

THEORY

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REFINEMENT OF THE Fe–C DIAGRAM ON THE BASIS OF RESULTS OF A THERMODYNAMIC ANALYSIS AND GENERALIZATION OF DATA FOR Fe–C AND Fe–C–Cr SYSTEMS¹

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The Fe–C system has been studied quite thoroughly. However, some aspects of the system remain underdeveloped or at least disputable. This refers especially to the carbide part of the diagram. There is no unanimous opinion on the nature of melting of cementite (congruent or incongruent) and its melting temperature. Light carbide phases other than cementite are not represented by the diagram and there is no correspondence between the low-temperature part of the diagram and existing experimental data on carbide transformations in tempering of quenched steel.

It is assumed in many textbooks, reference books, and monographs that the melting temperature of cementite is equal to 1500–1550°C or it is not given at all (i.e., the cementite liquidus is not extended to the stoichiometric composition of cementite). However, the results of some calculational and experimental works have shown that this temperature is much lower and lies in the 1200–1270°C range [1, 2].

The problems of the melting behavior of cementite and the expediency of representing the hypercementite region and the phase equilibrium in this region in the Fe–C diagram remain unsolved. Most often cementite is represented congruently to the melting chemical compounds and the diagram of the metastable equilibrium is restricted to the cementite composition. For this reason the diagram is often called the iron–cementite one. At the same time, it is known that the Fe–C system can contain one more metastable carbide with an Fe₇C₃ stoichiometry in addition to cementite. This carbide has been obtained experimentally at a high pressure [3] or by other special methods [4]. Its crystal structure is close to that of Cr₇C₃ carbide with a rhombic lattice [5]. The structure of hypercementite alloys with Fe₇C₃ carbides obtained at a pressure up to 90 kbar (9 GPa) has been studied in [3, 6]. This structure is represented by a mixture of Fe₃C and Fe₇C₃ carbides and is interpreted as eutectic. For this reason, it has been suggested that the hypercementite part of the Fe–C system should be represented by a diagram with a eutectic and congruent melting of cementite. In [6, 7] the open maxi-

imum of cementite corresponding to congruent melting of it is preserved in the diagram for atmospheric pressure. The presence of an open cementite maximum in a diagram of metastable equilibria has been assumed in a number of works of foreign researchers [1, 8]. However, the authors of [9] conclude that this representation is incorrect and a variant of the diagram having a peritectic transformation is more probable. This variant agrees with data obtained earlier by calculation [10] and with the variant suggested in [11].

All the suggested variants of the diagram are deficient because of their conjectural nature and the absence of sufficiently reliable proofs of existence, to say nothing of the absence of quantitative results on the phase equilibria of the Fe₇C₃ carbide with other phases.

The carbide phases formed in the decomposition of martensite are not represented by the diagram. The composition of these carbides is described, by various estimates, by formulas ranging from Fe₂C to Fe_{2.4}C, i.e., their stoichiometry is close to Fe₇C₃. By the data of [12], at 200–250°C these carbides are more stable thermodynamically than cementite.

The aim of the present work consists in refining the phase diagram for alloys of the metastable Fe–C system in the region of cementite and the hypercementite part (up to the Fe₇C₃ carbide) and estimating the thermodynamic conditions of equilibrium of Fe₇C₃ with the other phases.

We used two methodological approaches, namely, (1) a thermodynamic analysis of the Fe–C system with calculation of the position of the line of the cementite liquidus and (2) a thermodynamic analysis of the Fe–C–Cr system with

¹ Many concepts of the present paper contradict generally accepted notions.

² We invite the readers to take part in the discussion of the problem.

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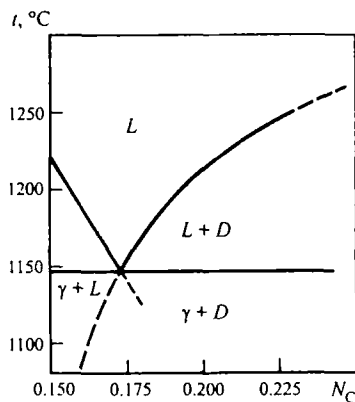
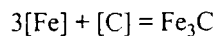


Fig. 1. A part of the Fe-C diagram in the region of the cementite liquidus. Calculated by Eq. (8).

recalculation of the results for the Fe-C system (i.e., for zero chromium content).

