore, another formula should be used to describe magnetite i.e. $(\text{Fe}+2, \text{Fe}+3)\text{T}1(\text{Fe}+2, \text{Fe}+3, \text{Zr}+4, \text{Va})\text{O}2(\text{Fe}+2, \text{Va})\text{I}2(\text{O}-2)_4$. Therefore, four end-members containing Zr+4 should appear $\text{Fe}+2\text{Zr}+42\text{Va}2\text{O}-24$, $\text{Fe}+3\text{Zr}+42\text{Va}2\text{O}-24$, $\text{Fe}+2\text{Zr}+42\text{Fe}+22\text{O}-24$ and $\text{Fe}+3\text{Zr}+42\text{Fe}+22\text{O}-24$. The Gibbs energy for two end-members can be derived

using electro-neutrality conditions and the other two end-members using reciprocal reactions.

Figure 1 shows the first two end-members together with $\text{Fe}+2\text{Fe}+22\text{Va}2\text{O}-24$ and $\text{Fe}+3\text{Fe}+22\text{Va}2\text{O}-24$ as well as electro-neutrality lines. Correspondingly, electro-neutrality reactions can be written as following:

The Gibbs energy of inverse spinel Sp1 (with Fe+2) is considered as sum of oxides ZrO₂ and FeO plus some positive parameter to be optimized:

$$G(\text{Fe}2\text{ZrO}4) = G(\text{ZrO}2) + 2 \cdot G(\text{FeO}) + V1;$$

On the other hand, the Gibbs energy of inverse spinel Sp1 is presented as:

$$2 \cdot G(\text{Fe}2\text{ZrO}4) = G(\text{Fe}+2\text{Zr}2\text{Va}2\text{O}4) + G(\text{Fe}+2\text{Fe}+22\text{Va}2\text{O}4) - 4 \cdot RT \ln(2);$$

The Gibbs energy of inverse spinel Sp2 (with Fe+3) is considered as the sum of oxides ZrO₂, FeO and Fe₂O₃ plus some positive parameter to be optimized:

$$4 \cdot G\text{Fe}+3(\text{Zr}+40.25\text{Fe}+20.75)\text{O}4 = 2 \cdot G\text{ZrO}2 + 6 \cdot G\text{FeO} + 2 \cdot G\text{Fe}2\text{O}3 + V2$$

On the other hand, the Gibbs energy of inverse spinel 2 is expressed as:

$$4 \cdot G(\text{Fe}+3(\text{Zr}+40.25\text{Fe}+20.75)\text{O}4) = G(\text{Fe}+3\text{Zr}2\text{Va}2\text{O}4) + 3 \cdot G(\text{Fe}+3\text{Fe}+22\text{Va}2\text{O}4) + 8 \cdot RT(0.25 \cdot \ln(0.25) + 0.75 \cdot \ln(0.75));$$

The Gibbs energies for the remaining two end-members $\text{Fe}+2\text{Zr}+42\text{Fe}+22\text{O}4$ and $\text{Fe}+3\text{Zr}+42\text{Fe}+22\text{O}4$ are obtained using the following reciprocal reactions:

Fig. 1 Electro-neutrality lines of the magnetite phase

The introduced changes into the description have not caused any substantial changes of the calculated phase diagram of the system presented in the work of Fabrichnaya and Pavlyuchkov [24].

The vertical section of ZrO_2 – Fe_2O_3 of the Zr–Fe–O phase diagram calculated for air atmosphere and for $P(\text{O}_2) = 0.0021$ bar are presented in Fig. 2 together with experimental data [32–34]. The isothermal section of ZrO_2 – FeO – Fe_2O_3 system is shown in Fig. 3.

5.2 Fe–Mg–O System

Based on the available experimental results, a re-assessment of the Fe–Mg–O system has been performed in order to achieve the compatibility with the current thermodynamic database.

The magnesioferrite phase with spinel structure was modelled using the following formula $(\text{Fe} + 2\text{Fe} + 3\text{Mg} + 2)\text{Fe} + 2\text{Fe} + 3\text{Mg} + 2\text{Va})_2(\text{O} - 2)_4$. The Gibbs energy for the spinel end-members in the Fe–O system were accepted from the description of Kjellqvist et al. [35] based on the description of Sundman. [36] The Gibbs energies of $\text{Mg} + 2(\text{Mg} + 2)2\text{Va}_2\text{O} - 24$ end-member were accepted from the work of Zienert and Fabrichnaya. [14] The Gibbs energies of $\text{Mg} + 2(\text{Fe} + 3)2\text{Va}_2(\text{O} - 2)_4$ and $\text{Fe} + 3(\text{Mg} + 2)2\text{Va}_2\text{O}_4$ were optimized to reproduce experimental thermodynamic data for MgFe_2O_4 and the degree of inversion. The heat capacity is in a reasonable agreement with the data presented by Jung et al. [12], corresponding to

the experimental data of King [37] and the adjusted data of Reznitskii et al. [38]. The heat capacity data were quite scattered. The heat capacity calculated from heat content measurements of Bonnicksen [39] are incompatible with room temperature data of King. [37] Data on CP from Barin and Platzki [40] were lower at high temperature than calculated one from the measurements of Bonnicksen. [39] The

Fig. 3 Calculated isothermal section of ZrO_2 – FeO – Fe_2O_3 of the Zr–Fe–O phase diagram at 1473 K with calculated oxygen partial pressure conditions in three phase areas. According to experimental data from Ref [22], oxygen partial pressure in the two phase field of Hal+T–ZrO₂ is in a range of $\lg P(\text{O}_2)$ from -11.82 to -9.21 ; Sp+T–ZrO₂– $\lg P(\text{O}_2)$ from -9.09 to -3.36

Fig. 2 Calculated vertical section of ZrO_2 – Fe_2O_3 of the Zr–Fe–O phase diagram at: (a) air; (b) $P(\text{O}_2) = 0.0021$ bar together with experimental data [32–34]

standard entropy of MgFe_2O_4 was determined by King [37] to be equal to $118.47 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. However, later in the book of Barin and Platzki [40] a substantially higher value of $123.8 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ was presented. It should be mentioned, that the value of standard entropy depends on the degree of inversion preserved in the measured substance and this phenomenon can explain the difference between different data.

In the present work a lower value of the standard entropy equal to $98.6 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ was obtained as the result of the optimization procedure. It should be mentioned that the data on the enthalpy of formation of MgFe_2O_4 obtained by solution calorimetry present high uncertainty. The calculated value of the enthalpy of formation of $-19.293 \text{ kJ}\cdot\text{mol}^{-1}$ at room temperature reasonably agreed with value of Navrotsky [41] equal to $-20.64 \text{ kJ}\cdot\text{mol}^{-1}$ obtained at 973 K . It should be noted that value obtained using acid solution calorimetry by Koehler et al. [42] at 298 K was substantially higher $-2.52 \text{ kJ}\cdot\text{mol}^{-1}$. The temperature difference should not cause such a large difference in the enthalpy of formation from oxides. The main source of uncertainty is the enthalpy of dissolution of MgO . The latest data of Navrotsky for dissolution of MgFe_2O_4 [43] in combination with data of Majzlan et al. [44] for dissolution of Fe_2O_3 and data of Navrotsky [45] for dissolution of MgO resulted in $-2.22 \text{ kJ}\cdot\text{mol}^{-1}$ for the enthalpy of formation of MgFe_2O_4 at 973 K which is reproduced within the uncertainty range in the present work $-7.315 \text{ kJ}\cdot\text{mol}^{-1}$. To reproduce the degree of inversion, mixing parameters were introduced. The calculated degree of inversion along with experimental data [46–53] is presented in Fig. 4.

The experimental data on the Fe_2O_3 – MgO system at air pressure, the FeO – MgO system in presence of metallic iron, isothermal sections at varying partial pressures of oxygen, Fe^{+3} content in halite phase ($\text{Mg}+2, \text{Fe}+2, \text{Fe}+3, \text{Va})_1(\text{O}-2)_1$ and other available data were used to optimise parameters of spinel, halite and liquid phases. A reasonable agreement between calculated and experimental data was obtained. The calculated phase diagram of the Fe_2O_3 – MgO system at air oxygen partial pressure is shown together with experimental data [54–58] in Fig. 5. The calculated diagram for the FeO – MgO system in presence of metallic Fe is presented in Fig. 6 along with experimental data. [59–68]

Isothermal sections at temperatures 1433 , 1573 and 1673 K along with calculated isobars are compared with experimental data [69–73] in Fig. 7.

