Nonisothermal reduction of oxides in carbon-saturated melts

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Abstract. The nonisothermal kinetics of carbon reduction of oxides in carbon-saturated melts has been studied. The numerical procedure involves the consecutive resolution and subtraction of individual peaks from a total evolution curve. The temperature-dependent background evolution and mixing effects in the gas system of the analyzer were also taken into account. The OxSeP original software allowing us to process FGA data has been realized for the modern TC-600 LECO gas analyzer. The problem of identification of oxides was found to be connected with the start temperature of carbothermal reduction of oxides \( T_s \). A considerable discrepancy between the equilibrium reduction temperatures of oxides calculated by thermodynamics and real values is observed. The identification OxID software, which includes a thermodynamic model of carbon reduction of oxide inclusions and dissociation of nitrides during the analysis, was developed. Results of numerous FGA studies of synthesized alloys and different steels are in a good agreement with experimental data obtained by X-ray microprobe analysis and quantitative metallography.

The content of oxide inclusions affects significantly the metal quality. Nonmetallic inclusions, which are present in a metal matrix in a significant amount, are known to be main sites of fatigue and tensile crack nucleation. The control of non-metallic inclusions allows us to predict the metal properties however modern methods of non-metallic inclusions evaluation are highly labor and time-consuming. Fractional Gas Analysis (FGA) method is a modified oxygen determination method realized under non-isothermal conditions. It is based on the difference in the thermodynamic stability of oxides. It provides a possibility to separate and identify the oxides in steel. First attempts to elaborate a hot extraction in a carrier gas technique for the separation of oxides from the steel samples upon monotonous or step-wise heating with IR detector have been realized in 80th [1]. It was noted that, the sequence of reduction of different oxides in a carbon saturated melt was predetermined by the standard Gibbs energy of their formation. The progress of earlier works was not, however, succeeded [2]. This fact was mainly attributed to two problems. The first one was the absence of numerical algorithm and software for processing of nonisothermal kinetic data. The second problem was the problem of oxide identifications related of the start temperatures of carbothermal reduction of oxides \( T_s \). The above problems have been worked on in recent years. First, to process the results of temperature ramped analysis an OxSeP original software has been developed and implemented on the modern TC-600 LECO gas analyzer [3]. The numerical procedure involved consecutive separation and subtraction of individual peaks from the total evolution curve followed by minimization of the sum of squared residuals. The temperature-dependent background evolutions as well as mixing effects in a gas system of analyzer were also treated by this model. Second, a thermodynamic model of carbon reduction of oxides in a molten sample, saturated with graphite during FGA was developed [4].

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The present study was aimed to the development of thermodynamic and kinetic aspects of nonisothermal reduction of oxides in carbon saturated melts as applied to the conditions of the fractional gas analysis method.

The oxide reduction processes in carbon saturated iron- and nickel-base melts were investigated in the furnace of TC-436 LECO analyzer using specially prepared synthetic alloys. It was established that the process of carbon reduction of oxides during the heating of sample in a carbon crucible of analyzer can be divided into three stages, which differ in the reaction conditions. The first stage continues from the moment of dropping a specimen into the heated graphite crucible to the start of its melting. Only oxygen adsorbed on the surface of sample can be extracted. The second stage is the specimen melting with the formation of a melt. The moment of the formation of a drop of a melt saturated with carbon in the graphite crucible is the start of the third stage, in which prerequisites for the oxide fractional separation arise. In so doing we suppose that the crucible heating rate with a sample is low, there are no temperature and concentration gradients in the melt and there is a thermodynamic equilibrium at every moment. With increasing temperature, the oxide particles $R_xO_y$ present in the melt are reduced with carbon with formation of CO bubbles nucleated on the particle surfaces. The reduction of the oxide in the carbon-saturated melt with the oxide-forming component passing into the solution develops according to the following reaction:

$$R_xO_y(s) + yCO(g) = xR + yCO_2(g)$$

where $R$ is the deoxidizing element; $x, y$ are the stoichiometric coefficients, $K_p$ is the reaction equilibrium constant characterizing the stability of oxides; $a_G, a_{R_xO_y}, a_q$ are carbon, oxide and deoxidizer activities, respectively and $p_{CO}$ is the partial pressure of carbon monoxide. Based on the equilibrium constant for considered reaction it is feasible to evaluate actual temperatures of oxide reduction beginning in the melt.

