Theoretical methods for calculating the structure and properties of cast iron based on Fe-C-Al systems

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Abstract. The main factor preventing the widespread introduction of Fe-C-Al system cast iron is the mismatch of the cast iron structure with the operating conditions. At the same time, there is no sufficiently simple and reliable technique in the literature for calculating the structure of iron of the Fe-C-Al system, taking into account both kinetic and thermodynamic factors and operating conditions. Theoretical methods of determination of structure and properties of cast iron of Fe-C-Al system are proposed on the basis of thermodynamic, kinetic analyses, as well as metallographic and X-ray phase investigations in relation to operating conditions.

1. Thermodynamic analysis of the processes of alloying cast iron with aluminum
To achieve the maximum service life of the part under the specified operating conditions it is necessary to provide a certain structure: the ratio of phase components; the number and shape of inclusions of graphite and carbides, the size of the eutectic grain; the type of metal matrix.

It is known that the structure of cast iron is determined by two factors: the thermodynamic activity of the components in the melt and crystallizing phases, as well as the cooling rate of the casting, which controls the diffusion processes in the solidifying casting.

Having the ability to analytically calculate the graphitization curve of cast iron taking into account thermodynamic factors, it is possible to predict the structure of cast alloys with a certain accuracy and manage it by complex alloying [1].

The carbon potential value is taken as a measure of iron's propensity to graphitization $\pi_{Ck}$

$$\pi_{Ck} = RT \ln a_C,$$

where $a_C$ - is the activity of carbon in the alloy, which can be calculated using the formula:

$$a_C = \gamma_C N_C,$$

where $\gamma_C$ - is the carbon activity coefficient; $N_C$ - is the atomic fraction of carbon.

Basically, the P.Wagner method [2] is used to calculate the activity of components present in cast iron, based on the decomposition of excess free energy into a Taylor series:

$$\ln \gamma_i = \ln \gamma_i^0 + \sum_{j=2}^{n} \rho_i^{(j)} N_j + \sum_{j=2}^{n} \rho_i^{(j)} N_j N_k + .. ,$$

where $\gamma_i^0$ and $\rho_i^{(j)}$ are the baseline and the coefficients of the Taylor series for the activity of component $i$.

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where \( \ln \gamma_i \) - is the activity coefficient of component \( i \); \( \ln \gamma_i^\infty \) - is the activity coefficient of component \( i \) in an infinitely dilute solution; \( e_i, \rho_i, \rho_i^{jk} \) - are the interaction parameters; \( N_j, N_k \) - are the atomic fractions of the components.

Meanwhile, the apparatus of interaction parameters was developed by P. Wagner for solutions close to infinite dilution. Its application to melts far from infinite dilution is unjustified, and for component-saturated allos, which include cast iron based on Fe-C-Si and Fe-C-Al systems, it is unacceptable.

Analysis of the available data on interaction parameters in the literature has shown that their values for infinitely dilute solutions and saturated solutions are different. Thus, Kulikov I. S. assumes the asymptotic character of the change in the value of interaction parameters during the transition from infinitely dilute solutions to saturated solutions [3]. In this paper, preference is given to the hyperbolic concentration dependence of the interaction parameters, which has a significant degree of curvature. As shown by the authors of [4], in principle, it is possible to select such interaction parameters for saturated solutions that differ in general from the interaction parameters of R. Wagner, substitution of which in the calculation formulas allows us to obtain satisfactory results, in this case, the main equation of the method takes the form:

\[
\ln \ln \gamma_i = \ln \gamma_i^\infty + \sum_{j=2}^{n} E_i^j N_j + \sum_{j=2}^{n} P_i^j N_j^2 + \sum_{j=2}^{n} \sum_{k=2}^{n} P_i^{jk} N_j N_k + \ldots ,
\]

(4)

where \( \gamma_i \) - is the activity coefficient of component \( i \) in a saturated solution; \( \gamma_i^\infty \) - is also, in an infinitely dilute solution; \( E_i^j \) - is the first - order interaction parameters for saturated solutions; \( P_i^j, P_i^{jk} \) - of the second order for saturated solutions.

