Calphad 62 (2018) 187–200

Contents lists available at ScienceDirect

Calphad

journal homepage: www.elsevier.com/locate/calphad

Addition of TiO_2 and Ti_2O_3 to the Al_2O_3-FeO-Fe_2O_3-MgO system

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ARTICLE INFO

Keywords:
Titanium oxides
Phase diagrams
Thermodynamic modelling
Titania Spinel
Pseudobrookite
Corundum

ABSTRACT

The Al_2O_3-FeO-Fe_2O_3-MgO-TiO_2-Ti_2O_3 system has been thermodynamically assessed using all available experimental data. Titanium was introduced into the thermodynamic description of the liquid phase as well as of solid solution phases such as MeO, Cubic Spinel, Titania Spinel, Corundum and Pseudobrookite. Particular attention was given to the phase Cubic Spinel which forms a wide miscibility range amongst Fe_3O_4-$TiFe_2O_4$-$TiMg_2O_4$-$TiMn_2O_4$. In addition, the present modelling of the phase Pseudobrookite allows the description of the experimentally determined mutual solubility between Al_2TiO_5, $MgTi_2O_5$, $FeTi_2O_5$, Fe_2TiO_5 and Ti_3O_5. 9 titanates as stoichiometric phases have also been included in the database.

1. Introduction

Titanium oxide containing systems are attractive materials in various industrial applications. Aluminum titanate in the form of tialite (Al_2TiO_5) is an interesting refractory ceramic with high melting temperature (1860 °C), excellent thermal shock resistance, low average thermal expansion coefficient and low thermal conductivity [1,2]. In addition, tialite has high heat capacity, chemical stability with respect to the molten non-ferrous metals (especially, aluminum) and molten glasses. These properties allow using of Al_2TiO_5 in aluminum foundry refractories, parts of internal combustion engines, diesel particulate filters, high temperature insulating coatings, in components of electrical and electronic devices used at high temperatures, thermocouple shields for temperature measurements of molten glass and non-ferrous metals and lately in coatings of substrates for silicon chips.

The oxide database containing the components CaO-MgO-Al_2O_3-CrO_x-FeO_x-MnO_x-ZnO-P_2O_5-SiO_2-Na_2O-K_2O-(CaF_2, CaS, CrS, FeS, MgS, MnS) has been thermodynamically assessed using all available experimental data on phase equilibria and thermodynamic properties [3]. This database is relevant for the development and production of refractory materials as well as for metallurgical slag applications, glass processing, or ash/slag formation during coal/biomass combustion and gasification. In the present study the titanium oxides TiO_2 and Ti_2O_3 have been integrated into the reduced core system MgO-Al_2O_3-FeO-Fe_2O_3. The experimental information on the thermodynamic properties of the titanium containing oxide systems (phase diagram, phase transition etc.) is used for the generation of Gibbs energy datasets for all known phases and compounds.

Ternary Me-Ti-O systems are not a subject of the present study, but some metallic-oxygen phases were adopted from other assessments with small modifications. The thermodynamic descriptions of the titanium-oxygen system given by Waldner and Eriksson [4] and Cancarevic and Zinkevich [5] were taken into account, the liquid phase was re-optimized in this work using the non-ideal associate solution model [6] with the associates Ti_2O_2, Ti_2O_3, Ti_2O_4 resulting from the two-sublattice ionic liquid model used by Waldner and Eriksson.

In order to reproduce the properties of binary and ternary subsystems in the Al_2O_3-FeO-Fe_2O_3-MgO-TiO_2-Ti_2O_3 system the Gibbs energy functions for all non-ideal phases have been generated using suitable thermodynamic models. The datasets are used for the reproduction and calculation of thermodynamic properties and the prediction of value in multicomponent systems in known as well as in unknown regions of temperature and composition.

The Gibbs energy of the liquid phase has been modelled using a non-ideal associate solution model proposed by Besmann and Spear [6]. This model has been successfully applied for the description of melts containing oxides and sulphides in our previous studies, e.g. [7–10].

