Standard Enthalpy of Formation of Crystalline Titanomagnetites (FeO)\textsubscript{x} \cdot TiO\textsubscript{2}

A. G. Ryabukhin\textsuperscript{a}, A. V. Roshin\textsuperscript{b}, and V. E. Roshin\textsuperscript{a}

\textsuperscript{a} Southern Ural State University, Chelyabinsk, Russia
\textsuperscript{b} Institute of Metallurgy and Materials Science (Southern Ural Branch), Ural Division, Russian Academy of Sciences, Chelyabinsk, Russia

e-mail: ant@met.susu.ac.ru

Received May 15, 2006

Abstract—A mathematical model developed previously is used to obtain equations for the calculation of the standard enthalpies of formation of some stoichiometric oxides and complex oxides of a variable composition in the Fe–O–Ti system. These entropies have been determined.

PACS numbers: 82.60.Cx

DOI: 10.1134/S003602950701003X

INTRODUCTION

It has been shown experimentally [1–3] that, upon metal reduction from oxides, an oxide crystal lattice transforms into a metal crystal lattice through the removal of oxygen anions to form charged anion vacancies in the oxide lattice. As vacancies are accumulated, the oxide composition changes gradually from the higher to lower oxide and, then, to a metal, passing through the formation of a number of compounds of variable composition (which are called berthollides). To describe the corresponding crystallochemical transformations and to perform their thermodynamic estimation, one has to know the fundamental thermodynamic characteristics (heat capacities, enthalpies, entropies, etc.) of such oxides.

There were several attempts to relate the properties of substances to the atomic nucleus charges. Empirical equations for solving various particular problems were obtained. However, these equations usually include the “effective” nucleus charge [4] numerically equal to the atomic number of an element with a variable correction coefficient, whose quantity was not grounded distinctly. The interesting model in [5–7] also has these drawbacks. Meanwhile, the specific features of interacting particles explicitly manifest themselves in their spatial arrangement. Indeed, it is interparticle interactions that determine the crystal systems of compounds with specific crystal-lattice parameters.

When developing our mathematical model for the calculation of the standard enthalpy of oxide formation, we borrowed the idea of the dependence of the standard enthalpy of formation on the specific (per unit nucleus charge) enthalpy \( h \) and composition [5–7] and the ideas from tested models [8, 9] for the calculation of the heat capacity and entropy. These ideas proposed to divide a composition–property field into solid-solution regions and to introduce the concepts of a crystal-forming (CF) component and a bulk structural constant \( K \).

Every nucleus charge is taken to have the same enthalpy; therefore, the specific enthalpy is an effective quantity and can be determined from the relation

\[ h = \frac{-\Delta_f H}{\Sigma Z}, \]

where \( \Sigma Z \) is the sum of the nucleus charges (atomic numbers of the elements) with regard for the oxide composition.

The dependence of \( h \) on the composition \( x \) (\( x \) is the mole fraction of oxygen per mole of the metal) can be expressed by the linear equation [8, 9]

\[ h = a + Kx, \]

where \( a \) is the specific enthalpy of formation of the crystal-forming component.

The whole field of a composition–enthalpy diagram is divided into solid-solution regions in which crystal-forming components are distinguished. A metal is always a crystal-forming component in the first solid-solution region. Since \( \Delta_f H = 0 \) for a metal, the \( h = f(x) \) dependence in any \( M–O \) system always starts at zero. In other solid-solution regions, any stable oxide with a known composition, structure, and enthalpy of formation can be taken as a crystal-forming element. However, in this case, the parameter \( x \) should take into account the oxygen that is contained in the crystal-forming oxide. Therefore, Eq. (2) for other solid-solution regions with an oxide as a crystal-forming component takes the form

\[ h = h(CF) + K(x - x(CF)). \]
Since the value of $K$ is different in each region and depends on a combination of the structural constants and coordination numbers of the lattices conjugated at region boundaries, the coordinates of the boundaries are determined by the simultaneous solution of corresponding Eqs. (3).

In [9, 10], we showed that the standard enthalpy of formation of binary $d$- and $p$-element oxides of an arbitrary composition can be calculated using this procedure. It seems necessary to check the possibility of using this mathematical model for the calculation of the standard enthalpy of formation for more complex oxide systems, in particular, for the crystalline titanomagnetites $(\text{FeO})_x \cdot \text{TiO}_2$. In this case, $x$ is the number of FeO moles per mole of TiO$_2$. The calculation of the standard heat capacities and entropies of these complex oxides using similar procedures [11] showed that the system under study contains two solid-solution regions with a boundary at $x = 1$, which corresponds to ilmenite FeO · TiO$_2$.

### FIRST SOLID-SOLUTION REGION ($X \leq 1$)

In this region, titanium dioxide (rutile) is a CF element. Therefore, an equation for the specific enthalpy has the form

$$h_1((\text{FeO})_x \cdot \text{TiO}_2) = h(\text{TiO}_2) - K_1(x - x(\text{TiO}_2)),$$

where $x$ is the fraction of FeO in the (FeO)$_x \cdot$ TiO$_2$ complex oxide. Since the CF substance (rutile) contains no FeO, $x(\text{TiO}_2) = 0$. Rutile crystallizes in a tetragonal structure (t-2). The outer boundary of the region is ilmenite FeO · TiO$_2$ or FeTiO$_3$ with an hcp-2 structure. The sequential transition from the t-2 ($k_t = \sqrt{2} - 1$) to the hcp-2 structure ($k_{\text{hcp}} = \frac{8}{3\sqrt{3}}$) corresponds to a bulk structural constant $K_1' = k_t \times k_{\text{hcp}} = \left(\sqrt{2} - 1\right) \frac{8}{3\sqrt{3}} = 0.6377$. The coordination number is 12 and, therefore, $K_1 = 12K_1' = 12 \times 0.6377 = 7.6527$. Allowing for the numerical value of $K_1$ and $h(\text{TiO}_2) = 24.8508$ calculated using Eq. (1), we rewrite Eq. (3) in the form

$$h_1((\text{FeO})_x \cdot \text{TiO}_2) = h(\text{TiO}_2) - K_1 x = 24.8508 - 7.6527x.$$

### SECOND SOLID-SOLUTION REGION ($1 \leq X \leq 2$)

Ilmenite FeO · TiO$_2$ (FeTiO$_3$) with an hcp-2 structure is a CF component in this region. While it is gradually enriched in FeO, the hcp structure of ilmenite transforms into the spinel structure 2FeO · TiO$_2$ ($\text{Fe}_2\text{TiO}_4$ is a 2-4-type spinel, $k_{\text{sp}} = 3/4$). The bulk structural constant for a coordination number of six is equal to $K_2 = \frac{3\sqrt{3}}{8} \frac{3}{4} = 2.9228$, and Eq. (3) takes the form

$$h_2((\text{FeO})_x \cdot \text{TiO}_2) = h(\text{FeO} \cdot \text{TiO}_2) - K_2(x - x(\text{FeO} \cdot \text{TiO}_2)).$$

Taking into account that $h(\text{FeO} \cdot \text{TiO}_2) = 17.1981$, $K_2 = 2.9228$, and $x(\text{FeO} \cdot \text{TiO}_2) = 1$, we obtain

$$h_2((\text{FeO})_x \cdot \text{TiO}_2) = 17.1981 - 2.9228(x - 1) = 20.1209 - 2.9228x.$$