The thermodynamic parameters of cementite were calculated proceeding from the conditions of equilibrium of austenite and the melt with cementite. For the reaction of segregation of cementite from the solution



the equilibrium constant is

$$K_{\text{eq}} = \frac{a_{\text{Fe}_3\text{C}}}{a_{\text{Fe}}^3 a_{\text{C}}}, \quad (1)$$

where $a_{\text{Fe}_3\text{C}}$, a_{Fe} , and a_{C} are the activities of cementite, iron, and carbon respectively. In a first approximation, cementite can be treated as a stoichiometric compound and therefore its activity can be taken equal to 1.

The change in the free energy of the system during the reaction of segregation of cementite is determined from the equation

$$\Delta F = \Delta F^0 + RT \ln K_{\text{eq}}, \quad (2)$$

where ΔF^0 is the change in the free energy in the reaction that occurs under standard conditions (the standard state of carbon is graphite and that of iron is pure γ -iron). Under equilibrium conditions $\Delta F = 0$ and

$$\Delta F^0 = -RT \ln K_{\text{eq}} = RT (\ln a_{\text{C}} + 3 \ln a_{\text{Fe}}). \quad (3)$$

The activity of carbon a_{C_γ} and iron a_{Fe_γ} in austenite was calculated from the equations [13, 14]

$$\ln a_{\text{C}_\gamma} = \ln \frac{N_{\text{C}_\gamma} + \frac{4590}{T} (N_{\text{C}_\gamma} - N_{\text{C}_\gamma}^*) (2 - N_{\text{C}_\gamma} - N_{\text{C}_\gamma}^*)}{N_{\text{C}_\gamma}^*}, \quad (4)$$

$$\ln a_{\text{Fe}_\gamma} = \ln N_{\text{Fe}_\gamma} - \frac{4590}{T} N_{\text{C}_\gamma}^2, \quad (5)$$

where N_{C_γ} and N_{Fe_γ} are the atomic fractions of carbon and iron in austenite, respectively (in the case considered, under equilibrium of austenite and cementite); $N_{\text{C}_\gamma}^*$ is the solubility

of graphite in austenite expressed in atomic fractions; T is the Kelvin temperature.

Using (4) and (5) we find the temperature dependence of ΔF^0 for the austenite-cementite equilibrium:

$$\Delta F^0 = RT \left[\ln \frac{N_{\text{C}_\gamma}}{N_{\text{C}_\gamma}^*} + \frac{4590}{T} (N_{\text{C}_\gamma} - N_{\text{C}_\gamma}^*) (2 - N_{\text{C}_\gamma} - N_{\text{C}_\gamma}^*) + 3 \ln (1 - N_{\text{C}_\gamma}) - 3 \times \frac{4590}{T} N_{\text{C}_\gamma}^2 \right]. \quad (6)$$

Our calculation has shown that dependence (6) is virtually linear and can be described by a simple equation:

$$\Delta F^0 = 12,390 - 11.52T \quad (7)$$

(here ΔF^0 is measured in J/mole).

This equation differs somewhat from the familiar Richardson equation [5], although the results obtained from both equations agree well and their difference does not exceed the error of calculation by the Richardson equation. At the same time it is more expedient to use Eq. (7) because it has been derived from the conditions of phase equilibrium.

