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SCIENCE DIRECT
Computer Coupling of Phase Diagrams and Thermochemistry 30 (2006) 226–234
www.elsevier.com/locate/calphad

Critical thermodynamic evaluation and optimization of the MnO–SiO_2–"TiO_2"–"Ti_2O_3" system

Youn-Bae Kang[a,*,1], In-Ho Jung[b], Hae-Geon Lee[c]

[a] *Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Republic of Korea*
[b] *Research Institute of Industrial Science and Technology (RIST), Pohang 790-600, Republic of Korea*
[c] *Graduate Institute of Ferrous Technology (GIFT), Pohang University of Science and Technology (POSTECH), Pohang 790-784, Republic of Korea*

Received 5 February 2006; received in revised form 19 April 2006; accepted 8 May 2006
Available online 12 June 2006

Abstract

A complete review, critical evaluation, and thermodynamic optimization of phase equilibrium and thermodynamic properties of the MnO–SiO_2–"TiO_2"–"Ti_2O_3" systems at 1 bar pressure are presented. The molten oxide phase was described by the Modified Quasichemical Model. The Gibbs energies of the manganosite, spinel, pyrophanite and pseudobrookite and rutile solid solutions were taken from the previous study. A set of optimized model parameters for the molten oxide phase was obtained which reproduces all available reliable thermodynamic and phase equilibrium data within experimental error limits from 25 °C to above the liquidus temperatures over the entire range of compositions and oxygen partial pressure in the range of pO_2 from 10^{-20} bar to 10^{-7} bar. Complex phase relationships in these systems have been elucidated, and discrepancies among the data have been resolved. The database of model parameters can be used along with software for Gibbs energy minimization in order to calculate any phase diagram section or thermodynamic properties.

Keywords: MnO–SiO_2–TiO_2–Ti_2O_3; Solution thermodynamics; Non-metallic inclusion; Phase diagram

1. Introduction

MnO–SiO_2–TiO_x–MnS type inclusions have been recognized as one of the most effective inclusions for grain refinement of steel by acting as the nucleation site of ferrite in the austenite matrix. A number of investigations have been conducted to characterize the role of these inclusions on grain refinement [1–5]. Several researches on the liquidus and thermodynamic properties of the MnO–SiO_2–TiO_x–MnS system have been reported by several investigators [6–10]. However, many of those studies failed to control in a quantitative manner the oxygen potential, which plays a decisive role on the phase equilibria and thermodynamics of the system, and overlooked the possibility of formation of various solid solutions [6–10]. In the present study, phase equilibria and thermodynamics for the system of MnO–SiO_2–"TiO_2"–"Ti_2O_3" were investigated by a combination of experiments and thermodynamic modeling with careful consideration of the above mentioned facts. Experimental results have already been reported [11,12]. Thermodynamic optimization of the MnO–"TiO_2"–"Ti_2O_3" system is presented separately [13] and hence thermodynamic modeling on the MnO–SiO_2–"TiO_2"–"Ti_2O_3" system is given in the present paper.

2. Thermodynamic models

2.1. Molten oxide

The Modified Quasichemical Model was used for the molten oxide phase [14–17]. Short-range-ordering is taken into account by considering second-nearest-neighbor pair exchange reactions. For example, for the MnO–SiO_2–"TiO_2"–"Ti_2O_3" molten oxide, these reactions are:

$$(A-A)+(B-B)=2(A-B) \quad \Delta g_{AB} \tag{1}$$

where A and B are Mn, Si, Ti^{4+} and Ti^{3+}, and $(i-j)$ represents a second-nearest-neighbor $i-j$ pair. The parameters

* Corresponding author. Tel.: +1 514 340 4711x4303; fax: +1 514 340 5840.
E-mail address: youn-bae.kang@polymtl.ca (Y.-B. Kang).
[1] Present address: Centre de Recherche en Calcul Thermochimique (CRCT), École Polytechnique, Montreal, Quebec H3C 3A7, Canada.

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doi:10.1016/j.calphad.2006.05.002

Table 1
Optimized model parameters of the molten oxide in the MnO–SiO_2–"TiO_2"–"Ti_2O_3" system (J/mole)[a]

Liquid oxide: MnO–SiO_2–"TiO_2"–"$TiO_{1.5}$"[b]
For MnO–SiO_2–"TiO_2" system (Kohler-like symmetric) $q^{104}_{SiO_2,MnO,TiO_2} = -46024, \quad q^{001}_{SiO_2,MnO,TiO_2} = -19246.4$
For MnO–SiO_2–"$Ti_2O_{1.5}$" system (Kohler-like symmetric) $q^{101}_{SiO_2,MnO,Ti_2O_{1.5}} = -194388.64 + 83.68T,$

[a] The Gibbs energies of pure components of the liquid solution and of the other stoichiometric compounds and solid solutions in the MnO–SiO_2–"TiO_2"–"Ti_2O_3" system are taken from Refs. [13,18,19].

[b] Binary model parameters for the MnO–SiO_2, MnO–"TiO_2", SiO_2–"TiO_2", SiO_2–"Ti_2O_3", and "TiO_2"–"Ti_2O_3" systems of the Modified Quasichemical Model are shown in Refs. [13,18,25].

of the model are the Gibbs energies of these reactions, which may be expanded as empirical functions of composition. Although manganese can exist in the trivalent state in the slag at high oxygen partial pressures, in the present study only divalent manganese is considered, while trivalent and tetravalent titanium are considered to exist in the molten oxide.

