

Mathematical modeling of the kinetics of high-temperature processes in metal-slag systems

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Abstract

The possibilities of modeling the interactions of metallic and oxide melts with consideration of the thermodynamic and kinetic laws governing the occurrence of chemical reactions on the phase boundary are considered. It is concluded that a thermodynamic model can only answer the question of the direction of chemical reactions and the final composition of the phases only if an overall equilibrium state is achieved in the system. An analysis of the kinetics of individual reactions without allowance for their mutual influence does not provide a picture that faithfully reflects the real technological process. A method developed for kinetically analyzing the reactions taking place simultaneously on the phase boundary of a metallic melt with a slag or a flux is examined herein in this context. The method takes into account the diffusion of all reactants in the metallic and oxide phases, the temperature, the hydrodynamic conditions, the compositions of the reacting phases, and other factors. The proposed method is used to develop mathematical models of the following real technological processes: surfacing and welding of materials based on iron and Ni-Al alloys by coated electrodes and welding of galvanized steel sheet using a self-shielded flux-cored wire.

Introduction

The production of metallic materials with a required chemical composition and properties is a very difficult metallurgical problem, since it is accompanied by the occurrence of complicated high-temperature physicochemical processes.

The final composition of the products of a technological processes is determined both by the composition of the starting materials and by the technological parameters. The greatest contribution to shaping the composition of the products is made by the chemical reactions that take place on the various phase boundaries in a metal-slag-gas system.

The search for an efficient technology based on the use of the traditional empirical approach requires large expenditures of materials, labor, and time and ultimately does not always provide an optimal solution for the problem.

In recent years the methods of technical cybernetics, which explore so-called large systems, have been employed to solve complex metallurgical problems. The principal method for such an approach is mathematical modeling, which is essentially the performance of computer experiments [1–9].

The use of models permits significant shortening of the time for a scientific search and the performance of investigations that are very difficult or totally impossible to carry out on real objects. In particular, the main advantage of such an approach is the possibility of optimizing the technological process already in the planning stage.

The creation of faithful models with a rigorous scientific basis requires knowledge of the thermodynamics, kinetics, and mechanisms of chemical reactions taking place at high temperatures. The first and simplest stage in the modeling of physicochemical processes in metallurgical systems involves the use of thermodynamic methods. Without dwelling here on a detailed analysis of this stage, we note only that the most important data on the

directionality of individual chemical reactions subjected to mutual influences, as well as information on the final composition of the reacting phases after the achievement of overall equilibrium in the system under investigation, can be obtained in this case [7–9].

Such an approach is undoubtedly important for analyzing the theoretical laws governing the processes under investigation, but it can yield results of practical importance only in relatively rare cases.

In a real technological process, a large portion of the chemical reactions do not reach an equilibrium state; therefore, the problem of calculating the final composition of the products is associated with an analysis of the kinetics, i.e., the variation of the concentrations of all the components with time.

The physiochemical processes occurring in a metal-slag-gas system are analyzed in this context in this paper, the principles for developing a complete quantitative mathematical model of the interaction of the phases are described, and some results of mathematical modeling as applied to technological welding and surfacing processes are given.

Investigation of the kinetics of the interaction of metallic melts with oxide melts

A fairly large amount of experimental data on the kinetics of chemical reactions on a metal-slag interface has been obtained. Both general laws and individual steps of processes have been investigated with allowance for the influence of the temperature, composition, mixing rate, and other factors.

In most technological processes involved in the production of metals and alloys, the principal reactions determining the final composition of the products take place on the boundary of the metal with the slag. They are primarily redox reactions involving alloying elements and harmful impurities, as well as vaporization, gas-adsorption, and other processes. When the kinetics are analyzed, special attention is focused on revealing the nature of the individual rate-limiting steps of the overall heterogeneous reaction.

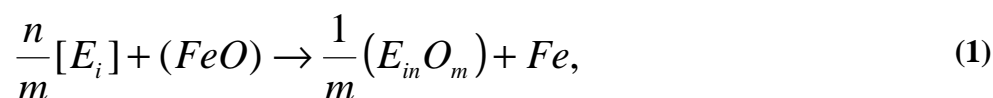
We note that the analysis of the kinetics and mechanism of individually occurring reactions does not present any special difficulties at the present time and that, as a rule, its results faithfully describe the real processes.

A kinetic analysis of the interaction of multicomponent metallic and slag melts with consideration of the mutual influence of reactions taking place in parallel is considerably more complicated.