The calculated dependences of oxygen partial pressure on the metal ratio $\text{Mg}/(\text{Mg}+\text{Fe})$ at temperatures 1273 , 1473 , 1573 and 1773 K are presented in Fig. 8 along with experimental data. [55, 56, 70, 71, 74–82] It should be noted that there are substantial deviations from experimental data at

Fig. 4 Inversion degree in the MgFe_2O_4 spinel with experimental data obtained by x-ray diffraction (XRD), Mossbauer and saturation magnetization (SM) measurements [46–53]

Fig. 5 Calculated phase diagram of the Fe_2O_3 – MgO system in air corresponding to $P(\text{O}_2)=0.21 \text{ bar}$ in comparison with experimental data [54–58]

1273 K for spinel composition in equilibrium $\text{Sp}+\text{Hal}$ and $\text{Sp}+\text{Fe}_2\text{O}_3$. Experimental data for spinel composition in equilibrium with halite are quite consistent in several experimental studies. [74, 75, 77, 78] However, with the selected binary descriptions and thermodynamic model for spinel and halite it was not possible to get better fit without serious deterioration of the fit to other experimental data. It should be noted that the experimental data at 1273 K were reproduced better in Ref. [12] where the associate model was

Fig. 6 Calculated phase diagram of the FeO-MgO system in equilibrium in the presence of metallic Fe^[59–68]

used for halite. As it can be seen from Fig. 8b and c the experimental results at 1473 and 1573 K are very well reproduced. Experimental data at 1773 K are very limited to evaluate their reliability.

6 Preliminary Calculations in the Fe-Mg-Zr-O System

The thermodynamic description of the Mg-Zr-O system based on the work of Pavlyuchkov et al.,^[18] as well as obtained thermodynamic descriptions for the Fe-Zr-O and Fe-Mg-O systems have been combined with the available binary systems^[5–10] in order to establish a thermodynamic database for the Fe-Mg-Zr-O system. The thermodynamic descriptions for Fe-O, Mg-O and Zr-O systems were accepted from the works of Kjellqvist et al.,^[6] Hallstedt^[10] and unpublished description of Wang,^[7] respectively. According to recommendations of SGTE, the Mg-Zr system was accepted from the work of Hämäläinen and Zeng.^[9] The Fe-Mg system was taken from Tibballs,^[5] Fe-Zr system from Saenko et al.^[8] The Fe-Mg-Zr ternary system was accepted as an extrapolation from the binaries.

The introduction of the ZrO₂ solubility in the spinel phase for the FeOx-MgO-ZrO₂ sub-system requires the definition of the Gibbs energies of four end-members: $\text{Mg}+2(\text{Zr}+4)\text{Va}2(\text{O}-2)_4$, $\text{Mg}+2(\text{Zr}+4)\text{Mg}+2(\text{O}-2)_4$, $\text{Mg}+2(\text{Zr}+4)\text{Fe}+2(\text{O}-2)_4$ and $\text{Fe}+2(\text{Zr}+4)\text{Mg}+2(\text{O}-2)_4$.

The Gibbs energy of the Mg₂ZrO₄ metastable compound (inverse spinel Mg(Mg_{0.5}Zr_{0.5})₂Va₂O₄) was estimated to be $G(\text{Mg}_2\text{ZrO}_4)=2 \cdot G(\text{MgO})+G(\text{ZrO}_2)+100000$.

Fig. 7 Calculated phase diagram section of the FeO-Fe₂O₃-MgO system along with calculated isobars at (a) 1433, (b) 1573 and (c) 1673 K with experimental data on oxygen partial pressure in lg(P(O₂)) in bar units [69–73]

(a)

(b)

(c)

(d)

The Gibbs energy of end-member $\text{Mg}+2(\text{Zr}+4)\text{ZrO}_2$ was derived using electro-neutrality condition:

Fig. 8 Calculated phase diagrams of the Fe–Mg–O system in dependence of oxygen partial pressure on metal ratio Mg/(Mg+Fe) at temperatures (a) 1273, (b) 1473, (c) 1573 and (d) 1773 K with experimental data [55, 56, 70, 71, 74–82]

$$0.5 \cdot G(\text{Mg} + 2\text{Zr} + 42\text{VaO} - 24) + 0.5 \cdot G(\text{Mg} + 2\text{Mg} + 22\text{VaO} - 24) - 2 \cdot RT \ln(2) = G(\text{Mg}2\text{ZrO}_4)$$

The Gibbs energies of other three end-members were obtained using reciprocal reactions

$$G(\text{Mg} + 2\text{Mg} + 22\text{VaO} - 24) = G(\text{Mg} + 2\text{Zr} + 42\text{VaO} - 24) + G(\text{Mg} + 2\text{Mg} + 22\text{Mg} + 22\text{O} - 24) - G(\text{Mg} + 2\text{Mg} + 22\text{VaO} - 24)$$

$$G(\text{Mg} + 2\text{Zr} + 42\text{Fe} + 22\text{O} - 24) = G(\text{Mg} + 2\text{Zr} + 42\text{VaO} - 24) + G(\text{Fe} + 2\text{Zr} + 42\text{Fe} + 22\text{O} - 24) - G(\text{Fe} + 2\text{Zr} + 42\text{VaO} - 24)$$

$$G(\text{Fe} + 2\text{Zr} + 42\text{Mg} + 22\text{O} - 24) = G(\text{Mg} + 2\text{Zr} + 42\text{Mg} + 22\text{O} - 24) + G(\text{Fe} + 2\text{Zr} + 42\text{Fe} + 22\text{O} - 24) - G(\text{Mg} + 2\text{Zr} + 42\text{Fe} + 22\text{O} - 24)$$

The ternary solubility in ZrO₂-based phases (cubic, tetragonal, monoclinic) and the liquid phase were modelled based on binary extrapolations. Solubility of ZrO₂ in halite was not modelled at the first stage due to absence of experimental data. The first calculations revealed unrealistically large solubility of ZrO₂ in spinel. To reduce ternary extension in spinel phase the Gibbs energy of Mg₂ZrO₄ formation was assumed to be equal to value of 100 kJ/mol. It should be noted that spinel phase is metastable in the ZrO₂-MgO system and therefore this parameter does not influence phase diagram of the binary system. A calculated isothermal section at 1873 K is presented in Fig. 9. However, further experimental investigations were necessary and calculated preliminary diagrams were used to select compositions for experimental studies.

Fig. 9 Calculated isothermal section of the FeOx–MgO–ZrO₂ system at 1873 K and air partial pressure of oxygen

7 Results of Experimental Study of the ZrO₂-MgO-FeOx System and Adjustment of its Thermodynamic Description

The results of XRD investigations of samples heat treated at 1523, 1673 and 1873 K are presented in Table 2. The results of microstructure investigations (SEM/EDX) confirmed phases found by XRD, but in several samples the microstructure indicated that some phases were formed during cooling and therefore were not in equilibrium during equilibration. The results of experimental studies indicated substantial extension of homogeneity range of cubic ZrO₂ based solid solution from the ZrO₂-MgO bounding system into the system ZrO₂-MgO-FeOx though cubic ZrO₂ is stabilized in ZrO₂-FeOx at much higher temperatures above 2200 K. The XRD investigation of samples heat treated at 1673 K indicated stability of cubic ZrO₂ solid solutions in ternary system below its stability range in the ZrO₂-MgO bounding system.

The investigation of phase relations at 1523 K indicated two three-phase assemblages Fe₂O₃+Sp+T-ZrO₂ in samples #1 and 2 and Sp+Halite+T-ZrO₂ in samples #4 and 5. Microstructure of samples #2 and 4 are presented in Fig. 10(a), (b). It should be noted that T-ZrO₂ stable phase at 1523 K transforms to monoclinic modification on cooling. The XRD phase identifications were confirmed by microstructural investigation. Precipitation of phases during cooling complicated the interpretation of XRD results. According to phase diagram of the Fe₂O₃-MgO system the Fe₂O₃ phase should not be stable at 1673 K. However, XRD investigation of samples #1 and 2 indicated presence of Fe₂O₃ phase together with T-ZrO₂ and spinel. The microstructure of sample #2 heat treated at 1673 K indicated precipitates of Fe₂O₃ which formed during cooling (see Fig. 10c). XRD investigation of samples #4 and 5 indicated three-phase equilibrium C-ZrO₂, halite and spinel. In sample #4 all three phases are observed as equilibrium phases. Microstructure investigation of sample #5 indicated precipitation of spinel phase within halite grains (see Fig. 10d). Spinel was observed in small amounts as separate grains, but mostly at the grain boundaries and as precipitates. Therefore, only traces of equilibrium spinel phase were observed in sample #5. Another three-phase equilibrium of T-ZrO₂, C-ZrO₂ and spinel was indicated in sample #6. Composition of C-ZrO₂ was measured to be 84 mol.% ZrO₂, 5 mol.% FeOx and 11 mol.% MgO. In sample #7 two-phase equilibrium of T-ZrO₂ and spinel phase was indicated. According to EDX measurements T-ZrO₂ phase contained 97 mol% of ZrO₂, 1 mol% MgO and 2 mol.% of FeOx.

