Experimental determination of interaction parameters in materials Fe-C-Al systems

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Abstract. Based on a sufficiently large amount of experimental data, the first-order interaction parameters for cast irons of the Fe-C-Al system are refined. The hyperbolic dependence of the first-order interaction parameters on the degree of saturation of cast iron with carbon is confirmed.

1. The method of experimental determination of interaction parameters
In order to clarify some values of interaction parameters (IP) for saturated solutions (SS), a series of experiments with cast iron melts based on the Fe-C-Al system in the Tamman furnace to determine the IP through experimentally obtained activity of the components was conducted. Experimental determination of carbon activity was carried out by the method of electromotive force (EMF) in the unit, the scheme of which is shown in Figure 1 [1].

Six identical alund caps were placed in the graphite cup, in which pre-melted samples of Fe-C and Fe-C-Al based alloys were placed, the chemical analysis of which is shown in Table 1 (* - average values of the results of six experiments).

2. Preparation for an experiment.
Measurement of temperature was carried out the platino-platinorodiyevy thermocouple of graduation of the PPR-1 with a diameter of electrodes of 0.3 mm. Thermocouple welding was performed on a graphite counter-electrode. The AC voltage during welding was 24 V.

Stabilising annealing was carried out in an atmosphere of purified argon by passing directly through an AC thermocouple with a force of 1.5 A for 2 minutes. After annealing, the thermoelectrodes were isolated with corundum capillaries and the junction was isolated with a length of corundum capillary with an inner diameter of 1 mm and an outer diameter of 2 mm.

This protective cap minimised thermal distortion. The end of the capillary was sealed with a mixture of liquid glass and Al₂O₃ (HDA grade), then dried at room temperature for 24 hours and calcined under 1273K in a Tamman furnace under argon atmosphere. Selection of thermocouples for experiments carried out by comparison of signals of thermal sensors with a signal of a control platino-platinorodiyevy pyrometer of P-0555 when heating them in common in Tamman’s furnace with a step to 100K. Thermocouples were selected, in which the variation of parameters at temperatures up to 1273K did not exceed ± 2K.
Figure 1. Experimental plant for determination of carbon activity in cast irons based on Fe-C-Al system: 1 - graphite cup; 2 - Tamman furnace; 3- millivoltmeter; 4- crate LTR; 5- switchboard

Table 1. * Chemical composition of samples

| № sample | The chemical composition of the samples, % prior to an experiment | after the experiment |
|----------|---------------------------------------------------------------|---------------------|
|          | C | A1 | C | A1 |
| 1        | 4,3 | - | 4,27 | - |
| 2        | 4,3 | 1,05 | 4,26 | 0,97 |
| 3        | 4,3 | 1,9 | 4,24 | 1,86 |
| 4        | 4,3 | 3,0 | 4,26 | 2,93 |
| 5        | 0,59 | - | 0,55 | - |
| 6        | 2,69 | - | 2,63 | - |

The original samples were melted in alundum crucibles. The charge was: carbonyl iron of V3 grade, powder of spectral graphite and aluminium of A0 grade. The mixture of starting components was weighed on the analytical weights of the VLR-200 to an accuracy of 0,001 g. Then, cups with a pre-calculated composition were placed in a Tamman furnace, heated to 1873K temperature, held at this temperature for 1 hour, then the melt was poured into graphite molds. In order to reduce aluminum burnout, it was introduced into the melt immediately before casting. The cast samples were treated to the desired size and their chemical composition as shown in Table 2 was determined.

The determination of activity by this method is based on the creation of a concentration cell. According to the Nernst equation of the EMF of the galvanic cell Me /electrolyte/ MeX2 is equal to [2,3]:

$$E = \frac{RT}{nF} \ln \frac{a_1}{a_2}$$

where $n$ is the number of electrons carried in the potentiating process; $F$ is Faraday constant 96484.56 KI/mol; $R$ is a universal gas constant of 8.31 J/(mol g); $a_1$, $a_2$ - activities of $X_1$ and $X_2$ components.
EMF shall be determined in a compensatory manner. In this case, there is no current in the circuit, and the element operates reversibly. The EMF value will be maximum, since there is no drop of potential inside the element. If one of the electrodes is taken as standard (the activity of the measured component is constant $a_{a_1} = \text{const}$), the activity of the $X_2$ component in the second electrode can be calculated from the value of EMF.

