Thermodynamic Analysis of the Deoxidation Ability of Aluminum in the Melt of the Fe–Cr–C System at 1600 °C

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Abstract. In the course of the present work, we performed a thermodynamic analysis of the deoxidation ability of aluminum in the melt of the Fe–Cr–C system at 1600 °C using the technique of constructing a special type of diagram – the surface of the solubility of components in a metal (SSCM), which binds changes in the composition of the metal melt with changes in the composition of deoxidation products. The calculation of the SSCM was based on the equilibrium constants of the reactions of the elements with oxygen interaction in a metal melt, as well as on the first-order interaction parameters (according to Wagner) of elements in liquid iron. During the calculation, the parameter $\alpha_{Al/Cr} = 0.023$ was estimated. Based on the results of the calculation of the SSCM, the concentration regions of the existence of non-metallic phases – deoxidation products in equilibrium with liquid metal were determined.

1. Introduction
In the production of chromium (including stainless) steels, special attention is paid to considering the possibility of oxidation of chromium and its transition from metal to non-metallic inclusions and even to slag. Such a process is highly undesirable and the technology of steelmaking should take into account the thermodynamic aspects of the interaction in the Fe–Cr–O system [1–7]. In order to avoid oxidation of chromium, elements with a sufficiently high affinity for oxygen, in particular aluminum, are introduced into the metal melt. The literature contains data on the thermodynamics of interactions in the Fe–Al–O system [8–15]. However, the literature on the thermodynamics of the interaction of aluminum with oxygen in the liquid metal of the Fe–Cr and Fe–Cr–C systems is very limited [16–18].

The aim of this work is a thermodynamic analysis of the deoxidation ability of aluminum in the melt of the Fe–Cr–C system at 1600 °C.

2. Methodology of thermodynamic modeling
A thermodynamic analysis of the interaction processes in the Fe–Cr–Al–O–C system was carried out using the technique of constructing the solubility surface of components in a metal (SSCM), which is a diagram linking the compositions of a liquid metal with the composition of the formed nonmetallic inclusions [19].

To construct the SSCM, data are needed on the equilibrium constants of high-temperature chemical reactions involving oxygen that occur in the melt of the system under study (table 1). The activity of the components of the oxide melt was calculated according to the theory of subregular ionic solutions, the energy parameters of which are given in table 2. The component activity (CrO) was calculated at zero parameters, which actually corresponds to modeling according to the theory of ideal ionic solutions. The features of this approach to the description of slag melt with the participation of
chromium oxides of different valencies are described in detail in [7]. The activities of the components of the solid solution of oxides \( \text{Al}_2\text{O}_3, \text{Cr}_2\text{O}_3 \) were calculated according to the theory of regular ionic solutions, the energy parameter of which is \( Q_{12} = +16737 \text{ J/mol} \). The activity of the components of the solid solution of spinels \( \text{FeAl}_2\text{O}_4, \text{FeCr}_2\text{O}_4 \) was determined by the theory of ideal ionic solutions. The activities of the components of the metal melt were calculated using the first-order interaction parameters (according to Wagner) of elements in liquid iron (table 3). The activity of a pure solid \( \text{Cr}_3\text{O}_4 \) compound was assumed to be unity. The activities of the components of the gas phase were determined through partial pressures.

Table 1. Equilibrium constants of high-temperature chemical reactions involving oxygen according to [7, 15, 20].

| Chemical reaction* | \( \log K = -\frac{A}{T} + B \) |
|-------------------|---------------------------------|
| \( (\text{FeO}) = [\text{Fe}] + [\text{O}] \) | 6320 | 4.734 |
| \( (\text{CrO}) = [\text{Cr}] + [\text{O}] \) | 12516 | 6.495 |
| \( (\text{Cr}_2\text{O}_3) = 2[\text{Cr}] + 3[\text{O}] \) | 36332 | 15.675 |
| \( (\text{Al}_2\text{O}_3) = 2[\text{Al}] + 3[\text{O}] \) | 58383 | 18.063 |
| \( (\text{FeCr}_2\text{O}_4)_{\text{s.s.}} = [\text{Fe}] + 2[\text{Cr}] + 4[\text{O}] \) | 50873 | 22.744 |
| \( (\text{FeAl}_2\text{O}_4)_{\text{s.s.}} = [\text{Fe}] + 2[\text{Al}] + 4[\text{O}] \) | 76069 | 27.365 |
| \( (\text{Cr}_2\text{O}_3)_{\text{s.s.}} = 2[\text{Cr}] + 3[\text{O}] \) | 41800 | 17.800 |
| \( (\text{Al}_2\text{O}_3)_{\text{s.s.}} = 2[\text{Al}] + 3[\text{O}] \) | 64000 | 20.480 |
| \( (\text{Cr}_3\text{O}_4)_{\text{s.s.}} = 3[\text{Cr}] + 4[\text{O}] \) | 56170 | 24.300 |
| \( \{\text{CO}\} = [\text{C}] + [\text{O}] \) | 1168 | -2.070 |
| \( \{\text{CO}_2\} = [\text{C}] + 2[\text{O}] \) | 9616 | 2.510 |