Solubilities in the solid state have been treated using the multi-sublattice approach based on the structure of the corresponding phases. In the present study there are four fundamental solid solution series with different structure which form wide completely miscible solid solutions at high temperatures. The first one called α-oxides $(Me)_m(Me)_{2-m}O_3$ with rhombohedral structure is described with the following end-members: Al_2O_3, Fe_2O_3, Ti_2O_3, $MgTiO_3$, $FeTiO_3$. The Cubic spinel phase with formula $Me_nMe_{3-n}O_4$ includes Fe_3O_4, $TiFe_2O_4$, $TiMg_2O_4$, $MgAl_2O_4$ as end-members. The phase with the composition

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https://doi.org/10.1016/j.calphad.2018.05.009
Received 5 April 2018; Received in revised form 24 May 2018; Accepted 25 May 2018

$Me_xTi_{3-x}O_5$ relating to the orthorhombic structure is modelled with the following end-members Al_2TiO_5, Mg_2TiO_5, Fe_2TiO_5, $FeTi_2O_5$ and Ti_3O_5. All these phases called in this work Corundum, Cubic spinel and Pseudobrookite, correspondingly, are modelled using sub-lattice models which allow the description of both the experimentally determined complete solubility at high temperatures and mutual solubility at lower temperatures. In the present assessment titanium appears also in additional solid solution phases such as monoxide MeO and Titania spinel. Titania spinel including iron as well as titanium in two different oxidation states, 2 +, 3 + and 3 +, 4 + respectively, was modelled to describe the corresponding phase relations in the complete oxide system under consideration. This resulted in the thermodynamic description of 5 binary and 7 ternary oxide systems, which will be given below.

2. Thermodynamic models

The present database contains a gas phase, a multi-component liquid phase, 5 solid solutions and a total of 35 solid stoichiometric compounds, including 9 titanates. The Gibbs energies of the pure oxides and stoichiometric compounds were taken from the SGTE Pure Substance database [11], thermodynamic descriptions of titanium oxides were taken from [4]. The crystal structure data of the pure stoichiometric titanates are collected in the Table 1. The thermodynamic descriptions of the stoichiometric titanates are presented in Table 2. The associates introduced into the liquid phase are collected in Table 3. All phases in the titanium oxides containing systems considered in the present work are given in Table 4 and are described below in more detail.

2.1. Slag phase

The Gibbs energy of the liquid phase in the system is represented by the modified non-ideal associate species model [6]. The basic species such as TiO_x have been adopted from the corresponding binary assessment of Waldner [4]. However, the present work will attend to the melt oxide species; the interactions between these oxides and other oxide species are responsible for the thermodynamic properties of the liquid phase. To provide equal weighting of each associate species with regard to its entropic contribution in the ideal mixing term, each species contains a total of two cations in its formula according to the model used [6]. In addition, interactions between associate species were introduced in order to fine tune the thermodynamic description.

The molar Gibbs energy of the solution is presented by a three-term expression with contributions of the reference part, the ideal and the excess part taking into account binary interactions as follows:

$$G_m = \sum x_i {}^\circ G_i + RT \sum x_i ln x_i + \sum \sum_{i<j} x_i x_j \sum_{v=0} L_{ij}^{(v)} (x_i - x_j)^v \quad (1)$$

where x_i is the mole fraction of phase constituent i (including the associate species), G_i° is the molar Gibbs energy of the pure phase constituent and $L_{ij}^{(v)}$ is an interaction coefficient between components i and j, according to the Redlich-Kister polynomial. and $L_{ij}^{(v)}$ with $v = 0, 1, 2$ are temperature dependent in the same way according to equation:

$${}^\circ G_i, L_{ij}^{(v)} = A + B*T + c*T*\ln(T) + D*T^2 + E*T^{-1} \quad (2)$$

Thermodynamic data for the liquid components are summarized in Table 3. In the system Ti-O the different oxides of titanium resulting from the two-sublattice ionic liquid model used by Waldner and Eriksson [4], namely Ti_2O_2, Ti_2O_3, Ti_2O_4, were considered. Their data have been taken from the reference with some modifications. The liquid phase of the binary oxide systems containing TiO_2 and Ti_2O_3 is described with similar sets of associates in order to provide a handle for the use in ternary assessments and later in quaternary systems. For systems of the type Me_2O_3-TiO_2 with Me = Al, Fe one associate species of the type $Me_2O_3{\cdot}TiO_2$ was included, while for MeO-TiO_2 systems with Me = Fe, Mg two associate species, $MeO{\cdot}TiO_2$ and $2MeO{\cdot}TiO_2$, and additionally $MeO{\cdot}2TiO_2$ for the MgO-TiO_2 system were introduced. Moreover, the species $MgO{\cdot}Ti_2O_3$ was added to reproduce the melting behavior in the corresponding MgO-TiO_2-Ti_2O_3 system containing titanium with oxidation states 3 + and 4 +. The Gibbs energy of the binary species $FeTiO_3$ and Al_2TiO_5 are taken from the SGTE Pure Substance database [11] without modifications, whereas $MgTiO_3$ and Mg_2TiO_4 were slightly modified to obtain a better agreement with experimental data on phase relations. The thermodynamic functions of the remaining binary species (Fe_2TiO_5, Fe_2TiO_4, $MgTi_2O_5$ and $MgTi_2O_4$) are modelled in the present work using the melting data of the corresponding solids. The interactions between liquid species are listed in Table 4.

