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Thermodynamic analysis of the SiO_2–NiO–FeO system

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Abstract

The evaluation of the thermodynamic properties and phase diagrams of the FeO–SiO_2, NiO–SiO_2 and SiO_2–NiO–FeO systems is presented in which a structural model is used for the liquid phase. This thermodynamic model is based on the assumption that each metallic oxide produces the depolymerization reaction of silica network with a characteristic free energy change. A least squares optimization program permits all available thermodynamic and phase diagram data to be optimized simultaneously for the binary systems. In this manner, data for these binary systems have been analyzed and represented with a small number of parameters. The binary structural model is extended to the ternary system assuming a random mixing of cations Fe^{2+} and Ni^{2+}, since the FeO–SiO_2 and NiO–SiO_2 binary systems exhibit similar thermodynamic behavior, that is comparable free energies of mixing.

1. Introduction

The reduction of non-ferrous metal values from slags is currently the subject of considerable research and development effort in the extractive metallurgy industry. The widespread introduction of new processes and the trend to the production of higher-grade mattes in the copper and nickel industries have led to increased metal losses to the slag phase during smelting. In order to estimate the loss of nickel to slags by dissolution during smelting and converting processes it is necessary to know the activity of nickel oxide as a function of composition in relevant (predominantly iron–silicate) slags. In this context some researchers [1–3] have conducted experimental studies of the solubility and activity of nickel oxide in iron–silicates based slags.

Many models have been proposed to calculate the thermodynamic properties of ordered solutions such as liquid silicates [4]. Lin and Pelton [5] developed a structural model for binary silicate systems MO–SiO_2 (M = Ca, Mn, Mg, etc.) where one single formalism applies over the entire composition range and accounts for two- and three-dimensional silicate network structure. Recently, the model has been examined in more depth and a general empirical expression for enthalpy has been written and an empirical non-configurational excess entropy has been added [6].

This structural model was also extended to ternary systems [7]. It is shown that, for systems SiO_2–AO–BO, random mixing of cations A^{2+} and B^{2+} occurs when the oxides AO and BO behave in a similar way with silicate. If the AO–SiO_2 and BO–SiO_2 binary systems exhibit similar thermodynamic behavior, that is comparable free energies of mixing, the properties of the ternary SiO_2–AO–BO can be extrapolated from those binary systems in a straightforward fashion. This condition is found in simple silicates such as SiO_2–MnO–MgO, SiO_2–FeO–MnO and SiO_2–FeO–MgO systems where the activities and liquidus temperatures calculated solely from data on the binary sub-systems are in good agreement with measured ternary data. The aim of the present work is to apply the structural model for the FeO–SiO_2 and NiO–SiO_2 binary systems and the extended model to calculate activities and phase diagram

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of the SiO_2–NiO–FeO system solely from the assessed parameters for the binary subsystems.

2. Structural model

2.1. Structural model for binary systems

A detailed development was given previously [6]. Only a brief summary will be presented here. For binary silicate systems it is generally accepted that all Si atoms are tetrahedrally bonded to four oxygen atoms The model is based on the depolymerization reaction of SiO_2:

$$\text{Si–O–Si} + \text{MO} = \text{Si–}\overset{\text{M}^{2+}}{\text{OO}}\text{–Si} \tag{1}$$

or, in shorthand notation

$$\text{O}^0 + \text{O}^{2-} = 2\text{O}^- \tag{2}$$

where O^0 is a bridging oxygen bonded to two silicon atoms, O^{2-} is a free oxygen ion, and O^- is an oxygen single bonded to one silicon atom. It is assumed that every silicon atom is bonded to four oxygen atoms. Thus, mass balance considerations require that

$$\text{N}_{\text{O}^0} = 2\text{X}_{\text{SiO}_2} - \frac{\text{N}_{\text{O}^-}}{2}, \tag{3}$$

$$\text{N}_{\text{O}^{2-}} = \text{X}_{\text{MO}} - \frac{\text{N}_{\text{O}^-}}{2}, \tag{4}$$

where X_{MO} and X_{SiO_2} are the mole fractions of the components and N_{O^0}, N_{O^-} and $N_{O^{2-}}$ are the number of moles of the various oxygen species per mole of solution. The first term of the configurational entropy is calculated by assuming a tetrahedral quasi-lattice in which the sites are occupied by O^{2-} ions and Si atoms (each associated with four oxygen atoms bonded to it); the second term is obtained by distributing the oxygen bridges (O^0) over the neighboring Si–Si pairs

$$\begin{aligned}\Delta\text{S}^{\text{c}} = -\text{R}\Bigg[&\text{X}_{\text{SiO}_2}\ln\left(\frac{\text{X}_{\text{SiO}_2}}{\text{X}_{\text{SiO}_2}+\text{N}_{\text{O}^{2-}}}\right) \\ &+\text{N}_{\text{O}^{2-}}\ln\left(\frac{\text{N}_{\text{O}^{2-}}}{\text{X}_{\text{SiO}_2}+\text{N}_{\text{O}^{2-}}}\right)\Bigg] - \text{R}\left[\text{N}_{\text{O}^0}\ln\left(\frac{\text{N}_{\text{O}^0}}{\text{N}_{\text{Si–Si}}}\right)\right. \\ &\left.+(\text{N}_{\text{Si–Si}}-\text{N}_{\text{O}^0})\ln\left(\frac{\text{N}_{\text{Si–Si}}-\text{N}_{\text{O}^0}}{\text{N}_{\text{Si–Si}}}\right)\right].\end{aligned} \tag{5}$$