*Note: the components of oxide melt are shown in parentheses, in the metal melt – in square brackets, solids are indicated in line brackets, and the gas phase – in braces.

Table 2. Energy parameters of the theory of subregular ionic solutions according to [21].

| System | \( Q_{ijkl} \) (J/mole) for oxide melt |
|--------|--------------------------------------|
| \( \text{FeO–Al}_2\text{O}_3 \) | \( Q_{1112} = +212 \) | \( Q_{1122} = -21502 \) | \( Q_{1222} = -11091 \) |
| \( \text{FeO–Cr}_2\text{O}_3 \) | \( Q_{1133} = 0 \) | \( Q_{1133} = +12115 \) | \( Q_{1333} = -60565 \) |
| \( \text{Al}_2\text{O}_3–\text{Cr}_2\text{O}_3 \) | \( Q_{2223} = +17155 \) | \( Q_{2223} = +34310 \) | \( Q_{2333} = +17155 \) |
| \( \text{FeO–Al}_2\text{O}_3–\text{Cr}_2\text{O}_3 \) | \( Q_{1123} = +12715 \) | \( Q_{1223} = +366 \) | \( Q_{1233} = -28293 \) |

Table 3. The first-order interaction parameters (according to Wagner) of elements in liquid iron \( e_{ij}^l \) (1600 °C).

| Element \( i \) | \( \text{Cr} \) | \( \text{Al} \) | \( \text{O} \) | \( \text{C} \) |
|-----------------|--------|--------|--------|--------|
| \( \text{Cr} \) | -0.0003 [22] | +0.023* [7] | -0.179 [22] | -0.120 [22] |
| \( \text{Al} \) | +0.012 [16] | +0.045 [23] | -1.980 [23] | +0.091 [22] |
| \( \text{O} \) | -0.055 [24] | -1.170 [11] | -0.200 [22] | -0.450 [22] |
| \( \text{C} \) | -0.024 [22] | +0.043 [22] | -0.340 [22] | +0.140 [22] |

*Note: data obtained in the course of this work.
3. Results and discussion

Figure 1 shows the results of the simulation of the SSCM of the Fe–Cr–Al–O system (in the absence of carbon in the metal melt). Data is given in logarithmic coordinates, concentrations are indicated in weight percent. In Figure 1(a) in region I, in equilibrium with a metal melt, an oxide melt (O.m.) of variable composition (FeO, Al2O3, Cr2O3, CrO) will form as deoxidation products; in region II – a solid solution of spinels [FeAl2O4, FeCr2O4]s.s.; in region III – a solid solution of oxides [Al2O3, Cr2O3]s.s.; in region IV – the Cr2O4 compound. According to Figure 1(a) the formation of an oxide melt is possible only at very low concentrations of aluminum (about 10–6 wt. %) and sufficiently low concentrations of chromium (not more than 0.01 wt. %). The Cr2O4 compound is formed at high chromium concentrations (about 10 wt. %) and [% Al] ≤ 10–4 wt. %.

In the presence of aluminum in a metal melt (starting from [% Al] = ~ 0.0001 wt. % and more) for any concentration of chromium, the only reaction product will be a solid solution of oxides [Al2O3, Cr2O3]s.s. The calculation procedure made it possible to determine the composition of the solid solution of oxides. When the oxygen concentration in the liquid metal is 0.01 wt. % (see Figure 1(a)): for the concentration of chromium in the metal [% Cr] = 0.1 wt. % in the composition of the solid solution of oxides the molar fraction of chromium oxide is equal to \( x_{CrO} = 0.0061 \); for [% Cr] = 1 wt. % \( x_{CrO} = 0.0070 \); for [% Cr] = 10 wt. % \( x_{CrO} = 0.1144 \). And already at a concentration of oxygen in the metal of 0.001 wt. % in the composition of the solid solution of oxides the molar fraction of chromium oxide does not exceed 0.0026.