3. Carrying out experiment

The cell with alloy samples was filled with ground synthetic slag having the following chemical composition, wt\%: $\text{Al}_2\text{O}_3 - 49$; $\text{CaO} - 43$; $\text{CaC}_2 - 4$; $\text{Al}_4\text{C}_3 - 4$.

The example in question concerns the definition of the interaction parameters of $E^C_{\text{C}}$ and $E^\text{AlC}_{\text{C}}$. After heating the cell, melting the slag and overheating the metal to 1873 K, the EMF value was measured sequentially on all cells. The graphite cup was covered with a graphite cap with 7 platinum electrodes secured therein, insulated with alund capillaries. Six electrodes were immersed in melts and the seventh in synthetic slag. The diagram of the experimental cell is shown in Figure 2 [4]. In order to avoid the effect of systematic errors, in particular thermo-EMF, occurring at the phase contact boundaries, EMF ratios were found. The results of the experiment are shown in Table 2 (* - average values of the results of six experiments).

![Figure 2](image)

**Figure 2.** Experimental cell for determination of interaction parameters of cast irons based on Fe-C-Al system: 1 - graphite cup; 2 - alund crucible; 3 is an alund capillary; 4 – cover; 5 - synthetic slag; 6 - platinum electrode

The interaction parameters of $E^C_{\text{C}}$ and $E^\text{AlC}_{\text{C}}$ are determined for certain carbon activities in Fe-C and Fe-C-Al systems.

| Sample No. | $E_i$, B | $E_i/E_1$ | $N_C$ | $N_A$ | $T,K$ | $S^C_{\text{H}}$ |
|------------|---------|-----------|-------|-------|-------|------------------|
| 1          | 0,052   | —         | 0,1733| —     | 1873  | 0,703            |
| 2          | -0,0021 | -0,0403   | 0,1717| 0,0186| 1873  | 0,769            |
| 3          | -0,00351| -0,0675   | 0,1703| 0,0335| 1873  | 0,833            |
| 4          | -0,00477| -0,0909   | 0,1686| 0,0523| 1873  | 0,932            |
| 5          | 0,2740  | 5,269     | 0,0269| —     | 1873  | 0,097            |
| 6          | 0,08377 | 1,611     | 0,1143| —     | 1873  | 0,440            |
The procedure for numerical determination of interaction parameters by experimentally determined carbon activities is as follows [5]. The activity of the component is known to be:

$$a_i = \gamma_i N_i$$  \hspace{1cm} (2)

where $\gamma_i$ is the activity coefficient of the $i$-th component; $N_i$ is the molar fraction of the $i$-th component.

In the Taylor series decomposition for the two-component Fe-C system, we have:

$$\ln \gamma_c = \ln \gamma_c^\infty + \varepsilon_c C N_C,$$  \hspace{1cm} (3)

where $\gamma_c$ is the carbon activity coefficient; $N_C$ is the atomic fraction of carbon; $\ln \gamma_c^\infty$ is the activity coefficient of carbon in an infinitely dilute solution; $\varepsilon_c$ is the interaction parameter of the first order with respect to carbon

$$\ln \gamma_c = \ln \gamma_c^\infty + \varepsilon_c C N_C,$$  \hspace{1cm} (4)

from where:

$$\varepsilon_c = \frac{\ln \gamma_c - \ln \gamma_c^\infty}{N_C},$$  \hspace{1cm} (5)

The value $\ln \gamma_c^\infty$ is determined from the ratio:

$$\ln \gamma_c^\infty = 2718/T - 2.02,$$  \hspace{1cm} (6)

