Thermodynamic study and modelling of iron-based melts for adequate prediction of modern ladle metallurgy processes

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Abstract. The representation of iron-based melts as associated liquids have been developed basing on the detail experimental investigation and analysis of available data on their thermodynamic properties and phase equilibria. It has allowed, for the first time, to interpret adequately the reactivity of the earth metals in the iron-based melts and to predict with high precision the reactions of metal refinement and non-metallic inclusions modifying in modern ladle metallurgy.

Progress in the development of metallurgy is mainly related to the development and introduction of novel technologies. The methods of out-of-furnace treatment of steel have radically changed the process of steel-making. The abilities of refining, alloying, finishing of the chemical composition of a metal allow one to decrease the content of harmful impurities and to improve the physico-chemical and mechanical properties of metallic materials. The development of the methods of melt treatment in a ladle has transformed the nonmetallic phases of steel. In most cases, their effect on the service properties of a metal is still insufficiently known. Therefore, the control of the composition of inclusions has become crucial in modern steel-making processes.

To predict the types and amounts of nonmetallic inclusions forming upon ladle treatment of steel, researchers widely use the methods of physicochemical simulation and calculation based on both laboratory and industrial data. Among them, metal deoxidation is very important.

The simulation of steel deoxidation is usually based on the thermodynamic methods of calculation of the equilibria and reactions in a metal-slag-gas system. The reactions between all components of liquid steel and dissolved oxygen and sulfur are taken into account. The most important reactions are the interaction of oxygen dissolved in iron with deoxidizers (R). To realize adequate numerical calculation of equilibrium for individual or combined reactions, it is necessary to know the complete and reliable data on thermodynamic properties of an oxide and a metallic phase that relate the component activities and concentrations and to know the corresponding deoxidation constants.

Traditional method for the description of the concentration-temperature dependences of the component activities in the melts of carbon and low-alloy steels is the use of the Wagner interaction parameters $e_i^j$. Their numerical values are either found from the results of independent thermodynamic measurements or chosen as free parameters when experimental data on the solubility products ($K^*$) of various phases are processed by regression analysis. This approach allows the reactions of single-component steel
deoxidation with aluminum and some other elements (Si, Mn, C, etc. [1]) to be interpreted with a satisfactory accuracy, though for limited temperature and composition ranges.

However, in the case of alkaline-earth metals, e.g., calcium, the calculated deoxidation constants do not agree with the solubility products, and the Wagner formalism leads to inadequate results. Numerous experimental studies show that the deoxidation constants calculated thermodynamically differ from the solubility product $K'(\text{CaO})$ by several orders of magnitude. This fact is likely to indicate intense interaction between calcium and oxygen atoms dissolved in liquid iron. However, attempts to take this interaction into account by ascribing high negative values to the parameters have been done.

An original approach to the problem was formulated in [2]. The thermodynamic properties of a metallic melt are approximated using the theory of associated liquids. Formation of $\text{R}^*\text{O}$ association complexes as a result of the interaction of atoms (monomeric particles) of deoxidizer element $\text{R}$ and oxygen is assumed. In some cases, additional reaction of the formation of $\text{R}_2^*\text{O}$ groups (in the general case, $\text{R}_p^*\text{O}$ groups) takes place:

$$\text{pR}+\text{O} = \text{Rp}^*\text{O}. \quad (1)$$

The forming solution is an ideal mixture of statistically (randomly) distributed monomeric solvent atoms, monomeric dissolved-element particles, and associates. The concentration of the structural constituents of the solution can be found from the equilibrium condition

$$K_{\text{R}_p^*\text{O}} = -\Delta g_{\text{R}_p^*\text{O}} / RT = a_{\text{R}_p^*\text{O}} / (a_{\text{R}}^p \cdot a_{\text{O}}), \quad (2)$$

where $\Delta g_{\text{R}_p^*\text{O}}$ is the Gibbs energy of formation of $\text{RpO}$ complexes with respect to the Henry standard state of the initial components $\text{R}$ and $\text{O}$. According to the theory of associated solutions, the activity of a component in a liquid mixture is equal to the activity of its monomeric particles.