2.2. Cubic spinel

Magnesium aluminate Al_2MgO_4 has the cubic spinel structure (space group *Fd-3m*) and Pearson symbol cF56 [12]. This spinel structure is present in many systems, e.g. as magnetite Fe_3O_4 in the Fe-O system, hercynite Al_2FeO_4 in the Al_2O_3-FeO system, magnesioferrite $MgFe_2O_4$ in MgO-Fe_2O_3 and also ulvöspinel Fe_2TiO_4 in FeO-TiO_2. In the Al_2O_3-MgO binary system the spinel phase is located in the middle of the phase diagram and exhibits a very wide experimentally determined solubility range [17–25]. Spinels $(A_{1-x},B_x)(B_{2-x},A_x)(O)_4$ have a very compact oxygen structure, with cations in tetragonal (T) and octahedral (O) coordination. A and B cations with variable valence are distributed in T and O sites, where x is the inversion parameter [26]. A thermodynamic assessment of the Al_2O_3-MgO system was carried out by Hallstedt [15] where the thermodynamic description of the Spinel phase with respect to normal (x = 0, AB_2O_4) and inverse spinel (x = 1, $B(B,A)O_4$) could reproduce the experimental data very well. Hallstedt [15] proposed the formula $(Al^{3+},\underline{Mg^{2+}})(\underline{Al^{3+}},Mg^{2+},Va)_2(Mg^{2+},\underline{Va})_2(O^{2-})_4$ assuming that the tetragonal and octahedral sublattices can be occupied by aluminum and magnesium cations while the oxygen ions form an fcc lattice [15]. The introduction of the third cation-ionic sublattice occupied by vacancies and magnesium cations allows to describe the deviation from the stoichiometry towards higher MgO-contents. The Gibbs energy of the phase Spinel was based on the Gibbs energies of 12 real and fictive compounds which Hallstedt [15] has estimated using reciprocal equations. Unfortunately the Gibbs energy of the fictive compound $G(Al^{3+}:Al^{3+}:Va:O^{2-})$ was set to be zero, which made the description of the Spinel phase in the binary system Fe-O by [16] and in the Al_2O_3-MgO system [15] incompatible. By the accepting

$${}^\circ G_{Al^{3+}:Fe^{2+}:Va:O^{2-}} = 0.5*{}^\circ G_{Fe^{2+}:Al^{3+}:Va:O^{2-}} + 0.5* \quad {}^\circ G_{Fe^{2+}:Fe^{2+}:Va:O^{2-}} \quad (3)$$

and also using the reciprocal equation

$${}^\circ G_{Al^{3+}:Al^{3+}:Va:O^{-2}} + {}^\circ G_{Fe^{2+}:Fe^{2+}:Va:O^{2-}} = {}^\circ G_{Fe^{2+}:Al^{3+}:Va:O^{2-}} + {}^\circ G_{Al^{3+}:Fe^{2+}:Va:O^{2-}} \quad (4)$$

Table 1
Crystal structure data of titanates [12].

Titanate	Name	Pearson Symbol	Space Group No	Prototype
Al_2TiO_5	Tialite	oC32	63	$TiFe_2O_5$
$FeTiO_3$	Ilmenite	hR30	148	TiFeO3
Fe_2TiO_4	Ülvospinel	cF56	227	$MgAl_2O_4$
Fe_2TiO_5	Kennedyite	oC32	63	$TiFe_2O_5$
$FeTi_2O_5$	Pseudobrookite	oC32	63	$TiFe_2O_5$
$MgTiO_3$	Geikielite	hR30	148	TiFeO3
Mg_2TiO_4	Qandilite	cF56	227	$MgAl_2O_4$
$MgTi_2O_4$	Qandilite	cF56	227	$MgAl_2O_4$
$MgTi_2O_5$	Karrooite	oC32	63	$TiFe_2O_5$