The interaction parameters of \( E_i^j \) and \( P_i^j, (P_i^{jk}) \), in contrast to \( e_i, \rho_i, (\rho_i^{jk}) \), depending on the degree of saturation of the solution with any component, are determined by the equation:

\[
E_i^j = f(T, S_H^i) = \varphi(T) \times \omega(S_H^i),
\]

(5)

where \( S_H^i \) - is the degree of saturation of the melt with component \( i \); \( \varphi (T) \) - is the temperature dependence of the interaction parameters [1].

Taking into account the critical concentrations of elements, we have the degree of saturation of the melt of cast iron based on the Fe-C-Al system with carbon:

\[
S_H^C = \frac{1,3 + 2,57 \times 10^{-3} \times t + 0,3\% Mn + 0,5\% Cr - 0,4\% Si - 0,35\% P - 0,1\% S - 0,5\% Al}{\% C}
\]

Taking the concentration dependence of the interaction parameters on the degree of saturation hyperbolic, we have:

\[
\omega(S_H^i) = \frac{1}{C + S_H^i} + D ,
\]

(7)

where \( C \) and \( D \) are coefficients calculated based on the following conditions: for \( S_H^i=0 \), \( E_i^j = \epsilon_i^\infty \); for \( S_H^i=1 \), \( E_i^j = \epsilon_i^\infty \). The calculated values of coefficients \( C \) and \( D \) are shown in table 1.

| \( i/j \) | \( C \) | \( D \) | \( i/j \) | \( C \) | \( D \) |
|----------|-------|-------|----------|-------|-------|
| C/C      | 0,795 | -0,258| C/Si     | 0,747 | -0,338|
| C/Mn     | 0,482 | -0,075| C/S      | 0,901 | -0,109|
| C/P      | 1,131 | 0,115 | C/Cr     | 0,725 | -0,380|
| C/Ni     | 0,853 | -0,173| C/Al     | 0,964 | -0,038|

Thus, the formula for calculating the first-order interaction parameters takes the form:

\[
E_i^j = \left( \frac{A}{T} + B \right) \left( \frac{1}{C + S_H^i} + D \right) ,
\]

(8)
where A and B are the temperature coefficients of the interaction parameters P.Wagner's.

The parameters of the second-order interaction are determined from the equations of quasi-chemical theory [5], applied to saturated melts:

\[ P_i = 0.15(E_i^2) - 0.5E_i, \quad P \beta_i = 0.05(E_i^2) + 0.1E_i(E_i - 5), \quad P_{i,j}^\beta = 2P_j + E_j - E_i, \]  

(9)

Unknown temperature dependencies, namely coefficients A and B of the function:

\[ \phi(T) = \frac{A}{T} + B \]

find from the equations:

\[ A = \varepsilon_i - \varepsilon_j, \quad B = \varepsilon_j - A \times 5.34 \times 10^{-4} \]  

Thus, the interaction parameters have the form:

\[
\begin{align*}
E_C^C &= \frac{(20603/T)}{0.795 + S_H^C} - 0.257 \quad E_C^{Ni} = \frac{(22476/T)}{0.747 + S_H^{Ni}} - 0.338 \\
E_C^{Al} &= \frac{(6176/T + 2)}{0.964 + S_H^{Al}} - 0.038 \quad E_C^{Mn} = \frac{(-4227/T - 0.44)}{0.482 + S_H^{Mn}} - 1.075 \\
E_C^{Cr} &= \frac{(-6424/T - 2.07)}{0.725 + S_H^{Cr}} - 0.38 \quad E_C^{Cu} = \frac{(4583/T + 0.55)}{0.853 + S_H^{Cu}} - 0.175 \\
E_C^{P} &= \frac{(6306/T + 3.66)}{1.131 + S_H^{P}} + 0.115 \quad E_C^{S} = \frac{(22476/T)}{0.901 + S_H^{S}} - 0.109
\end{align*}
\]