Let us briefly describe the method for the kinetic analysis of diffusion-controlled reactions that we previously developed [10]. The theoretical basis of the method consists of two assumptions:

- 1) under diffusion-controlled conditions the concentration ratio on the phase boundary for each reaction is close to the equilibrium value;
- 2) the rate of transfer of the reactants to the phase boundary or away from it is proportional to the difference between their concentrations in the bulk and on the boundary of the metallic and oxide melts.

The oxidation of elements in a metallic melt can be represented by the reaction



where $[E_i]$ is an element dissolved in the metallic melt.

Under diffusion-controlled conditions the concentration ratio on the phase boundary is specified by the expression [10]:

$$\frac{[FeO]_A}{[Fe]_A} = K_{Ei} \frac{(E_{in}O_m)_A^{1/m}}{[E_i]_A^{n/m}} \quad (2)$$

where K_{Ei} is the equilibrium concentration ratio, and the subscript A denotes the concentration on the phase boundary.

Taking into account that in a stationary regime the concentration of any component on the phase boundary C_j^A is related to its bulk concentration by the equality

$$C_j^A = C_j \left(1 \pm \frac{V_j}{V_j^l} \right) \quad , \quad (3)$$

where V_j is the rate of mass transport of reactant $j \left(\frac{mol}{cm^2 \cdot S} \right)$, and V_j^l is the limiting diffusion flux. In our case j can refer to $[E_i]$ and $(E_{in}O_m)$.

From (2) and (3) we obtain

$$\frac{(FeO)_A}{[Fe]_A} = X = K_{Ei} \frac{(E_{in}O_m)_A^{1/m} \left(1 + \frac{V_{E_{in}O_m}}{V_{E_{in}O_m}^l} \right)^{\frac{1}{m}}}{[E_i]_A^{n/m} \left(1 - \frac{V_{E_i}}{V_{E_i}^l} \right)^{\frac{n}{m}}} \quad . \quad (4)$$

Using V_i to denote the rate of reaction (1) and taking into account the stoichiometry of this reaction

$$V_{FeO} = V_{Fe}; \quad V_i = \frac{m}{n} V_{Ei} = m V_{E_{in}O_m} \quad (5)$$

we find that V_i is the fraction of the diffusion flux of ferrous oxide V_{FeO} consumed in the oxidation of element i :

$$V_{FeO} = V_1 + V_2 + \dots V_i = \sum V_i = \sum \frac{m}{n} V_{Ei} \quad (6)$$

With allowance for (4) and (5) it was found that [10]

$$V_{FeO} = \frac{\frac{(FeO)}{[Fe]} - X}{\frac{X}{V_{Fe}^l} + \frac{(FeO)}{[Fe]V_{FeO}^l}} \quad (7)$$

For $n = 1$:

$$V_{E_i} = \frac{\frac{X^m - K_{E_i}^m (E_i O_m)}{[E_i]}}{\frac{X^m}{V_{E_i}^l} + \frac{K_{E_i}^m (E_i O_m)}{[E_i]V_{E_i O_m}^l}} \quad (8)$$

and for $n = 2$:

$$V_{E_i} = V_{E_i}^l \left[1 + \mathbf{a}_i \frac{V_{E_i}^l}{4V_{E_i2O_m}^l} - \sqrt{\left(1 + \mathbf{a}_i \frac{V_{E_i}^l}{4V_{E_i2O_m}^l} \right)^2 - 1 + \mathbf{a}_i} \right] \quad (9)$$

where $\mathbf{a}_i = \frac{K_{E_i}^m (E_{i2} O_m)}{X^m [E_i]^2}$.

The proposed method of kinetic analysis permits determination of the fluxes of reactants to the phase boundary (or away from it) and the rates of their passage through the boundary, rather than the rates of the individual reactions. Therefore, the calculation results do not depend on which of all the possible reactions are considered. It is sufficient that they be algebraically independent and contain one common reactant.

We used the method of kinetic analysis described above to model and optimize real technological processes [2, 7, 11].

The complexity of the processes occurring in the production of metallic materials is due to the simultaneous occurrence of numerous physical and chemical processes involving liquid, solid, and gaseous phases, their high temperatures, the complex character of hydrodynamic and thermal fluxes, and the nonstationary course of the processes.

This complexity is manifested in the large number of parameters specifying the course of the processes and their interrelationship. The object of modeling in the analysis of physicochemical processes in metallurgical systems is a system that includes several phases:

metal, slag, gas, and solid phases, in which diverse chemical and physical processes take place.

We developed general mathematical models of welding and surfacing by coated electrodes and flux-cored wires. The quantitative versions of the models relating to the surfacing of turbine blades by materials based on Ni-Al alloys [2] and to the welding of galvanized steel [7, 11] permitted the creation of fundamentally new welding materials (coated electrodes and flux-cored wires) and optimization of the technological process already in the development stage.

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