The binary model parameters obtained by evaluation/optimization of all data in the MnO–SiO_2 [18], MnO–"TiO_2" [13], MnO–"Ti_2O_3" [13], "TiO_2"–"Ti_2O_3" [13], SiO_2–"TiO_2" [25] and SiO_2–"Ti_2O_3" [25] binary sub-systems are given in references along with the second-nearest-neighbor "coordination numbers" of Mn, Si, Ti^{4+} and Ti^{3+} used in the Modified Quasichemical Model. For the MnO–"TiO_2"–"Ti_2O_3" and the SiO_2–"Ti_2O_3"–"TiO_2" systems, a Toop-like "asymmetric approximation" [20,21] was used with MnO and "Ti_2O_3" as the "asymmetric components", respectively, in order to estimate the Gibbs energy of the ternary liquid from the binary Gibbs energy parameters. No ternary parameters were used for any of the ternary systems. In the case of the MnO–SiO_2–"TiO_2" and the MnO–SiO_2–"Ti_2O_3" systems, Kohler-like "symmetric approximation" [20,21] was used. In order to reproduce the measured experimental data in the MnO–SiO_2–"TiO_2"–"Ti_2O_3" system, two optimized ternary model parameters were added in the MnO–SiO_2–"TiO_2" system and one optimized ternary model parameter with a temperature dependence term was added in the MnO–SiO_2–"Ti_2O_3" system during the present study. The optimized ternary model parameters are listed in Table 1.

2.2. Solid solutions

Several solid solutions in the MnO–SiO_2–"TiO_2"–"Ti_2O_3" system such as manganosite, spinel, pyrophanite, pseudobrookite and rutile were modeled using the Henrian solution model or Compound Energy Formalism; the optimized model parameters for the solutions were given in the previous article [13]. No ternary solid solution was observed in the previous study [12].

2.3. Stoichiometric compounds

SiO_2 (quartz, tridymite and cristobalite), Mn_2SiO_4 (tephroite), $MnSiO_3$ (rhodonite) and several Magnéli phases

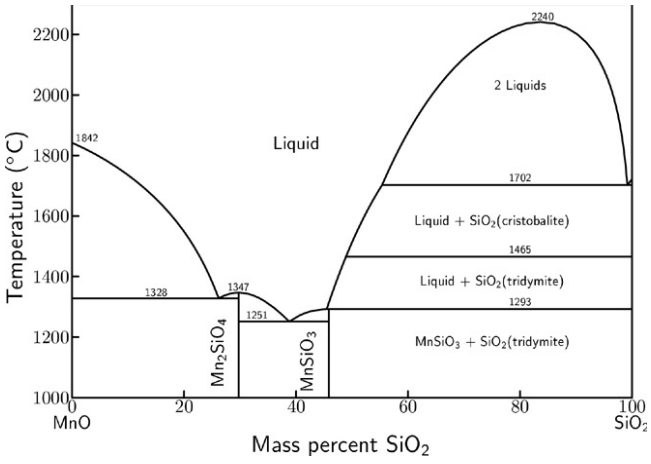

Fig. 1. Optimized phase diagram of the MnO–SiO_2 system by Eriksson et al. [18].

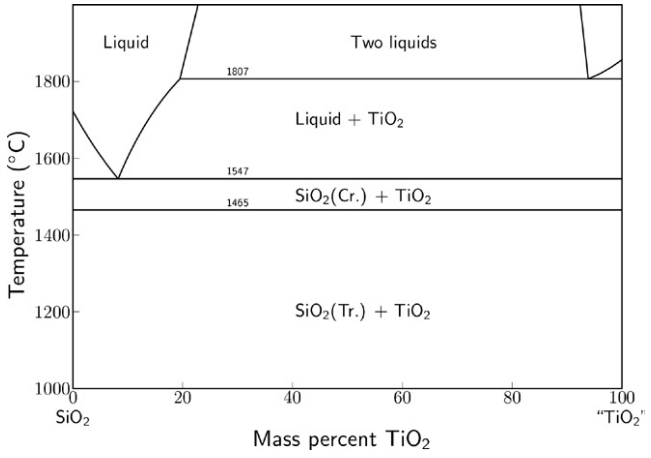

Fig. 2. Optimized phase diagram of the SiO_2–"TiO_2" system by Pelton and Eriksson [25].

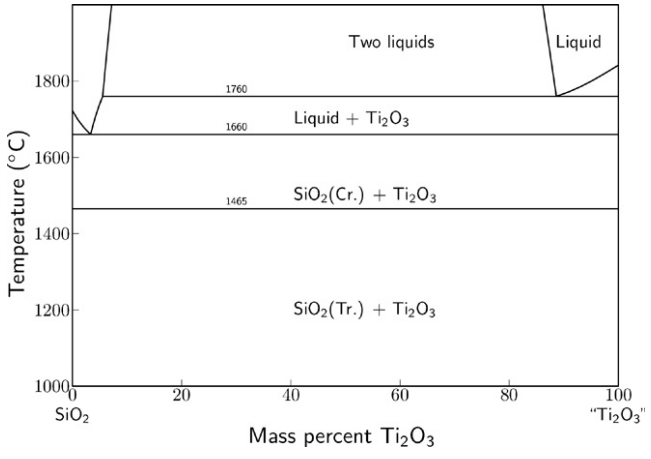

Fig. 3. Optimized phase diagram of the SiO_2–"Ti_2O_3" system by Pelton and Eriksson [25].

(Ti_nO_{2n-1}, $n \geq 4$) were considered as stoichiometric compounds. Although the small solubility of titanium oxide in SiO_2 (less than 3.5 mass pct) [12] and that of manganese oxide in Magnéli phase (less than 2.3 mass pct) was observed [22], it