Based on the foregoing, a program was developed for calculating the carbon activity \( a_C \) and the carbon potential \( \pi_C \) for the systems Fe-C-Al, Fe-C-Si, Fe-C-Mn, Fe-C-Cr, Fe-C-Cu, Fe-C-S, Fe-C-P. The results of calculating the carbon potential \( \pi_C \) depending on the percentage of components for the systems Fe-C-Al, Fe-C-Si, Fe-C-Mn, Fe-C-Cr, Fe-C-Cu, Fe-C-S, Fe-C-P are presented in table 2.

Table 2. Influence of elements on the carbon potential value \( \pi_C \).

| Element | Percent | \( \pi_C \), J/mol | Element | Percent | \( \pi_C \), J/mol |
|---------|---------|--------------------|---------|---------|--------------------|
| Al      | 1.0     | 952.3              | Al      | 2.0     | 1185.4             |
| Al      | 3.0     | 1318.5             | Al      | 4.0     | 1334.8             |
| Si      | 1.0     | 1156.2             | Si      | 2.0     | 1506.3             |
| Si      | 3.0     | 1669.3             | Si      | 4.0     | 1679.9             |
| Cr      | 1.0     | -20.7              | Cr      | 2.0     | -672.4             |
| Cr      | 3.0     | -1325.1            | Cr      | 4.0     | -1981.1            |
| Mn      | 1.0     | 425.5              | Mn      | 2.0     | 218.6              |
| Mn      | 3.0     | 7.3                | Mn      | 4.0     | -207.6             |
| Cu      | 1.0     | 758.2              | Cu      | 2.0     | 943.4              |
| Cu      | 3.0     | 1021.3             | Cu      | 4.0     | 1056.6             |
| S       | 0.1     | 735.3              | S       | 0.2     | 839.5              |
| S       | 0.3     | 942.1              | S       | 0.4     | 1044.3             |
| P       | 0.1     | 694.2              | P       | 0.2     | 764.1              |
| P       | 0.3     | 830.3              | P       | 0.4     | 895.9              |

2. Relationship between the structure and applications of cast iron based on the Fe-C-Al system

The use of cast iron based on the Fe-C-Al system for one purpose or another assumes their well-defined phase composition. The analysis of literature data, and, in particular, works [6 -13] allowed to establish the structure for cast iron based on the Fe-C-Al system of the appropriate purpose and the desirability of a particular structural component. Table 3 shows data on the chemical composition, structure, desirability of structural components and applications of cast iron based on the Fe-C-Al system.
Knowing the chemical composition of cast iron, the calculation of the carbon potential of UCS, which for various types of castings has the following values: 0.9-1.2 kJ/mol for corrosion-resistant; 0.6-0.85 kJ/mol for heat-resistant; 1.1-2.2 kJ/mol for wear-resistant; 1.5-3.5 kJ/mol for castings without bleaching; 1.2-2.5 kJ/mol for heat-resistant castings; 1.7-2.0 kJ/mol for high-strength castings.

Table 3. Scope and desirability of structural components of cast iron based on the Fe-C-Al system.

| Structural component | Field of application |
|----------------------|----------------------|
|                      | Castings without the chill (chill casting; thin-walled) | Heat-resistant casting (coquilles, molds) | Corrosion-resistant casting (crucibles, retorts) | Heat-resistant casting (furnace fittings) | Wear-resistant casting (guides, bearings) | Casting with special properties |
| Doped ferrite        | -                    | +                    | ++                    | +                    | -                    | +                    |
| Cementite            | -                    | -                    | +                    | -                    | +                    | -                    |
| Perlite A            | +                    | +                    | -                    | -                    | ++                   | +                    |
| Perlite B            | +                    | ++                   | +                    | +                    | ++                   | +                    |
| Graphite             | +                    | +                    | -                    | +                    | +                    | ++                   |
| γ’-phase             | -                    | -                    | ++                   | -                    | ++                   | ++                   |
| Al4C3 and other carbides | -                    | -                    | +                    | -                    | +                    | +                    |

Based on the calculations, the thermodynamic part of the nomogram is constructed (figure 1), which connects the percentage of components in cast iron based on the Fe-C-Al system with the carbon potential of \( \pi_{\text{Cu}} \) and the scope of application of cast iron for castings of a particular purpose.