The value of ΔF^0 can be expressed in terms of the parameters of the melt. In this case we can use expressions of types (2) and (6) but with allowance for the change in the chemical potential of iron $\Delta\mu_{\text{Fe}}^{L-\gamma}$ in melting. We used the value of $\Delta\mu_{\text{Fe}}^{L-\gamma}$ presented in [15]. After some transformations we obtain

$$\Delta F^0 = RT \left[\ln \frac{N_{\text{CL}}}{N_{\text{CL}}^*} + \frac{10,720}{T} (N_{\text{CL}} - N_{\text{CL}}^*) (2 - N_{\text{CL}} - N_{\text{CL}}^*) + 3 \ln (1 - N_{\text{CL}}) - 3 \times \frac{10,720}{T} N_{\text{CL}}^2 \right] - 3\Delta\mu_{\text{Fe}}^{L-\gamma}. \quad (8)$$

Joint solution of Eqs. (7) and (8) gives the temperature dependence of the solubility of cementite in the melt. This dependence is plotted in Fig. 1. It can be seen that the temperature of the liquidus line for the stoichiometric cementite composition is much lower than that assumed earlier and is close to 1260-1270°C. Similar results have been obtained experimentally in [2]. However, the results of our calculation do not answer the question of the melting behavior of cementite (congruent or incongruent).

We used the second approach to solve this problem and determine the conditions of equilibrium of the phases of the Fe-C system (the melt, austenite, ferrite, and cementite) with Fe_7C_3 carbide. It is based on the techniques of thermodynamic analysis of ternary systems developed by the author of [16] and makes it possible to calculate and plot sections of phase diagrams for such systems. This method can involve the approximate equation of Hellert [1] and modified and refined equations relating the thermodynamic activities of the components of a complex system to the coefficients of the interphase distribution of the elements. The method, its equations, and the admissible calculation errors are described in [16]. In the present work I modified the equations in order to

reduce the calculation errors. In the new equations the assumptions used by Hellert are partially compensated by the averaged values of the carbon contents in the phases of the alloyed and unalloyed alloys. An analysis has shown that for chromium-bearing alloys (about 5% Cr in the austenite) the calculation error due to the use of a refined equation is equal to ~3%, whereas for the Hellert equation it is about five times higher.

As applied to the Fe–C–Cr system the refined equations can be represented in the form

$$\ln \frac{a_C^{\text{Cr}}}{a_C^0} = \beta_C^{\text{Cr}} N_{\text{Cr}}, \quad (9)$$

$$\beta_C^{\text{Cr}} = - \frac{(K_{\text{Cr}} - 1) + (N_{\text{C(av)}}'' - K_{\text{Cr}} N_{\text{C(av)}}')}{(K_{\text{Cr}} - 1) N_{\text{C}} + (N_{\text{C(av)}}'' - K_{\text{Cr}} N_{\text{C(av)}}')}, \quad (10)$$

where a_C^{Cr} and a_C^0 are the thermodynamic activities of carbon in the alloyed and unalloyed alloys, respectively; N_{C} and N_{Cr} are the atomic fractions of carbon and chromium in the alloy; β_C^{Cr} is a coefficient allowance for the effect of chromium on the thermodynamic activity of carbon in the alloy; K_{Cr} is the coefficient of the distribution of chromium between the high-carbon and low-carbon phases of the alloy; $N_{\text{C(av)}}' = \frac{1}{2}(N_{\text{C}_0}' + N_{\text{C}}')$ and $N_{\text{C(av)}}'' = \frac{1}{2}(N_{\text{C}_0}'' + N_{\text{C}}'')$ are the mean equilibrium carbon contents (in atomic fractions) in the low-carbon and high-carbon phases of the two-phase alloy, respectively (here N_{C_0}' and N_{C_0}'' are the equilibrium carbon contents in the phases of the unalloyed alloy, N_{C}' and N_{C}'' are the same quantities in the phases of the alloyed alloy).

As a rule, this method is used in going from binary systems to ternary or more complex ones. The initial data for such an analysis are the phase diagrams of the corresponding binary systems, the thermodynamic activities of the components in the binary systems, and the coefficients of the interphase distribution of the elements, commonly determined experimentally.