The analysis indicates that a high-accuracy thermodynamic description of iron-based dilute solutions can be reached using the simplifying assumption that the activity coefficients of associated complexes are equal to unity. Then, we can rewrite equation (2) in the form

$$K_{\text{M}_p^*\text{O}} = X_{\text{R}_p^*\text{O}} \left( \frac{a_{\text{R}_p}^p \cdot a_{\text{O}}}{\gamma_{\text{R}} \cdot \gamma_{\text{O}}} \right)^{\text{X}_{\text{R}_p}^*}, \quad (3)$$

where $X_i$ are the mole fractions of the components and $\gamma_i$ are the activity coefficients that take into account the interaction of only monomeric-metal (deoxidizer) and oxygen particles. These activity coefficients can be represented in terms of the Wagner concept. The same approach has been used also for approximation of thermodynamic properties of the melts with sulfur. The number of associates, their composition, and the thermodynamic functions of formation are free parameters. They are determined from the available experimental data using regression analysis. The values of Gibbs energy of formation of associates in liquid iron are presented in the table.

The formulated approach has allowed the adequate interpretation of the experimental data on the deoxidizing capacity of all elements, including alkaline-earth metals [3-9]. This is illustrated by the results of calculation of the CaO solubility in liquid iron using the assumption that CaO associates exist (figure 1). For comparison, figure 1 also shows the deoxidizing capacity of calcium calculated using the formalism of Wagner interaction parameters [10]. It is seen that not only the concentrations corresponding to the saturation of an Fe-Ca-O melt by the CaO oxide, but also the shapes of the saturation curves are different.
Figure 1. The concentrations of calcium and oxygen dissolved in liquid iron at 1873 K in equilibrium with solid CaO according to (points) the reported experimental data, (solid line) the calculation of this work, and (dashed line) the calculation of [10].

The positive result in the interpretation of the reactivity of calcium in Fe-Ca-O mixtures allowed us to use the approach formulated to describe the Fe-Ca-Al-O melt during the complex deoxidation of steel with aluminum and calcium. Figure 2 shows the calculated isothermal section (at 1873 K) of the stability diagram of inclusions in the Fe-Al-Ca-O system, which presents the solubility of deoxidation products in liquid metal. The boundaries of phase-precipitation fields are seen to be parallel to the aluminum.
Figure 2. Isothermal section (at 1873 K) of the inclusion diagram of the Fe-Ca-Al-O system calculated in this work.

Table. Optimized Energies of Associate Formation in Liquid Fe.

| Associate | $\Delta g^{o}$/J/mol | Reference |
|-----------|-----------------------|-----------|
| C*O       | -40000                | This work |
| Mn*O      | -20920                | [2]       |
| Si*O      | -30000                | This work |
| Ca*O      | 310500                | This work |
| Al*O      | -108614               | [2]       |
| Al$_2$*O  | -179912               | [2]       |
| Ca*S      | -265000               | This work |
| S*O       | -44750                | This work |
concentration axis. The positions of these lines are consistent with the data of many experimental works [11-14]. For comparison, the calculation of [15], in which the thermodynamic properties of iron melts were approximated using the Wagner formalism with only first-order interaction parameters, results in the shift of the phases precipitation boundaries toward high concentration of dissolved calcium as the aluminum content increases. The calculation performed in [16] using the Wagner formalism with allowance for second-order interaction parameters gives the boundaries of phase-precipitation fields represented complicated curves with minima.

It is important that the difference in the Fe-Ca-Al-O diagrams at $T=1873$ K (Figs. 2-4) can be grounded physically. In the approach based on the concepts of association, calcium and aluminum compete for oxygen. As aluminum is added to Fe-Ca-O melt at constant [Ca] and [O] concentrations, Al*O and Al$_2$*O associates form at the expense of a decrease in the fraction and amount of Ca*O complexes. As a sequence, the number of monomeric Ca particles and, hence, the Ca activity increases. Therefore, the slopes of the phase boundaries in the Fe-Ca-Al-O diagram with respect to the aluminum concentration axis decrease, and they become virtually parallel.

This work was supported by the Russian Foundation for Basic Research, project no. 05-08-18144a.

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