Based on this part of the nomogram, it is possible to select a cast iron composition based on the Fe-C-Al system that would provide a given set of mechanical and special properties, i.e. the required quality, taking into account the need for structural components and the possibility of their stabilization with additional alloying. Correction of the carbon potential is made by adding an appropriate amount of graphitizing or carbidostabilizing element, which is calculated based on the additivity of the carbon potential value [14].

2.1. Kinetic calculations

The construction of the kinetic part of the diagram is based on the well-known equations of the theory of casting formation. The calculation is based on determining the speed of solidification of a flat casting and the duration of solidification [15].

The linear speed of solidification of castings of various configurations is determined by:

\[
U = \frac{b_4 \varrho_E}{L_E \rho_3^{0.5}} \left[ I + 2b_4 \varrho_E (k + 1) \frac{I}{L_E \rho_3^{0.5} (\sqrt{t} - \sqrt{t_1})} \right]^{k+1},
\]

where \( l_0 \) is a characteristic size of the casting, m; \( k \) - coefficient taking into account the configuration of the casting (\( k=0 \) for flat, \( k=1 \) for cylindrical, \( k=2 \) for the ball); \( L_E \) is the specific heat of crystallization of the eutectic, \( j/kg\); \( \rho_3 \) is the density of the alloy, \( kg/m^3\); \( b_4 \) is the coefficient of the heat storage capacity of the form \( W\times S^{0.5}/(m^2K)\); \( \varrho_E = T_E-T_f \) excess eutectic temperature, K; \( t_1 \) - time of full cooling of the casting.

Thus, knowing the mass and thickness of the casting wall, it is possible to calculate the linear speed of solidification for forms with different values of \( b_4 \) at different pouring temperatures. Carried out calculations of the linear velocity of the solidification of cast iron for flat castings. The results were obtained at \( b_4=1377 \) W*s/(m2*K) (typical molding mixture for cast iron based on the Fe-C-Al system); \( T_f=293K\); \( \rho_1=6850 \) kg/m³; \( \rho_3=7000 \) kg/m³; \( c_1=838 \) j/(kg*K); \( L_E=215000 \) j/kg; \( T_E=1420K\); \( T_{\text{filling}}=1673K\); \( T_f=298K\).
In order to establish a quantitative assessment of the effect of the solidification rate on the graphite phase, x-ray diffraction [16,17] and metallographic studies of cast iron based on the Fe-C-Al system of the first graphite region (up to 8% Al) were performed.

Based on x-ray and metallographic analyses, a quantitative relationship was established between the graphite phase and the rate of solidification of cast iron based on the Fe-C-Al system of the first graphite structural region. Table 4 shows the results of the research.

### Table 4. Quantitative dependence of the graphite phase of cast iron based on the Fe-C-Al system on the solidification rate.

| Sample diameter, mm; solidification rate U mm / s | Aluminum content, % | \( \frac{C_{\text{graphite}}}{C_{\text{total}}} \) |
|---------------------------------|-----------------|-----------------|
| 30<s<40 U=0,06                        | 1 2 3 4 5 6 7 8   |
| 20<s<30 U=0,91                        | 0,65 0,90 0,98 0,88 0,72 0,52 0,33 0,17 |
| 10<s<20 U=0,135                       | 0,55 0,75 0,78 0,60 0,37 0,20 0,12 0,07 |
| 6<s<10 U=0,165                        | 0,50 0,58 0,40 0,20 0,13 0,06 0,06 0,02 |

This allowed us to construct the kinetic part of the nomogram (figure 1). The relationship between the structural components (perlite, ferrite, carbides) and the \( \frac{C_{\text{graphite}}}{C_{\text{total}}} \) is carried out using the well-known equation [7]:

\[
\frac{C_{\text{graphite}}}{C_{\text{total}}} = 1 - e^{-\frac{K}{t}},
\]

where \( K \) is the graphitization constant of cast iron proposed by N. G. Girshovich.