In the present work the method is used to solve the inverse problem that consists in going from a ternary Fe–C–Cr system to a binary Fe–C one in the regions where the Fe_7C_3 carbide is in equilibrium with the other phases. In this case the most reliable isothermal sections of the Fe–C–Cr diagram, constructed experimentally and published in [17–19], are used as the initial data. These sections correspond to the four-phase equilibria of $\alpha + \gamma + D + \varepsilon$ (760°C), $\gamma + L + D + \varepsilon$

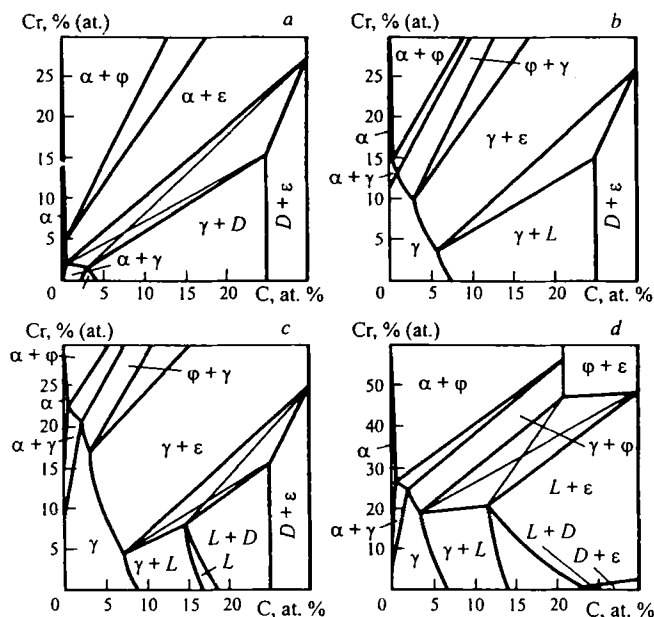


Fig. 2. Isothermal sections of the Fe–C–Cr diagram: a) for 760°C; b) for 1000°C; c) for 1175°C; d) for 1255°C.

(1175°C), $\gamma + L + D + \phi$ (1255°C) and the three-phase equilibrium of $\gamma + D + \varepsilon$ at 1000°C. They are presented in Fig. 2 after recalculation of the mass fractions of carbon and chromium into atomic fractions and some correction aimed at matching the sections with each other and with the Fe–C diagram. Here α is used to denote ferrite, γ is used for austenite, D for cementite, L for the melt, ε for carbide ($\text{Fe, Cr})_7\text{C}_3$, and ϕ for carbide $(\text{Cr, Fe})_{23}\text{C}_6$.

Table 1 presents the initial data for calculating the equilibrium content N_{C} of carbon in the phases of Fe–C alloys (from the Fe–C diagram) and the thermodynamic activity of carbon a_{C} in the biphasic regions of the Fe–C system (in accordance with the data of [2, 12–15]).

The carbon content N_{C_0} in Table 1 refers to the phase of the biphasic region that is given first. For example, $N_{\text{C}_0(\gamma-L)}$ is the solubility of carbon in the phase L that is in equilibrium with the γ -phase, and $N_{\text{C}_0(L-\gamma)}$ is the solubility of carbon in the γ -phase under the same biphasic equilibrium.

The transition from the Fe–C–Cr system to the Fe–C system occurs through three-phase regions (conode triangles) in isothermal sections of the Fe–C–Cr diagram, for example, through the $\gamma-D-\varepsilon$ triangle (Fig. 2). Taking into ac-

TABLE 1

$t, ^\circ\text{C}$	a_{C}^0					N_{C_0}						
	$D-L$	$D-\gamma$	$D-\alpha$	$L-\gamma$	$\gamma-\alpha$	$L-D$	$\gamma-D$	$\alpha-D$	$L-\gamma$	$\gamma-L$	$\gamma-\alpha$	$\alpha-\gamma$
760	–	1.24	1.19	–	0.62	–	0.041	0.0029	–	–	0.023	0.0015
1000	–	1.101	–	–	–	–	0.072	–	–	–	–	–
1175	1.20	1.036	–	0.875	–	0.184	0.096	–	0.164	0.086	–	–
1255	2.24	–	–	0.476	–	0.235	–	–	0.139	0.070	–	–