Microstructure investigation of sample #1 heat treated at 1873 K indicated partial melting of sample and

Table 2 Sample compositions and results of characterization by XRD

Sample	Nominal / measured sample composition [mol.%]			Temperature, [K]/ Annealing time in days	Phases according to XRD results	Vol. %	Lattice parameters, [Å]			
	ZrO ₂	FeO _x	MgO				a	b	c	β [°]
#1	10.0/11.5	80.0/77.7	10.0/10.8	1523/10	M–ZrO ₂	19	5.1470	5.2065	5.3151	99.206
					Fe ₂ O ₃	10	5.0374	...	13.752	...
					Spinel	71	8.3732	...	...	...
				1673/7	M–ZrO ₂	14	5.1456	5.2046	5.3147	99.233
					Fe ₂ O ₃	40	5.0402	...	13.755	...
					Spinel	46	8.3776	...	...	...
				1873/5	M–ZrO ₂	26	5.1468	5.2000	5.3187	99.197
					Fe ₂ O ₃	14	5.0443	...	13.732	...
					Spinel	60	8.3738	...	...	...
				1523/10	M–ZrO ₂	15	5.1476	5.2046	5.3253	99.212
					Fe ₂ O ₃	52	5.0494	...	13.778	...
					Spinel	33	8.3740	...	...	...
#2	10.0/11.3	70.0/69.4	20.0/19.4	1673/7	M–ZrO ₂	19	5.1485	5.2040	5.3161	99.231
					Fe ₂ O ₃	10	5.0393	...	13.749	...
					Spinel	71	8.3764	...	...	...
				1873/5	M–ZrO ₂	14	5.1445	5.2001	5.3174	99.147
					Fe ₂ O ₃	38	5.0386	...	13.753	...
					Spinel	48	8.3752	...	...	...
	10.0/10.0	60.0/60.5	30.0/29.5	1523/10	M–ZrO ₂	19	5.1504	5.2034	5.3147	99.213
					Spinel	81	8.4014	...	...	...
					Spinel	85	8.4049	...	...	...
				1673/7	M–ZrO ₂	15	5.1502	5.2056	5.3156	99.227
					Spinel	85	8.4049	...	...	...
					Spinel	85	8.4056	...	...	...
				1873/5	M–ZrO ₂	5	5.1448	5.2001	5.3174	99.146
					C–ZrO ₂	10	5.076	...	...	...
					Spinel	85	8.4056	...	...	...
#4	10.0/112	45.0/41.1	45.0/47.6	1523 / 10	M–ZrO ₂	17	5.1506	5.2054	5.3147	99.218
					MgO	23	4.2127	...	...	...
					Spinel	60	8.4060	...	...	...
				1673/7	Spinel	72	8.4130	...	...	...
					C–ZrO ₂	14	5.0709	...	...	...
					MgO	14	4.2110	...	...	...
				1873/5	Spinel	59	8.4270	...	...	...
					C–ZrO ₂	6	5.0760	...	...	...
					MgO	35	4.2137	...	...	...
#5	10.0/11.3	15.0/14.2	75.0/74.5	1523/10	M–ZrO ₂	20	5.1499	5.2058	5.3143	99.208
					MgO	62	4.2127	...	...	...
					Spinel	18	8.4009	...	...	...
				1673/7	Spinel	21	8.4000	...	...	...
					C–ZrO ₂	15	5.0699	...	...	...
					MgO	64	4.2101	...	...	...
				1873/5	Spinel	21	8.4052	...	...	...
					C–ZrO ₂	19	5.0598	...	...	...
					Spinel	19	5.0598	...	...	...

Table 2 continued

Sample	Nominal / measured sample composition [mol.%]			Temperature, [K]/ Annealing time in days	Phases according to XRD results	Vol. %	Lattice parameters, [Å]			
	ZrO ₂	FeO _x	MgO				a	b	c	β [°]
#6	50.0/54.6	30.0/29.3	20.0/16.2	1523/10	MgO	60	4.2105			
					M–ZrO ₂	68	5.1509	5.2062	5.3154	99.235
					Spinel	32	8.4047			
				1673/7	M–ZrO ₂	51	5.1495	5.2011	5.3141	99.140
					C–ZrO ₂	17	5.087			
					Spinel	32	8.4087			
				1873/5	M–ZrO ₂	46	5.1523	5.1970	5.3181	99.124
					C–ZrO ₂	6	5.076			
					Spinel	47	8.3787			
					Fe ₂ O ₃	1	5.0380	-	13.772	
#7	80.0/80.9	12.0/11.9	8.0/8.1	1523/10	M–ZrO ₂	88	5.1518	5.2073	5.3166	99.236
					Spinel	12	8.4079			
				1673/7	M–ZrO ₂	90	5.1518	5.2049	5.3161	99.235
					Spinel	10	8.4076			
				1873/5	M–ZrO ₂	85	5.1548	5.1842	5.3269	99.018
					C–ZrO ₂	6	5.087			
					Spinel	9	8.4087			

crystallization of binary eutectic spinel+T–ZrO₂ (see Fig. 10e). Precipitation of Fe₂O₃ occurring during cooling was also indicated. The measured composition of binary eutectic was 79 mol.% FeO_x, 7 mol.% MgO and 14 mol.% ZrO₂. Three-phase equilibrium C–ZrO₂+T–ZrO₂+spinel was found in samples #6 and 7 and C–ZrO₂+spinel+halite in samples #4 and 5 using XRD. Microstructure investigation of these samples #4 and 5 heat treated at 1873 K indicated precipitation of spinel within grains of halite. Microstructure of sample #4 is shown in Fig. 11(f). C–ZrO₂, spinel and halite are equilibrium phases. Some precipitates of spinel formed on cooling can be observed inside halite grains. The composition of C–ZrO₂ in equilibrium with spinel and halite was measured to be 75 mol.% ZrO₂, 10 mol.% FeO_x and 15 mol.% MgO. The composition of spinel phase in equilibrium with halite and C–ZrO₂ was established to be 4 mol.% ZrO₂, 60 mol.% FeO_x and 36 mol.% MgO based on SEM/EDX data for sample #4. It should be noted that in sample #5 spinel phase was found only within halite grains and therefore it precipitated during cooling. Therefore, in equilibrium phases in sample #5 were halite and C–ZrO₂.

To model solubility of ZrO₂ in halite phase the Gibbs energy of fictive end-member of Zr+4O–2 with halite structure was accepted from the advanced description of MgO–ZrO₂ system [83].

To fit calculated phase equilibria to the obtained experimental results additional binary mixing parameters were introduced into description of cubic ZrO₂ solid solution i.e. mixing between Fe+2 and Mg+2 as well as mixing between Fe+3 and Mg+2:

$$0L(\text{Fe}+2, \text{Mg}+2; \text{O}-2) = 0L(\text{Fe}+2, \text{Mg}+2; \text{Va})$$

$$= -1.7 \cdot 10^5 \text{ J/mol};$$

$$0L(\text{Fe}+3, \text{Mg}+2; \text{O}-2) = 0L(\text{Fe}+3, \text{Mg}+2; \text{Va})$$

$$= -1.7 \cdot 10^5 \text{ J/mol}.$$

The calculated isothermal sections of phase diagram ZrO₂–MgO–FeO_x at 1523, 1673 and 1873 K and air partial pressure of oxygen are presented in Fig. 11(a)–(c) together with experimental data of the present work. The phase fraction diagram (Fig. 11d) calculated for the composition of sample #1 indicated formation of liquid in two-phase field at 1859 K. The calculated composition of liquid phase was 84 mol.% FeO_x, 5 mol.% MgO and 11 mol.% ZrO₂ which is in reasonable agreement with experimentally measured composition of binary eutectic.

The derived thermodynamic description of the ZrO₂–MgO–FeO_x system was merged with binary descriptions Zr–Fe, Zr–Mg, Zr–O, Mg–O, Fe–O and Mg–Fe as mentioned above.