The equality of the chemical potentials of graphite of crucible and of carbon dissolved in the liquid corresponds to the attainment of equilibrium of the reaction between the graphite crucible and the molten specimen. According to the Gibbs phase rule, the system consists of four phases ($\Phi$), i.e., oxide, graphite, melt, and gas, and five components (C), namely, oxide - $R_xO_y$, $M$, graphite - $C$, oxide-forming component - $R$, and $CO$, between which one independent reaction (r) is possible. Thus, the number of degrees of freedom of the system is equal to two, i.e., $\Phi = 2 + (C-r) - \Phi = 2$. Thus, at a specified pressure, the temperature of oxide reduction is unambiguously predetermined by the concentration of the element $R$ in the analytical melt. The oxide reduction in the presence of a strong carbide forming elements can be accompanied by the formation of corresponding carbide phases. There is a point in the phase equilibrium diagram where in this case, in a presence of the five phases (oxide, graphite, melt, and gas $R_xO_y$, $M$, graphite $C$, component - $R$, $CO$ and carbide $R_xC_y$) coexists with six components ($R_xO_y$, $M$, $C$, $R$, $CO$ and carbide $R_xC_y$) and one independent reaction are possible. In this case at a given pressure the variance of the system is equal to zero. Then for alloys with $R$ concentration more than $R_{cr}$, oxide is reduced at the temperature independent on the $R$ concentration.

The next fundamental principles of oxide identification in the FGA method can be specified as follows.

For a given melt composition, each oxide has its own temperature field of the carbon reduction. The lower temperature of this field ($T_i$) can be thermodynamically calculated as a temperature of the start of reduction.

Based on the Gibbs energy equation, we can, in the absence of oxide-metal mutual solubility, estimate directly the temperature, at which the carbon monoxide vapor pressure reaches a desired value:

$$\Delta G \equiv y(\Delta G^{eq}_{CO} + RTlnp_{CO}) + RTxh_n(X_{R_y}) - \Delta G_{R_xO_y} = 0,$$
where $X_R$, $\gamma_R$ are the mole fraction and activity coefficient of deoxidizer in the melt; $T$ (K) is a temperature; $\Delta G^0_{CO}$ is the change in the standard free energy of the CO formation (J/mole); $\Delta G_{R_2O_3}$ is the standard free energy of the oxide formation from pure liquid metal and gaseous oxygen (J/mole).

The thermodynamic estimation of the $T_s$ for the FGA carbon reduction of silica, alumina and titanium oxides in iron and nickel-based melts depending on the deoxidizer concentration is illustrated in figure 1. The oxides in samples were determined using wet chemical analysis and SEM equipped with X-ray microprobe analyzer. The calculated $T_s$ increases with increasing Si, Al and Ti concentrations in analytical melt. Comparison of experimental (points) and calculated results shows their good agreement. The temperatures of oxide reduction beginning ($T_s$) significantly depend on the oxide forming element concentration in the melt.

The shape of the FGA peaks was especially investigated using different model iron based and steel samples. In the experiments, the samples were heated in the carbon crucible of furnace of analyzer with a heating rate of 1.7–1.9 K/s. Figure 2 presents the analytical curves of carbon reduction of alumina(1) and silica(2) inclusions in iron base samples; and (3) alumina in stainless steel samples. All of the curves are plotted on nondimensional coordinates: $\nu(t)$ is the conversion rate equal to conversion rate divided on the oxygen quantity; $t$, $t_M$ are time coordinates, (s); and (4) is $\nu'(t)$ derivative. It was established that the similarity of the different peaks and conversion rate $\nu(t)$ is independent on the oxide composition, aluminum and silica concentrations in the melt and oxygen content (total surface of peaks). The analytical curve can be approximated by a sum of individual peaks. The shape of individual peak was modeled in terms of the following formula:

$$I(T) = I_1 \cdot \exp \left\{ \frac{E}{kT} \cdot \frac{T - T_m}{T_m - T_0} - \int_{T_0}^{T} e^{-E/kT'}dT' \right\}$$

where $T_m$ is the temperature of the peak’s maximum and $I_1$ is the peak’s height. The $k$, $E$ are the model parameters, such as the reaction rate constant and activation energy, were calculated for the real curve $I(T)$ on the dedicated section near the maximum by the equation.
Figure 2. FGA curves of alumina (1) and silica (2) inclusions in iron-based samples; (3) alumina in stainless steel samples plotted on nondimensional coordinates. $v(t)$ is the relative intensity; $t$, $t_M$ — time coordinates, s; (4) $v'(t)$ derivative of (1).

The analytical curve $I_s(t)$ was approximated by the sum of the selected peaks:

$$I_s(t) = \sum_{j=1}^{p} I_{x,j} \varphi_j(t, \tilde{t}_{x,j}, k_j, E_j),$$

where $p$ is the peaks number in the analytical curve. The $I_{i,j}$ optimum values were calculated by minimization of the functional:

$$\Phi(I') = \sum_{i=1}^{n} \left( I_i' - \sum_{j=1}^{n} I_{i,j} \varphi_j(t_i) \right)^2$$

It was found that the reliability of the OxSeP algorithm provides the good repeatability of the experimental results.

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