Thus, knowing \( \frac{C_{\text{graphite}}}{C_{\text{total}}} \) in cast iron based on the Fe-C-Al system, from figure 1, it is possible to determine its structure.

#### 2.2 Diagram of the mechanical properties of cast irons based on the Fe-C-Al system

Based on the analysis of an extensive experimental material, as well as works [18,19], it is established that the tensile strength \( \sigma_b \) of cast iron based on the Fe-C-Al system depends on the content of carbon and aluminum in them. The least squares polynomial approximation allowed us to find the mathematical dependence of \( \sigma_b = f(Al) \) for different \( C_{\text{total}} = \text{const} \). The equations describing the ultimate strength \( \sigma_b \) from the aluminum content, with a fixed carbon content in cast iron based on the Fe-C-Al system, written as a polynomial have the form:

\[
\sigma_b = a_0 + a_1x + a_2x^2 + \ldots + a_mx^m,
\]

The correlation between the tensile strength \( \sigma_b \) (in kg / mm²) and the Brinell hardness can be expressed by the equation [19]:

\[
HB = 100 + 3,1\sigma_b,
\]
Figure 1. Nomogram for calculating the structure, properties and applications of cast irons of the Fe-C-Al system: 1-4 carbon content in: 1 - 2.5% C; 2 to 3% C; 3 - 3.5% C; 4 - 4% C; linear speed of solidification U depending on the wall thickness S of the flat casting: 5 -10 kg, 6 - 100 kg; the effect of the solidification rate U on the graphite phase С / С tot. in cast iron: 7 - from 1% Al to 8%; 8 - heat resistant casting; 9 - wear-resistant casting; 10 - corrosion-resistant casting; 11 - casting without whitewash; 12 - heat-resistant casting; 13 - high strength casting

Figure 1 shows an example of the use of the nomogram for the manufacture of chill molds from heat-resistant material based on the Fe-C-Al system, with an average cast wall thickness of 25 mm and a weight of 80 kg.

On the kinetic part of the nomogram, drawing the horizontal from the point corresponding to 25 mm to the intersection with the line G = 80 kg and lowering the vertical, we determine that with a casting wall thickness of 25 mm and a mass of 80 kg, the linear solidification rate in the center of the casting is 0.073 mm / s. On the surface of the casting, the linear solidification speed is 0.155 mm / s.

On the thermodynamic part of the nomogram, drawing a horizontal line from the region of heat-resistant cast irons to the lines $\pi_{CAl}$=$f(\% i)$, we find that the composition of cast iron based on the Fe-C-Al system for aluminum and silicon should be as follows: Al = 2.0% ; Si = 1.0%.

At these solidification rates and Al=2.0%, the amount of Cg / C tot. on the surface of the casting and in the center is 0.46 and 0.84, respectively. To determine the structure of cast irons based on the Fe-C-Al system, we draw a horizontal line from the points $C_{\text{graphite}} / C_{\text{total}} = 0.84$ and $C_{\text{graphite}} / C_{\text{total}} = 0.46$ to the intersection with the line $C_{\text{graphite}} / C_{\text{total}} = 1-\text{e}^{-Ks}$, and lowering the vertical, we find that the structure of cast iron in the center of the casting will be perlite-ferrite with a predominance of perlite and graphite, and on the surface of the casting it will be pearlite with graphite and carbides. To determine the hardness and strength of cast iron, we use the diagram of mechanical properties. Draw a vertical line from point A1 = 2% to the intersection with the line C = 3.5%, then draw a horizontal line to find that the average values of hardness and strength are respectively HB = 193 and $\sigma_b = 300$ MPa.
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