The obtained thermodynamic description for the Fe–Mg–Zr–O system is presented in Table 3.

Fig. 10 (a)–(f) Microstructure of samples after heat treatments: #2 at 1523 K (dark grey phase is spinel, grey is Fe_2O_3 and white is T-ZrO_2). #4 at 1523 K (black phase is halite, grey phase is spinel and white phase is T-ZrO_2). #2 at 1673 K (dark grey is spinel, white is T-ZrO_2 , light grey stripes are precipitate of Fe_2O_3). #5 at 1673 K (dark

phase is halite, grey is spinel and white is C-ZrO_2). #1 at 1873 K (dark grey phase is spinel, white phase T-ZrO_2 , grey stripes are precipitates of Fe_2O_3 and liquid phase crystallized as eutectic spinel+ T-ZrO_2). #4 at 1873 K (dark phase is halite, grey is spinel and white is C-ZrO_2)

8 Implication of Thermodynamic Modelling for the Development of the TRIP-Matrix-Composites

For the simulation of interfacial reactions between ceramic particles and the steel matrix as well as for the evaluation of the compatibility of materials, a thermodynamic database for the major sub-system Fe-Mg-Zr-O has been

developed using experimental results of the present work. Conditions for TMC production using the powder-metal-lurgical conventional sintering method were temperature ranging at 1623–1673 K and protective gas atmosphere of technical argon with partial pressure of oxygen of $P(\text{O}_2) \approx 1 \times 10^{-4}$ bar.

Therefore, isothermal sections of the FeO-MgO-ZrO_2 system were calculated at the temperatures of the sintering

Fig. 11 (a)–(d) Calculated isothermal sections at 1523 K (a), 1673 K (b), 1873 K (c) along with experimental data of this work and phase fraction diagram for composition 10 mol.% ZrO₂, 10 mol.% MgO and 80 mol.% FeO_x (d)

process, i.e. at 1623 and 1673 K in a presence of a small amount of iron (iron mole fraction $x(\text{Fe})=10^{-5}$) in order to consider possible reactions in the ceramic material. Calculated results are presented in Fig. 12(a), (b). Based on the performed calculations, it can be concluded, that the solubility of the FeO in the T-ZrO₂ is insignificant and reaches around 2 mol. %. It should be noted that according to calculations at 1673 K, C-ZrO₂ also forms in presence of metallic Fe in ternary system although being unstable in bounding system ZrO₂–FeO_x.

Further thermodynamic calculations have been performed in order to estimate possible reactions between Mg-PSZ and pure iron accounting the partial pressure of

oxygen. It should be noted that due to the oxidized surface of the metal powder, a local equilibrium with an increased partial pressure of oxygen should be also considered. During the conventional sintering of TMC, the atmosphere of the technical argon ($P(\text{O}_2) = 1 \times 10^{-4}$ bar) should be taken into account, as well as the ideal conditions of sintering where $P(\text{O}_2) \rightarrow 0$. The calculated vertical section between Mg–PSZ and pure Fe at $P(\text{O}_2)=10^{-4}$ bar and $P(\text{O}_2) \rightarrow 0$ are presented in Fig. 13. Based on the calculated diagram shown in Fig. 13(a), it can be concluded that even low partial pressure of oxygen ($P(\text{O}_2)=10^{-4}$ bar) is enough for the oxidation of iron and the appearance of the spinel phase. Thermodynamic calculations showed that the

Table 3 Thermodynamic functions for the Fe–Mg–Zr–O system (J/mol)

Phase	Sublattice model	Optimized parameters
Gas (O ₂)		0GO2= +2·GHSEROO +R·T·ln(P);
Ionic liquid	(Fe+2,Mg+2,Zr+4)P (O–2,Va,FeO3/2)Q	0GFe+2:O–2IonicLiquid=+4·GFEOLIQ;
		0GZr+4:O–2IonicLiquid=+2·GZRO2LIQ;
		0GFe+2:VaIonicLiquid=+GFELIQ;
		0GMg+2:VaIonicLiquid=+GMGLIQ;
		0GMg+2:O–2IonicLiquid=+2·GMGOLIQ;
		0GZr+4:VaIonicLiquid=+GZRLIQ;
		0GFeO3/2IonicLiquid=–89819 +39.962·T +2.5·GFEOLIQ;
		0LFe+2,Zr+4:O–2IonicLiquid= –17320.87;
		1LFe+2,Zr+4:O–2IonicLiquid= –3683;
		0LFe+2:O–2,FeO3/2IonicLiquid= –26362;
		1LFe+2:O–2,FeO3/2IonicLiquid= +13353;
		0LFe+2:O–2,VaIonicLiquid= +176681–16.368·T;
		1LFe+2:O–2,VaIonicLiquid= –65655 +30.869·T;
		0LZr+4:O–2,FeO3/2IonicLiquid= +41044.94;
		1LZr+4:O–2,FeO3/2IonicLiquid= –17769.3;
		0LZr+4:O–2,VaIonicLiquid= +75166.0715 –55.2382004·T;
		1LZr+4:O–2,VaIonicLiquid= +39057.4913;
		0LFe+2,Zr+4:VaIonicLiquid= –85196.3 +12.829·T;
		1LFe+2,Zr+4:VaIonicLiquid= –1655.5;
		0LFe+2:Va,FeO3/2IonicLiquid= +110000;
		0LFe+2,Mg+2:VaIonicLiquid= +61343 +1.5·T;
		1LFe+2,Mg+2:VaIonicLiquid= –2700;
		0LFe+2,Mg+2:O–2IonicLiquid= –20000;
		0LMg+2:O–2,VaIonicLiquid= +182000 +26.8·T;
		0LMg+2:Va,FeO3/2IonicLiquid= –65000;
		0LMg+2,Zr+4:O–2IonicLiquid= –68195.5443;
		1LMg+2,Zr+4:O–2IonicLiquid= +35835.397;
BCC	(Fe,Mg,Zr)1(O,Va)3	0GFe:VaBCC= GHSERFE;
		0GFe:OBCC= GHSERFE +1.5·GO2GAS +195·T;
		0GZr:VaBCC= GZRBCC;
		0GZr:OBCC= 3·GHSEROO +GZRBCC –52652.008;
		0GMg:VaBCC= GHSERMG +3100 –2.1·T;
		0GMg:OBCC= GHSERMG +1.5GO2GAS +106 +195·T;
		TCFe:VaBCC= 1043;
		B0Fe:VaBCC= 2.22;
		0LFe:O,VaBCC= –517548 +71.83·T;
		0LFe,Zr:VaBCC= –33689.998 +8.76457·T;
		1LFe,Zr:VaBCC= –11176.623 +7.6257·T;
		0LZr:O,VaBCC= –1754239 +336.32517·T;
FCC	(Fe,Mg,Zr)1(O,Va)1	0GFe:VaFCC= GFEFCC;
		0GFe:OFCC= GFEFCC +0.5·GO2GAS +65·T;
		0GZr:VaFCC= +7600 –0.9·T +GHSERZR;
		0GZr:OFCC= GHSEROO +GHSERZR +7600 –0.9·T;
		0GMg:VaFCC= +2600 –0.9·T +GHSERMG;
		0GMg:OFCC= 0.5·GO2GAS +GHSERMG +65·T;
		TCFe:VaFCC= –201;
		B0Fe:VaFCC= –2.1;
		0LFe:O,VaFCC= –168758 +19.17·T;
		0LFe,Zr:VaFCC= –16847.9 –3.5611·T;
HCP	(Fe,Mg,Zr)1(O,Va)0.5	0GFe:VaHCP= GFEHCP;
		0GFe:OHCP= GFEHCP +0.5·GHSEROO +32.5·T;
		0GZr:VaHCP= GHSEZR;
		0GZr:OHCP= 0.5·GHSEROO +GHSEZR –286427.906 +43.223·T;
		0GMg:VaHCP= GHSERMG;