With an increase in aluminum concentration, the oxygen concentration in the metal melt decreases and may decrease to 0.0003 wt. %, which indicates a high deoxidizing ability of aluminum in iron-chromium melts. The results are consistent with experimental data from Ohta et al. [17]; there are some deviations for 20 wt. % chromium (see Figure 1(b)), which can be associated with the concentration limitations of the interaction parameters during the calculation.

Figure 2 shows the results of the simulation of the SSCM of the Fe–Cr–Al–O–C system for carbon concentrations of 0.1 wt. % (low carbon steel) and 0.4 wt. % (medium carbon steel). In addition to areas II – IV, which coincide in designations with Figure 1(a), when carbon appears in the metal melt, a region V arises, where the gas phase \{CO, CO2\} (the product of the interaction of carbon and oxygen dissolved in liquid iron) is in equilibrium with the metal melt.

In the presence of carbon at 1600 °C, the formation of an oxide melt as nonmetallic inclusions is thermodynamically unlikely (region I is not shown in the diagrams), and the formation of a spinel solid solution is possible only at 0.1 wt. % carbon in the metal. For low-carbon steels (see Figure 2(a)), the formation of the gas phase as a deoxidation product is possible only at extremely low concentrations of aluminum in the metal melt. The deoxidation pattern at [% C] = 0.1 wt. % in the presence of aluminum is as follows: starting from [% Al] = ~ 0.0001 wt. % and more for any concentration of chromium, the only interaction product will be a solid solution of oxides [Al2O3, Cr2O3]s.s. The composition of the solid solution of oxides is as follows: when the oxygen concentration in the liquid metal is 0.01 wt. % (see Figure 2 (a)) depending on the concentration of chromium in the liquid metal, the molar fraction of chromium oxide varies from \( x_{CrO} = 0.0005 \) ( [% Cr] = 0.01 wt. %) to \( x_{CrO} = 0.0910 \) ( [% Cr] = 10 wt. %). And already at a concentration of oxygen in the metal of 0.001 wt. % in the composition of the solid solution of oxides, the molar fraction of chromium oxide does not exceed 0.0022.

For a carbon concentration of 0.4 wt. % (see Figure 2 (b)) the probability of gas formation increases, but still, at practically significant aluminum concentrations (starting from 0.001 wt. % and more) [Al2O3, Cr2O3]s.s. will act as nonmetallic inclusions with a predominance of aluminum oxide in the composition of the solid solution (the molar fraction of chromium oxide does not exceed 0.0229).

Figure 2(a) shows the results of the simulation of the SSCM of the Fe–Cr–Al–O system (in the absence of carbon in the metal melt). Data is given in logarithmic coordinates, concentrations are indicated in weight percent. In Figure 2(a) in region I, in equilibrium with a metal melt, an oxide melt (O.m.) of variable composition (FeO, Al2O3, Cr2O3, CrO) will form as deoxidation products; in region II – a solid solution of spinels [FeAl2O4, FeCr2O4]s.s.; in region III – a solid solution of oxides [Al2O3, Cr2O3]s.s.; in region IV – the Cr2O4 compound. According to Figure 1(a) the formation of an oxide melt is possible only at very low concentrations of aluminum (about 10–6 wt. %) and sufficiently low concentrations of chromium (not more than 0.01 wt. %). The Cr2O4 compound is formed at high chromium concentrations (about 10 wt. %) and [% Al] ≤ 10–4 wt. %.

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Figure 1. The surface of the solubility of components in a metal of the Fe–Cr–Al–O system at 1600 °C: (a) a general view with iso-oxygen sections; (b) iso-compositional sections for 10 and 20 wt. % chromium. 1 – our simulation results; 2 and 3 – experimental data according to Ohta et al. [17] for 10 and 20 wt. % Cr accordingly.
Figure 2. The surface of the solubility of components in a metal of the Fe–Cr–Al–O–C system at 1600 °C: (a) [% C] = 0.1 wt. % and (b) [% C] = 0.4 wt. %.

4. Conclusions
According to the thermodynamic calculation and its graphical representation in the form of SSCM diagrams, it was established that at practically significant aluminum concentrations (corresponding to the actual technological process of deoxidation) in the metal melt of the Fe–Cr–Al–O–C system, the main reaction product is solid solution of oxides \( \text{Al}_2\text{O}_3, \text{Cr}_2\text{O}_3 \) \(_{\text{s.s.}}\) with a predominance of aluminum oxide in the composition of the solid solution. With an increase in aluminum concentration, the oxygen concentration in the metal decreases and may decrease to 0.0003 wt. %, which indicates a high deoxidizing ability of aluminum in iron-chromium melts.
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