The value of $\gamma_c$ is determined from the ratio of $\gamma = a_C/N_C$ at known experimental values of $a_C$ and $N_C$. For three-component Fe-C-Al system-based interaction parameters value $\varepsilon_{AlC}$ be determined similarly:

$$\ln \gamma_c = \ln \gamma_c^\infty + \varepsilon_c C N_C + \varepsilon_{Al} N_{Al},$$  \hspace{1cm} (7)

$$\varepsilon_{Al} = \frac{\ln \gamma_c - \ln \gamma_c^\infty - \varepsilon_c C N_C}{N_{Al}},$$  \hspace{1cm} (8)

from known experimental $a_C, N_C, N_{Al}$ data. The results of the experiment are shown in Table 3 (* - average values of the results of six experiments).

From the results of the experiment, it can be seen that the change in the value of the parameters of the reaction of $\varepsilon_c$ in the transition from infinitely diluted solutions to saturated solutions is practically constant. The following experiment was conducted to clarify the change in $\varepsilon_{AlC}$ interaction parameters in the transition from infinitely diluted solutions to saturated solutions.

**Table 3.** Results of experimental determination of interaction parameters.

| Sample No. | $N_C$ | $N_{Al}$ | $a_C$ | $\varepsilon_c$ | $\varepsilon_{Al}$ | $T$, $K$ |
|------------|-------|----------|-------|-----------------|-------------------|--------|
| 1          | 0.173 | —        | 0.607 | 10.53           | —                 | 1873   |
| 2          | 0.1717| 0.0186   | 0.623 | 10.81           | 2.79              | 1873   |
| 3          | 0.1703| 0.0335   | 0.634 | 11.07           | 2.78              | 1873   |
| 4          | 0.168 | 0.0523   | 0.644 | 11.38           | 2.77              | 1873   |
| 5          | 0.0269| —        | 0.0203| 9.65            | —                 | 1873   |
| 6          | 0.1143| —        | 0.215 | 10.51           | —                 | 1873   |

4. Method of experimental determination of concentration dependence of interaction parameters

Experiments with Fe-C-Al melts in the Tamman furnace were performed to clarify the nature of the transition curve of the interaction parameters of $\varepsilon_{AlC}$ from infinite dilution to a saturated state and to confirm the accepted hyperbolic dependence on the degree of saturation of the solution with carbon.

Experimental determination of the concentration dependence was performed by measuring EMF with a certain content of carbon and aluminum. The scheme of the experimental installation is shown in figure 1. The installation consists of a Tamman resistance furnace with a built-in PPR-1...
thermocouple with a secondary device SH-4500, a switch and a potentiometer for measuring the EMF of samples.

In a graphite Cup 1 (Figure 2), five alund crucibles were placed, in which pre-melted samples of Fe-C-Al alloys were placed, the chemical analysis of which is shown in table 4 (* - average values of the results of six experiments).

Alloys were synthesized in a Tamman furnace in alund crucibles from B3-grade carbonyl iron, spectral graphite powder and A0-grade aluminum. In order to reduce aluminum burnout, it was introduced into the melt immediately before casting. To top of graphite cells filled with ground synthetic slag of the following composition, wt%: Al$_2$O$_3$ - 49; CaO - 43; CaC$_2$ - 4; Al$_4$C$_3$ - 3.

The experiment is based on the same principle as determining the interaction parameters of $E_{CC}$ and $E_{AlC}$ in an iron carbon melt.

After heating the cell, melting the slag and overheating the metal to 1873 K, the EMF values on all cells were measured. The influence of iron activity was neglected due to the practical absence of iron ions in the slag. In order to avoid the effect of systematic errors, in particular thermo-EMF, occurring at phase contact boundaries, EMF relations were found.

The results of the experiment are shown in Table 5(* - average values of the results of six experiments).

Further, EALC interaction parameters for different carbon content, i.e., from infinite dilution state to saturated state, were calculated from the found EMF values using the method of experimental determination of interaction parameters.