Table 3 continued

Phase	Sublattice model	Optimized parameters
Fe ₂ Zr	(Fe,Zr) ₂ (Zr,Fe) ₁	0GMg:OHCP= GHSERMG +0.5·GHSEEROO +50·T; 0LZr:O,VaHCP= −37876.6552 +17.2915·T; 1LZr:O,VaHCP= −4471.39; 0LFe,Zr:VaHCP= +57696; 0GFe:ZrFe ₂ Zr= −112156 +438.584634·T −79.10388·T·ln(T) −0.006825·T ² +330106.042·T−1; 0GFe:FeFe ₂ Zr= +3·GHSERFE +15000; 0GZr:ZrFe ₂ Zr= +3·GHSERZR +15000; 0GZr:FeFe ₂ Zr= +112156 −438.584634·T +79.10388·T·ln(T) +0.006825·T ² −330106.042·T−1 +30000; TCFe:VaFe ₂ Zr= 585; B0Fe:VaFe ₂ Zr= 1.4; 0LFe,Zr:FeFe ₂ Zr= +56000; 0LFe,Zr:ZrFe ₂ Zr= +56000; 0LFe:Zr,FeFe ₂ Zr= −23000 +22.512·T; 0LZr:Zr,FeFe ₂ Zr= −23000 +22.512·T;
hex.−Fe ₂ Zr	(Fe) ₂ (Zr,Fe) ₁	0GFe:Zrhex.−Fe ₂ Zr= −113000 +440.1791·T −79.10388·T·ln(T) −0.006825·T ² +330106.042·T−1; 0GFe:Fehex.−Fe ₂ Zr= +3·GHSERFE +15000; 0GFe:Zr,Fehex.−Fe ₂ Zr= −1533.1 +3.095·T;
FeZr ₂	(Fe) ₁ (Zr) ₂	0GFe:ZrFeZr ₂ = +GHSERFE +2·GHSERZR −44258.83 −2.7322·T;
FeZr ₃	(Fe) ₁ (Zr) ₃	0GFe:ZrFeZr ₃ = −80910.01 +519.882937·T −97.864·T·ln(T) −0.0141·T ² +144140.86·T−1;
M−ZrO ₂	(Fe+2,Fe+3,Mg+2,Zr+4) ₁ (O−2,Va) ₂	0GFe+2:O−2M−ZrO ₂ = +GWUSTITE +GHSEEROO +120000 +11.5263·T; 0GFe+3:O−2M−ZrO ₂ = +0.5·GFE2O ₃ +0.5·GHSEEROO +100000 +9.35108255·T; 0GZr+4:O−2M−ZrO ₂ = +GZRO2M; 0GFe+2:VaM−ZrO ₂ = +GWUSTITE −GHSEEROO +120000 +11.5263·T; 0GFe+3:VaM−ZrO ₂ = +0.5·GFE2O ₃ −1.5·GHSEEROO +100000 +9.35108255·T; 0GZr+4:VaM−ZrO ₂ = +GZRO2M −2·GHSEEROO; 0GMg+2:O−2M−ZrO ₂ = +GMGOSOL +GHSEEROO +120000 +11.5263·T; 0GMg+2:VaM−ZrO ₂ = +GMGOSOL −GHSEEROO +120000 +11.5263·T;
T−ZrO ₂	(Fe+2,Fe+3,Mg+2,Zr+4) ₁ (O−2,Va) ₂	0GFe+2:O−2T−ZrO ₂ = +GWUSTITE +GHSEEROO +60000 +11.5263·T; 0GFe+3:O−2T−ZrO ₂ = +0.5·GFE2O ₃ +0.5·GHSEEROO +9.35108255·T +50000; 0GZr+4:O−2T−ZrO ₂ = +GZRO2T; 0GFe+2:VaT−ZrO ₂ = +GWUSTITE −GHSEEROO +60000 +11.5263·T; 0GFe+3:VaT−ZrO ₂ = +0.5·GFE2O ₃ −1.5·GHSEEROO +9.5108255·T +50000; 0GZr+4:VaT−ZrO ₂ = +GZRO2T −2·GHSEEROO; 0GMg+2:O−2T−ZrO ₂ = +GMGOSOL +GHSEEROO +60000 +11.5263·T; 0GMg+2:VaT−ZrO ₂ = +GMGOSOL −GHSEEROO +60000 +11.5263·T; 0LMg+2,Zr+4:O−2T−ZrO ₂ = +50000; 0LMg+2, Zr+4:VaT−ZrO ₂ = +50000; 0LFe+2, Zr+4:O−2T−ZrO ₂ = +50000; 0LFe+2, Zr+4:VaT−ZrO ₂ = +50000; 0LFe+3, Zr+4:O−2T−ZrO ₂ = +10000; 0LFe+3, Zr+4:VaT−ZrO ₂ = +10000;
C−ZrO ₂ Fluorite	(Fe+2,Fe+3,Mg+2,Zr+4) ₁ (O−2,Va) ₂	0GFe+2:O−2C−ZrO ₂ = +GWUSTITE +GHSEEROO +45000 +11.5263·T; 0GFe+3:O−2C−ZrO ₂ = +0.5·GFE2O ₃ +0.5·GHSEEROO +9.35108255·T +50000; 0GZr+4:O−2C−ZrO ₂ = +GZRO2C; 0GFe+2:VaC−ZrO ₂ = +GWUSTITE −GHSEEROO +45000 +11.5263·T; 0GFe+3:VaC−ZrO ₂ = +0.5·GFE2O ₃ −1.5·GHSEEROO +9.35108255·T +50000; 0GZr+4:VaC−ZrO ₂ = +GZRO2C −2·GHSEEROO; 0GZr+4:VaC−ZrO ₂ = +GMGOSOL −GHSEEROO +45000 +11.5263·T; 0GZr+4:VaC−ZrO ₂ = +GMGOSOL +GHSEEROO +45000 +11.5263·T; 0LMg+2,Zr+4:O−2C−ZrO ₂ = +2550.15; 0LMg+2,Zr+4:VaC−ZrO ₂ = +2550.15; 0LFe+2,Zr+4:O−2C−ZrO ₂ = +15000; 0LFe+2,Zr+4:VaC−ZrO ₂ = +15000; 0LFe+3,Zr+4:O−2C−ZrO ₂ = +9250;