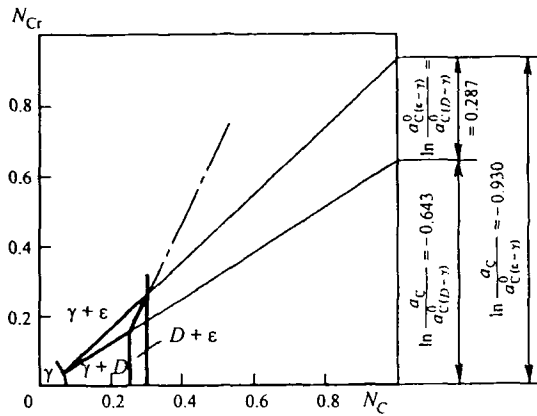


Fig. 3. Geometric evaluation of the difference in the values of the thermodynamic activity of carbon in biphasis regions of the Fe-C-Cr and Fe-C systems at 1000°C.

count that the thermodynamic activity of carbon in this triangle is constant and the same for all the alloys, including the corresponding boundary conodes of the biphasis regions, we can pass from the $\gamma_0 D_0$ conode (in the Fe-C system) to a conode triangle (i.e., to the boundary conode γD) and then from the boundary conodes $D\epsilon$ and $\gamma\epsilon$ of the triangle to the corresponding conodes $D_0\epsilon_0$ and $\gamma_0\epsilon_0$ in the Fe-C system and calculate the thermodynamic activities of carbon on these conodes.

As an example, we present a detailed calculation for a temperature of 1000°C.

The coefficient $\beta_{C(D-\gamma)}^{Cr}$ for cementite in the biphasis region $D-\gamma$ was calculated by Eq. (10). For the case considered it can be written in the form

$$\beta_{C(D-\gamma)}^{Cr} = - \frac{(K_{Cr}^{D-\gamma} - 1) + (N_C^D - K_{Cr}^{D-\gamma} N_{C(av)}^\gamma)}{K_{Cr}^{D-\gamma} (N_C^D - N_{C(av)}^\gamma)} \quad (11)$$

In correspondence with the section of the Fe-C-Cr diagram at 1000°C presented in Fig. 2 and with allowance for the stoichiometry of cementite we obtain $N_C^D = 0.25$, $N_{C(av)}^\gamma = 0.064$, $K_{Cr}^{D-\gamma} = 4.457$, and $\beta_{C(D-\gamma)}^{Cr} = -4.128$. In accordance with Eq. (9) we can write

$$\ln a_C = \ln a_{C(D-\gamma)}^0 + \beta_{C(D-\gamma)}^{Cr} N_{Cr}^D \quad (12)$$

for the carbon activity in the three-phase region, where N_{Cr}^D is the equilibrium content of chromium in the cementite for the

three-phase equilibrium $\gamma-D-\epsilon$, $N_{Cr}^D = 0.156$. The calculation gives $\ln a_C = -0.548$ and $a_C = 0.578$.

In correspondence with Eqs. (10) and (9) we calculate the values of $\beta_{C(\epsilon-D)}^{Cr}$, $\beta_{C(\epsilon-\gamma)}^{Cr}$, $a_{C(\epsilon-D)}^0$, and $a_{C(\epsilon-\gamma)}^0$ for the Fe-C system, namely,

$$\beta_{C(\epsilon-D)}^{Cr} = - \frac{(K_{Cr}^{\epsilon-D} - 1) + (N_C^\epsilon - K_{Cr}^{\epsilon-D} N_C^D)}{K_{Cr}^{\epsilon-D} (N_C^\epsilon - N_C^D)} \quad (13)$$

$$\beta_{C(\epsilon-\gamma)}^{Cr} = - \frac{(K_{Cr}^{\epsilon-\gamma} - 1) + (N_C^\epsilon - K_{Cr}^{\epsilon-\gamma} N_{C(av)}^\gamma)}{K_{Cr}^{\epsilon-\gamma} (N_C^\epsilon - N_{C(av)}^\gamma)} \quad (14)$$

$$\ln a_{C(\epsilon-D)}^0 = \ln a_C - \beta_{C(\epsilon-D)}^{Cr} N_{Cr}^\epsilon \quad (15)$$

$$\ln a_{C(\epsilon-\gamma)}^0 = \ln a_C - \beta_{C(\epsilon-\gamma)}^{Cr} N_{Cr}^\epsilon \quad (16)$$