$N_{Si–Si}$ is the number of moles of neighboring Si–Si pairs per mole of solution. Since there are now O^{2-} ions as well as Si atoms on the quasi-lattice sites, $N_{Si–Si}$ is given by

$$\text{N}_{\text{Si–Si}} = 2\text{X}_{\text{SiO}_2}\left(\frac{\text{X}_{\text{SiO}_2}}{\text{X}_{\text{SiO}_2}+\text{N}_{\text{O}^{2-}}}\right), \tag{6}$$

where once again the co-ordination number of the quasi-lattice is assumed to be four. The structural model assumes that Reaction (1) is associated with a Gibbs energy change containing an enthalpic (ω) and entropic (η) term

$$\Delta\text{H} = \left(\frac{\text{N}_{\text{O}^-}}{2}\right)\omega, \tag{7}$$

$$\text{S}^{\text{nc}} = \left(\frac{\text{N}_{\text{O}^-}}{2}\right)\eta. \tag{8}$$

Finally, ω and η are expanded as polynomials

$$\omega = \omega_0 + \omega_1\text{X}_{\text{SiO}_2} + \omega_2\text{X}^2_{\text{SiO}_2} + \cdots \tag{9}$$

$$\eta = \eta_0 + \eta_1\text{X}_{\text{SiO}_2} + \eta_2\text{X}^2_{\text{SiO}_2} + \cdots \tag{10}$$

The coefficients ω_i and η_i are the parameters of the model which are obtained by optimization of the data. Given a composition, X_{SiO_2}, and values of the parameters ω_i and η_i, the actual value of N_{O^-} can be calculated by minimizing the Gibbs energy at constant X_{SiO_2}, ω and η

$$\Delta\text{G} = \Delta\text{H} - \text{T}(\Delta\text{S}^{\text{c}} + \text{S}^{\text{nc}}), \tag{11}$$

$$\begin{aligned}2\left[\frac{\partial\Delta\text{G}}{\partial\text{N}_{\text{O}^-}}\right]_{\text{X}_{\text{SiO}_2},\omega,\eta} &= (\omega-\eta\text{T}) - \text{RT}\left[\ln\left(\frac{\text{N}_{\text{O}^{2-}}}{\text{X}_{\text{SiO}_2}+\text{N}_{\text{O}^{2-}}}\right)\right. \\ &\quad+\ln\left(\frac{\text{N}_{\text{O}^0}}{\text{N}_{\text{Si–Si}}}\right) - \left(1+\frac{\text{N}_{\text{Si–Si}}}{\text{X}_{\text{SiO}_2}+\text{N}_{\text{O}^{2-}}}\right) \\ &\quad\left.\times\ln\left(\frac{\text{N}_{\text{Si–Si}}-\text{N}_{\text{O}^0}}{\text{N}_{\text{Si–Si}}}\right)\right] = 0.\end{aligned} \tag{12}$$

Substitution of Eqs. (3), (4) and (6) into (12) gives an equation in terms of X_{MO} (or X_{SiO_2}) and N_{O^-}, which can be solved numerically at a fixed composition and for given values of the parameters ω_i and η_i to give N_{O^-}. This value can then be substituted back into Eqs. (3)–(5), (7) and (8) to give ΔS and ΔH.

Since all integral and partial properties are expressed in terms of the same parameters (ω_i and η_i) all available data (phase diagrams, activities, enthalpies, etc.) can be considered in one simultaneous least-squares optimization. For the present model, a non-linear least-squares optimization program was written. Copies of this software may be obtained by contacting the authors.

2.2. Structural model for ternary systems

Let us consider the general SiO_2–AO–BO ternary system where A and B are divalent cations. Let us assume also that these cations can mix randomly in a quasilattice. The mass balance considerations (3) and (4) requires now that

$$\text{N}_{\text{O}^0} = 2\text{X}_{\text{SiO}_2} - \frac{\text{N}_{\text{O}^-}}{2}, \tag{13}$$

$$\text{N}_{\text{O}^{2-}} = (\text{X}_{\text{AO}} + \text{X}_{\text{BO}}) - \frac{\text{N}_{\text{O}^-}}{2}. \tag{14}$$