Table 3 continued

Phase	Sublattice model	Optimized parameters
Halite	(Fe+2,Fe+3,Mg+2,Va)1(O–2)1	$0\text{LFe}+3,\text{Zr}+4:\text{VaC}-\text{ZrO}_2 = +9250;$ $0\text{GFe}+2:\text{O}-2\text{Halite} = +\text{GWUSTITE};$ $0\text{GFe}+3:\text{O}-2\text{Halite} = +1.25\cdot\text{AWUSTITE} +1.25\cdot\text{GWUSTITE};$ $0\text{GMg}+2:\text{O}-2\text{Halite} = +\text{GMGOSOL};$ $0\text{GVa}:\text{O}-2\text{Halite} = +0;$ $0\text{LFe}+2,\text{Mg}+2:\text{O}-2\text{Halite} = +19369.9567-12\cdot\text{T};$ $1\text{LFe}+2,\text{Mg}+2:\text{O}-2\text{Halite} = -3758.04262;$ $0\text{LFe}+3,\text{Mg}+2:\text{O}-2\text{Halite} = +68236.7774-30\cdot\text{T};$ $1\text{LFe}+3,\text{Mg}+2:\text{O}-2\text{Halite} = -6748.0443;$ $0\text{LFe}+2,\text{Fe}+3:\text{O}-2\text{Halite} = -12324;$ $1\text{LFe}+2,\text{Fe}+3:\text{O}-2\text{Halite} = +20070;$
Spinel	(Fe+2,Fe+3,Mg+2)1(Fe+2,Fe+3,Mg+2,Zr+4,Va)2(Fe+2,Mg+2,Va)2(O–2)4	$0\text{GFe}+2:\text{Fe}+2:\text{Fe}+2:\text{O}-2\text{Spinel} = +9\cdot\text{GFE3O}_4 +\text{DFE3O}_4;$ $\text{TCFe}+2:\text{Fe}+2:\text{Fe}+2:\text{O}-2\text{Spinel} = 848;$ $\text{B0Fe}+2:\text{Fe}+2:\text{Fe}+2:\text{O}-2\text{Spinel} = 44.54;$ $0\text{GFe}+3:\text{Fe}+2:\text{Fe}+2:\text{O}-2\text{Spinel} = +9\cdot\text{GFE3O}_4 +\text{DFE3O}_4 -\text{BFE3O}_4;$ $\text{TCFe}+3:\text{Fe}+2:\text{Fe}+2:\text{O}-2\text{Spinel} = 848;$ $\text{B0Fe}+3:\text{Fe}+2:\text{Fe}+2:\text{O}-2\text{Spinel} = 44.54;$ $0\text{GFe}+2:\text{Zr}+4:\text{Fe}+2:\text{O}-2\text{Spinel} = +2\cdot\text{GZRO}_2\text{C} +4\cdot\text{GWUSTITE} +23.0524394\cdot\text{T} +10000$ $+ \text{DFE3O}_4 -5\cdot\text{GFE3O}_4 -2\cdot\text{BFE3O}_4;$ $0\text{GFe}+2:\text{Fe}+3:\text{Fe}+2:\text{O}-2\text{Spinel} = +9\cdot\text{GFE3O}_4 +\text{DFE3O}_4 -\text{BFE3O}_4;$ $\text{TCFe}+2:\text{Fe}+3:\text{Fe}+2:\text{O}-2\text{Spinel} = 848;$ $\text{B0Fe}+2:\text{Fe}+3:\text{Fe}+2:\text{O}-2\text{Spinel} = 44.54;$ $0\text{GFe}+3:\text{Fe}+3:\text{Fe}+2:\text{O}-2\text{Spinel} = +9\cdot\text{GFE3O}_4 +\text{DFE3O}_4 -2\cdot\text{BFE3O}_4;$ $\text{TCFe}+3:\text{Fe}+3:\text{Fe}+2:\text{O}-2\text{Spinel} = 848;$ $\text{B0Fe}+3:\text{Fe}+3:\text{Fe}+2:\text{O}-2\text{Spinel} = 44.54;$ $0\text{GFe}+3:\text{Zr}+4:\text{Fe}+2:\text{O}-2\text{Spinel} = +2\cdot\text{GZRO}_2\text{C} +2\cdot\text{GFE2O}_3 +6\cdot\text{GWUSTITE} +10000 +37.40388\cdot\text{T}$ $-19\cdot\text{GFE3O}_4 +\text{DFE3O}_4 -\text{BFE3O}_4;$ $0\text{GFe}+2:\text{Va}:\text{Fe}+2:\text{O}-2\text{Spinel} = +7\cdot\text{GFE3O}_4 +\text{DFE3O}_4 +\text{CFE3O}_4 -\text{BFE3O}_4;$ $\text{TCFe}+2:\text{Va}:\text{Fe}+2:\text{O}-2\text{Spinel} = 848;$ $\text{B0Fe}+2:\text{Va}:\text{Fe}+2:\text{O}-2\text{Spinel} = 44.54;$ $0\text{GFe}+3:\text{Va}:\text{Fe}+2:\text{O}-2\text{Spinel} = +7\cdot\text{GFE3O}_4 +\text{DFE3O}_4 +\text{CFE3O}_4 -2\cdot\text{BFE3O}_4;$ $\text{TCFe}+3:\text{Va}:\text{Fe}+2:\text{O}-2\text{Spinel} = 848;$ $\text{B0Fe}+3:\text{Va}:\text{Fe}+2:\text{O}-2\text{Spinel} = 44.54;$ $0\text{GFe}+2:\text{Fe}+2:\text{Va}:\text{O}-2\text{Spinel} = +7\cdot\text{GFE3O}_4 +\text{BFE3O}_4;$ $\text{TCFe}+2:\text{Fe}+2:\text{Va}:\text{O}-2\text{Spinel} = 848;$ $\text{B0Fe}+2:\text{Fe}+2:\text{Va}:\text{O}-2\text{Spinel} = 44.54;$ $0\text{GFe}+3:\text{Fe}+2:\text{Va}:\text{O}-2\text{Spinel} = +7\cdot\text{GFE3O}_4;$ $\text{TCFe}+3:\text{Fe}+2:\text{Va}:\text{O}-2\text{Spinel} = 848;$ $\text{B0Fe}+3:\text{Fe}+2:\text{Va}:\text{O}-2\text{Spinel} = 44.54;$ $0\text{GFe}+2:\text{Zr}+4:\text{Va}:\text{O}-2\text{Spinel} = +2\cdot\text{GZRO}_2\text{C} +4\cdot\text{GWUSTITE} +10000 +23.0524394\cdot\text{T} -7\cdot\text{GFE3O}_4 -$ $\text{BFE3O}_4;$ $0\text{GFe}+2:\text{Fe}+3:\text{Va}:\text{O}-2\text{Spinel} = +7\cdot\text{GFE3O}_4;$ $\text{TCFe}+2:\text{Fe}+3:\text{Va}:\text{O}-2\text{Spinel} = 848;$ $\text{B0Fe}+2:\text{Fe}+3:\text{Va}:\text{O}-2\text{Spinel} = 44.54;$ $0\text{GFe}+3:\text{Fe}+3:\text{Va}:\text{O}-2\text{Spinel} = +7\cdot\text{GFE3O}_4 -\text{BFE3O}_4;$ $\text{TCFe}+3:\text{Fe}+3:\text{Va}:\text{O}-2\text{Spinel} = 848;$ $\text{B0Fe}+3:\text{Fe}+3:\text{Va}:\text{O}-2\text{Spinel} = 44.54;$ $0\text{GFe}+3:\text{Zr}+4:\text{Va}:\text{O}-2\text{Spinel} = +2\cdot\text{GZRO}_2\text{C} +2\cdot\text{GFE2O}_3 +6\cdot\text{GWUSTITE} -21\cdot\text{GFE3O}_4 +10000$ $+37.40388\cdot\text{T};$ $0\text{GFe}+2:\text{Va}:\text{Va}:\text{O}-2\text{Spinel} = +5\cdot\text{GFE3O}_4 +\text{CFE3O}_4;$ $\text{TCFe}+2:\text{Va}:\text{Va}:\text{O}-2\text{Spinel} = 848;$ $\text{B0Fe}+2:\text{Va}:\text{Va}:\text{O}-2\text{Spinel} = 44.54;$ $0\text{GFe}+3:\text{Va}:\text{Va}:\text{O}-2\text{Spinel} = +5\cdot\text{GFE3O}_4 +\text{CFE3O}_4 -\text{BFE3O}_4;$ $\text{TCFe}+3:\text{Va}:\text{Va}:\text{O}-2\text{Spinel} = 848;$ $\text{B0Fe}+3:\text{Va}:\text{Va}:\text{O}-2\text{Spinel} = 44.54;$ $0\text{GMg}+2:\text{Mg}+2:\text{O}-2\text{Spinel} = +\text{MGMGMG};$