The results of the experiments are shown in Table 6 (* - average values of the results of six experiments) and Figure 3.

| Sample No. | $E_{i}, mB$ | $E_{i}/E_3$ | $N_C$ | $N_{Al}$ | $T,K$ | $S_{C}'$ |
|------------|-------------|-------------|-------|---------|-------|----------|
| 1          | 0.356       | -75.26      | 0.00897 | 0.0618  | 1873  | 0.044    |
| 2          | 0.226       | -47.78      | 0.0351  | 0.0624  | 1873  | 0.177    |
| 3          | 0.131       | -27.59      | 0.0763  | 0.0603  | 1873  | 0.399    |
| 4          | 0.0436      | -9.21       | 0.129   | 0.055   | 1873  | 0.694    |
| 5          | -0.0047     | -          | 0.1685  | 0.054   | 1873  | 0.942    |

The results of the experiments are shown in Table 6 (* - average values of the results of six experiments) and Figure 3.

| Sample No. | $\% C$ | $\% Al$ | $a_c$ | $E_{AlC}'$ |
|------------|-------|--------|-------|------------|
| 1          | 0.2   | 3.1    | 0.00778 | 5,254      |
| 2          | 0.8   | 3.2    | 0.03882 | 4,321      |
| 3          | 1.8   | 3.2    | 0.12776 | 3,578      |
| 4          | 3.2   | 3.05   | 0.37535 | 3,071      |
| 5          | 4.3   | 3.1    | 0.64469 | 2,552      |
5. Conclusions
The parameters of the interaction of the first order of $\varepsilon_{CC}$ and $\varepsilon_{AlC}$ are more precisely determined experimentally. It is found that the $\varepsilon_{AlC}$ parameters change from 5.524 to 2.352 in the transition from infinite dilution to a saturated state, obeying a hyperbolic dependence. The parameters of the $\varepsilon_{CC}$ interaction during the transition from infinite dilution to a saturated state change from 9.65 to 10.53, and the $a_C$ carbon activity changes from 0.0078 to 0.644.

The obtained values of the interaction parameters of the first order quite satisfactorily agree with the literature data [6-11], which confirms the adequacy of the experimental results.

References
[1] V. Grachev, V. Kupryashin, *The methodology for determining the interaction parameters and its application for assessing the equilibrium of the crucible reaction*, Structure and properties of metal and slag melts, Ufa Scientific Center of the Academy of Sciences of the USSR, pp.31 – 32 (1986)
[2] K. Wagner, *Thermodynamics of alloys*, (Moscow, Metallurgizdat, 1957)
[3] C. Lupis, J.lliott, *Generalized interaction coefficients*, Actametallurgica., v. 14(4), pp. 529 – 538 (1966).
[4] A. Burkov, A. Fedotov, A. Kasyanov, R. Panteleev, T. Nakama, *Methods and devices for measuring thermo-EMF and electrical conductivity of thermoelectric materials at high temperatures*, Scientific and technical Bulletin of information technologies, mechanics and optics, v.15(2), pp. 173-195 (2015)
[5] V. Grigoryan, L. Belyanchikov, A.Stomakhin, *Theoretical foundations of electric steelmaking processes*, (Moscow, Metallurgy, 1987)
[6] K. Lupis, *Chemical thermodynamics of materials*, (Moscow, Metallurgy, 1989)
[7] G. Sigworth, J. Elliot F, *The thermodynamics of liquid dilute iron alloys*, Metal science Journal, v. 8(9), pp. 298...310 (1974)
[8] A. Zhukov, *On the thermodynamic activity of carbon in iron carbon alloys*, Metallurgy and fuel, v. 5, pp. 51-54 (1962)
[9] T. Sabirzanov, *Determination of interaction parameters by solubility of components*, Melting of foundry alloys, pp. 9-12 (1982)
[10] E. Filipov, S. Filipov, *The nature of the activities and their theoretical definition for double iron alloys*, University News. Ferrous metallurgy, v. 1, pp. 9-14 (1967)
[11] P. Neumann, Dotsoh. *Thermodunamios Fe - C - Si melts with particular emphasis on the oxidation behavior of carbon and silicon*, "Met. Cast.", pp. 31-55(1974)