Table 3 continued

Phase	Sublattice model	Optimized parameters
Fe ₂ O ₃	(Fe+3,Zr+4) ₂ (O–2,Va) ₁ (O–2) ₃	0GMg+2:Va:Mg+2:O–2Spinel= +GMGVAMG;
		0GMg+2:Mg+2:Va:O–2Spinel= +GMGMG;
		0GMg+2:Va:Va:O–2Spinel= +GMGVA;
		0GMg+2:Fe+3:Va:O–2Spinel= +GMGFE3NO;
		TCMg+2:Fe+3:Va:O–2Spinel= 689.5;
		B0Mg+2:Fe+3:Va:O–2Spinel= 1.0;
		0GFe+3:Mg+2:Va:O–2Spinel= +2·GMGFE3IN –7·GFE3O4 +BFE3O4 +23.05244·T;
		TCFe+3:Mg+2:Va:O–2Spinel= 689.5;
		B0Fe+3:Mg+2:Va:O–2Spinel= 1.0;
		0GFe+2:Mg+2:Va:O–2Spinel= +2·GMGFE3IN –7·GFE3O4 +2·BFE3O4 +23.05244·T;
		0GMg+2:Fe+2:Va:O–2Spinel= +GMGFE3NO +BFE3O4;
		0GMg+2:Fe+2:Mg+2:O–2Spinel= +GMGMGMG +GMGFE3NO +BFE3O4 –GMGMG +500000;
		0GMg+2:Fe+3:Mg+2:O–2Spinel= +GMGMGMG +GMGFE3NO –GMGMG +500000;
		0GFe+2:Mg+2:Mg+2:O–2Spinel= +GMGMGMG +2·GMGFE3IN –7·GFE3O4 +2·BFE3O4 +23.05244·T –GMGMG;
		0GFe+3:Mg+2:Mg+2:O–2Spinel= +GMGMGMG –7·GFE3O4 +BFE3O4 +23.05244·T –GMGMG +500000;
		0GMg+2:Fe+2:Fe+2:O–2Spinel= +2·GFE3O4 +DFE3O4 +GMGFE3NO +500000;
		0GFe+2:Mg+2:Fe+2:O–2Spinel= +DFE3O4 +2·GMGFE3IN –5·GFE3O4 +23.05244·T +500000;
		0GMg+2:Fe+3:Fe+2:O–2Spinel= +2·GFE3O4 +DFE3O4 –BFE3O4 +GMGFE3NO +500000;
		0GFe+3:Mg+2:Fe+2:O–2Spinel= +DFE3O4 +2·GMGFE3IN –5·GFE3O4 +BFE3O4 +23.05244·T +500000;
		0GFe+2:Fe+3:Mg+2:O–2Spinel= +GMGMGMG +2·GMGFE3IN –7·GFE3O4 +2·BFE3O4 +23.05244·T –2·GMGMG +GMGFE3NO +1000000;
		0GFe+3:Fe+2:Mg+2:O–2Spinel= +GMGMGMG –7·GFE3O4 +2·BFE3O4 +23.05244·T –2·GMGMG +GMGFE3NO +1000000;
		0GFe+3:Va:Mg+2:O–2Spinel= –7·GFE3O4 +BFE3O4 +23.05244·T –GMGMG +GMGVAMG +500000;
		0GFe+2:Va:Mg+2:O–2Spinel= +2·GMGFE3IN –7·GFE3O4 +2·BFE3O4 +23.05244·T –GMGMG +GMGVAMG +500000;
		0GFe+2:Fe+2:Mg+2:O–2Spinel= +GMGMGMG +2·GMGFE3IN –7·GFE3O4 +3·BFE3O4 +23.05244·T –GMGMG +GMGFE3NO +1000000;
		0GFe+3:Fe+3:Mg+2:O–2Spinel= +GMGMGMG –7·GFE3O4 +3·BFE3O4 +23.05244·T –2·GMGMG +GMGFE3NO +1000000;
		0GMg+2:Va:Fe+2:O–2Spinel= +GMGVA +2·GFE3O4 +DFE3O4 –BFE3O4 +500000;
		0GMg+2:Mg+2:Fe+2:O–2Spinel= +GMGMG +2·GFE3O4 +DFE3O4 –BFE3O4 +500000;
		0GMg+2:Zr+4:Va:O–2Spinel= +2·GMGZRO4 –GMGMG +23.05244·T;
		0GMg+2:Zr+4:Mg+2:O–2Spinel= +2·GMGZRO4 –GMGMG +GMGMGMG +23.05244·T;
		0GMg+2:Zr+4:Fe+3:O–2Spinel= +2·GMGZRO4 –GMGMG +23.05244·T +2·GFE3O4 +DFE3O4 –BFE3O4;
		0GMg+2:Zr+4:Fe+2:O–2Spinel= +2·GZRO2C –GMGMG +GMGMGMG +23.05244·T +GWUSTITE +1000 –7·GFE3O4 –BFE3O4;
		0LFe+3,Mg+2:Mg+2:Va:O–2Spinel= –162358.584;
		0LFe+3,Mg+2:Fe+3:Va:O–2Spinel= –32110.6041;
		0LFe+3:Fe+3,Mg+2:Va:O–2Spinel= +44188.8675;
		0LMg+2:Fe+3,Mg+2:Va:O–2Spinel= +90042.1775;
		0GFe+3:O–2:O–2Corundum= +GFE2O3 +GHSEROO;
		0TCFe+3:O–2:O–2Corundum= –2867;
		0B0Fe+3:O–2:O–2Corundum= –25.1;
		0GZr+4:O–2:O–2Corundum= +2·GZRO2C +50000;
		0GFe+3:Va:O–2Corundum= +GFE2O3;
		0GZr+4:Va:O–2Corundum= +2·GZRO2C –GHSEROO +50000;
		0TCFe+3:Va:O–2Corundum= –2867;
		0B0Fe+3:Va:O–2Corundum= –25.1;
		0LFe+3,Zr+4:Va:O–2Corundum= +120000;
		0LFe+3,Zr+4:O–2:O–2Corundum= +120000;

Table 3 continued

Phase	Sublattice model	Optimized parameters
Functions	(Temperature limits)	
<i>GHSEROO</i>	(298–1000)	$-3480.87 - 25.503038 \bullet T - 11.136 \bullet T \bullet \ln(T) - 0.005098888 \bullet T^2 + 6.61846 \bullet 10^{-7} T^3 - 38365 \bullet T^{-1}$
	(1000–3300)	$-6568.763 + 12.65988 \bullet T - 16.8138 \bullet T \bullet \ln(T) - 5.95798 \bullet 10^{-4} \bullet T^2 + 6.781 \bullet 10^{-9} \bullet T^3 + 262905 \bullet T^{-1}$
	(3300–6000)	$-13986.728 + 31.259625 \bullet T - 18.9536 \bullet T \bullet \ln(T) - 4.25243 \bullet 10^{-4} \bullet T^2 + 1.0721 \bullet 10^{-8} \bullet T^3 + 4383200 \bullet T^{-1}$
<i>GO2GAS</i>	(298–1000)	$-6961.74451 - 76729.7484 \bullet T^{-1} - 51.0057202 \bullet T - 22.2710136 \bullet T \bullet \ln(T) - 0.0101977469 \bullet T^2 + 1.32369208 \bullet 10^{-6} \bullet T^3$
	(1000–3300)	$-13137.5203 + 525809.556 \bullet T^{-1} + 25.3200332 \bullet T - 33.627603 \bullet T \bullet \ln(T) - 0.00119159274 \bullet T^2 + 1.35611111 \bullet 10^{-8} \bullet T^3$
	(3300–6000)	$-27973.4908 + 8766421.4 \bullet T^{-1} + 62.5195726 \bullet T - 37.9072074 \bullet T \bullet \ln(T) - 8.50483772 \bullet 10^{-4} \bullet T^2 + 2.14409777 \bullet 10^{-8} \bullet T^3$
<i>GHSEFE</i>	(298–1811)	$+1225.7 + 124.134 \bullet T - 23.5143 \bullet T \bullet \ln(T) - 0.00439752 \bullet T^2 - 5.8927 \bullet 10^{-8} \bullet T^3 + 77359 \bullet T^{-1}$
	(1811–6000)	$-25383.581 + 299.31255 \bullet T - 46 \bullet T \bullet \ln(T) + 2.29603 \bullet 1031 \bullet T^{-9}$
<i>GFEFCC</i>	(298–1811)	$-236.7 + 132.416 \bullet T - 24.6643 \bullet T \bullet \ln(T) - 0.00375752 \bullet T^2 - 5.8927 \bullet 10^{-8} \bullet T^3 + 77359 \bullet T^{-1}$
	(1811–6000)	$-27097.396 + 300.25256 \bullet T - 46 \bullet T \bullet \ln(T) + 2.78854 \bullet 1031 \bullet T^{-9}$
<i>GFEHCP</i>	(298–1811)	$-3705.78 + 12.591 \bullet T - 1.15 \bullet T \bullet \ln(T) + 6.4 \bullet 10^{-4} \bullet T^2 + \text{GHSEFE}$
	(1811–6000)	$-3957.195 + 5.249009 \bullet T + \text{GHSEFE} + 4.9251 \bullet 1030 \bullet T^{-9}$
<i>GFELIQ</i>	(298–1811)	$+12040.17 - 6.55843 \bullet T - 3.67516 \bullet 10^{-21} \bullet T^7 + \text{GHSEFE}$
	(1811–6000)	$+14544.751 - 8.01055 \bullet T + \text{GHSEFE} - 2.29603 \bullet 1031 \bullet T^{-9}$
<i>GFEOLIQ</i>	(298–6000)	$-137252 + 224.641 \bullet T - 37.1815 \bullet T \bullet \ln(T)$
<i>GFE2O3</i>	(298–3000)	$-858683 + 827.946 \bullet T - 137.0089 \bullet T \bullet \ln(T) + 1453810 \bullet T^{-1}$
<i>GWUSTITE</i>	(298–3000)	$-279318 + 252.848 \bullet T - 46.12826 \bullet T \bullet \ln(T) - 0.0057402984 \bullet T^2$
<i>AWUSTITE</i>	(298–3000)	$-55384 + 27.888 \bullet T$
<i>GFE3O4</i>	(298–3000)	$-161731 + 144.873 \bullet T - 24.9879 \bullet T \bullet \ln(T) - 0.0011952256 \bullet T^2 + 206520 \bullet T^{-1}$
<i>DFE3O4</i>	(298–3000)	$+402520 - 30.529 \bullet T$
<i>BFE3O4</i>	(298–3000)	$+46826 - 27.266 \bullet T$
<i>CFE3O4</i>	(298–3000)	$+120730 - 20.102 \bullet T$
<i>GHSEZR</i>	(130–2128)	$-7827.595 + 125.64905 \bullet T - 24.1618 \bullet T \bullet \ln(T) - 0.00437791 \bullet T^2 + 34971 \bullet T^{-1}$
	(2128–6000)	$-26085.921 + 262.724183 \bullet T - 42.144 \bullet T \bullet \ln(T) - 1.342896 \bullet 1031 \bullet T^{-9}$
<i>GZRBCC</i>	(130–2128)	$-525.539 + 124.9457 \bullet T - 25.607406 \bullet T \bullet \ln(T) - 3.40084 \bullet 10^{-4} \bullet T^2 - 9.729 \bullet 10^{-9} \bullet T^3 + 25233 \bullet T^{-1} - 7.6143 \bullet 10^{-11} \bullet T^4$
	(2128–6000)	$-4620.034 + 1.55998 \bullet T + \text{GHSEZR} + 1.4103476 \bullet 1032 \bullet T^{-9}$
<i>GZRLIQ</i>	(130–2128)	$+18147.69 - 9.080812 \bullet T + \text{GHSEZR} + 1.6275 \bullet 10^{-22} \bullet T^7$
	(2128–6000)	$-8281.26 + 253.812609 \bullet T - 42.144 \bullet T \bullet \ln(T)$
<i>GZRO2M</i>	(298–6000)	$-1126163.54 + 424.890806 \bullet T - 69.3875137 \bullet T \bullet \ln(T) - 0.00375880141 \bullet T^2 + 683000 \bullet T^{-1}$
<i>GZRO2T</i>	(298–6000)	$+5468 - 4 \bullet T + \text{GZRO2M}$
<i>GZRO2C</i>	(298–6000)	$+10336 - 4 \bullet T + \text{GZRO2T}$

Table 3 continued

Phase	Sublattice model	Optimized parameters
<i>GZRO2LIQ</i>	(298–6000)	+87027 −29.17432•T +GZRO2C
<i>GCORUND</i>	(298–600)	−1707351.3 +448.021092•T −67.4804•T•ln(T) −0.06747•T ² +1.4205433•10−5•T ³ +938780•T−1
	(600–1500)	−1724886.06 +754.856573•T −116.258•T•ln(T) −0.0072257•T ² +2.78532•10−7•T ³ +2120700•T−1
	(1500–3000)	−1772163.19 +1053.4548•T −156.058•T•ln(T) +0.00709105•T ² −6.29402•10−7•T ³ +12366650•T−1
<i>GHSERMG</i>	(298–3000)	−8367.34 +143.677875•T −26.1849782•T•ln(T) +4.858•10−4•T ² −1.393669•10−6•T ³ +78950•T−1−14130.185 +204.718543•T −34.3088•T•ln(T) +1.038192•10+28•T−9
<i>GMGLIQ</i>	(298–923)	+8202.243 −8.83693•T +GHSERMG −8.0176•10−20•T ⁷
	(923–3000)	+8690.316 −9.392158•T +GHSERMG −1.038192•10+28•T−9
<i>GMGOLIQ</i>	(298–1700)	−549098.33 +275.724634•T −47.4817•T•ln(T) −0.00232681•T ² +4.5043•10−8•T ³ +516900•T−1
	(1700–2450)	−585159.646 +506.06825•T −78.3772•T•ln(T) +0.0097344•T ² −8.60338•10−7•T ³ +8591550•T−1
	(2450–3100)	+9110429.75 −42013.7634•T +5298.548•T•ln(T) −1.30122485•T ² +5.8262601•10−5•T ³ −3.24037416•109•T−1
	(3100–5100)	−632664.468 +589.239555•T −84•T•ln(T)
<i>GMGOSOL</i>	(298–1700)	−619428.502 +298.253571•T −47.4817•T•ln(T) −0.00232681•T ² +4.5043•10−8•T ³ +516900•T−1
	(1700–3100)	−655489.818 +528.597187•T −78.3772•T•ln(T) +0.0097344•T ² −8.60338•10−7•T ³ +8591550•T−1
	(3100–5000)	−171490.159 −1409.43369•T +163.674142•T•ln(T) −0.044009535•T ² +1.374896•10−6•T ³ −1.72665403•108•T−1
	(5000–5100)	−722412.718 +617.657452•T −84•T•ln(T)
<i>GALAL</i>	(298–6000)	+1.5•GCORUND −0.5•GHSEROO
<i>NSPINEL</i>	(298–6000)	+GMGOSOL +GCORUND −23204.5143 −32.2303298•T +4.31045184•T•ln(T)
<i>ISPINEL</i>	(298–6000)	+NSPINEL +18002.9059 −0.398945666•T
<i>GMGMG</i>	(298–6000)	+NSPINEL +2•ISPINEL −2•GALAL +23.0525839•T
<i>MGVA</i>	(298–6000)	+NSPINEL +8•GALGAMMA −6•GALAL +44.9540891•T +102792.122
<i>GMGGAMMA</i>	(298–6000)	+GMGOSOL +24319.9053
<i>GMGMGMG</i>	(298–6000)	+8•GMGGAMMA −NSPINEL −2•ISPINEL +2•GALAL
<i>GALGAMMA</i>	(298–6000)	+GCORUND +27140.4693 −11.3005601•T
<i>GMGVAMG</i>	(298–6000)	+8•GMGGAMMA −NSPINEL −4•ISPINEL +8•GALGAMMA −2•GALAL−23.0525839•T +44.9540891•T +102792.122
<i>GMGFE3IN</i>	(298–6000)	−1491536.06 +847.138581•T −139.0343•T•ln(T) −0.04400522•T ² +4.8464667•10−7•T ³ +1215870.5•T−1
<i>GMGZRO4</i>	(298–6000)	+GZRO2C +2•GMGOSOL +100000
<i>GANCA</i>	(298–6000)	+23000
<i>GMGFE3NO</i>	(298–6000)	+GMGFE3IN +GANCA

spinel phase dissolves ZrO_2 in the range from 1.2 to 1.8 mol.% at the temperatures of the sintering. Moreover, up to 5 mol.% of MgO could be dissolved in the spinel phase. Such substantial diffusion of MgO from Mg-PSZ to the spinel phase could cause a destabilization of the Mg-PSZ ceramics. At the same time, T- ZrO_2 provides a quite limited solubility of iron cations, which reaches only 1.3 mol.%. In the case of $\text{P}(\text{O}_2) \rightarrow 0$, the solubility of iron oxides in T- ZrO_2 is insignificant (Fig. 13b). For a good performance of TMC, a strong adhesion between the metallic and the ceramic components is required in order to

transmit stresses between different phases. Powder-metalurgical techniques i.e. conventional sintering applied for TMC production provide no crystallographic coherent interface between the components due to the random particle orientation.^[84] Besides this, for additional increase of strength most of the reinforcing zirconia should be present in tetragonal phase after the sintering process. Therefore, a certain thermal stability of the tetragonal phase at the sintering conditions needs to be achieved, so that the phase transformation can occur during mechanical loading of the composite material. In order to attain the best adhesion

Fig. 12 (a), (b) Calculated isothermal sections of the FeO-MgO-ZrO₂ system at 1623 K (a) and 1673 K in presence of iron $x(\text{Fe})=10-5$

Fig. 13 (a), (b) Calculated vertical section of Mg-PSZ (ZrO₂-10 mol.% MgO)-Fe at: (a) $\text{P}(\text{O}_2)=10^{-4} \text{ bar}$; (b) $\text{P}(\text{O}_2) \rightarrow 0$

between the metallic matrix and ceramics, an optimization of the adhesion promoters such as oxides of Mn and Ti can be performed and therefore further development of thermodynamic databases of oxide and metallic system.

9 Conclusions

In the present work the thermodynamic description of the MgO-FeOx system was performed based on the available experimental data. To be consistent with the descriptions of the ZrO₂-MgO system [83] and description of the ZrO₂-FeOx system [24] was slightly modified in the present study.

The phase equilibria in the ZrO₂-MgO-FeOx system were experimentally investigated at 1523, 1673 and 1873 K at air partial pressure of oxygen. Investigation of samples using XRD and SEM/EDX allowed to determine phases co-existing in equilibrium. Melting of Fe-rich sample was observed at 1873 K and composition of binary eutectic were determined.

Based on the obtained results thermodynamic parameters of the ZrO₂-MgO-FeOx system were derived to reproduce experimental results. Calculated composition of binary eutectic is in a good agreement with experimental data.

The derived thermodynamic description of oxide system was merged with available binary descriptions to obtain the description of the Zr-Fe-Mg-O system which was applied to model interfacial phase relations in TMC.

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Funding Open Access funding enabled and organized by Projekt DEAL.

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