We use the section at 1000°C (Fig. 2) and the stoichiometry of the carbides to obtain $N_C^D = 0.25$, $N_C^\epsilon = 0.30$, $N_{C(av)}^\gamma = 0.065$, $K_{Cr}^{\epsilon-D} = 1.67$, $K_{Cr}^{\epsilon-\gamma} = 7.43$. After the calculation we arrive at

$$\beta_{C(\epsilon-D)}^{Cr} = -6.610; \beta_{C(\epsilon-\gamma)}^{Cr} = -3.579; \ln a_{C(\epsilon-D)}^0 = 1.171.$$

$$a_{C(\epsilon-D)}^0 = 3.225; \ln a_{C(\epsilon-\gamma)}^0 = 0.383, \text{ and } a_{C(\epsilon-\gamma)}^0 = 1.467.$$

The values of $a_{C(\epsilon-D)}^0$ and $a_{C(\epsilon-\gamma)}^0$ can also be determined without calculation by plotting them geometrically on the basis of a geometric interpretation of the changes in the thermodynamic activities of the components in biphasis regions of ternary systems suggested in [20]. A plot is presented in Fig. 3 for the biphasis equilibria $\gamma-\epsilon$ and $D-\gamma$. For the phase γ we used the mean values of the solubility of carbon ($N_{C(av)}^\gamma = 0.064$ for the $\gamma-D$ equilibrium and $N_{C(av)}^\gamma = 0.065$ for the $\gamma-\epsilon$ equilibrium).

In correspondence with the geometric interpretation, the solutions to Eq. (9) for the biphasis regions considered correspond to the segments cut by the continuations of the conodes on a line parallel to the axis of ordinates and passing through the point $N_C = 1$. This is done using the following rule of signs: if the cut segment lies above the axis of abscissas the activity of the component considered (carbon in our case) decreases, if it lies below the axis of abscissas the activity increases. In correspondence with this rule the lengths of the segments in Fig. 3 are given with minus sign.

It follows from Fig. 3 and Eq. (9) that for both biphasis regions we have

$$\ln a_{C(\epsilon-\gamma)}^0 = \ln a_{C(D-\gamma)}^0 - 0.643 + 0.930.$$

Since $a_{C(D-\gamma)}^0 = 0.101$, we have $\ln a_{C(\epsilon-\gamma)}^0 = 0.383$ and $a_{C(\epsilon-\gamma)}^0 = 1.467$, i.e., the result is the same as calculated above. We see that at least a preliminary estimate of the

TABLE 2

t, °C	a_C	a_C^0 in biphasis regions			
		$\epsilon + D$	$\epsilon + L$	$\epsilon + \gamma$	$\epsilon + \alpha$
760	0.656 ± 0.020	4.253 ± 0.255	-	1.687 ± 0.101	1.559 ± 0.094
1000	0.578 ± 0.017	3.226 ± 0.194	-	1.467 ± 0.088	-
1175	0.547 ± 0.016	2.732 ± 0.164	1.696 ± 0.102	1.365 ± 0.082	-
1255	0.337 ± 0.010	-	2.516 ± 0.151	1.232 ± 0.074	-

effect of the alloying elements on the thermodynamic conditions of the phase equilibria can be obtained by a simple geometric construction without calculation. For example, it is clear from Fig. 3 that the Fe – C system has a region where the D and ϵ carbides are in equilibrium but the thermodynamic activity of carbon is so high ($a_{C(\epsilon-D)}^0 > 3$) that this equilibrium can hardly be fixed without the development of graphitization of both phases.

A similar thermodynamic calculation and plotting has been conducted for the temperatures of the four-phase equilibria (790, 1175, and 1255°C). The results obtained are presented in Table 2 with the errors due to the calculation method used.

The calculated results were used to construct the diagram of the thermodynamic activity of carbon in the Fe – C system, where the biphasic regions with a ϵ -phase (Fe_7C_3) are represented by the principal line and a band that allows for the maximum possible calculation error (Fig. 4). Figure 4a presents the diagram in the conventional $t(^{\circ}C) - a_C$ coordinates without the bottom part that characterizes the $\alpha - D$ and $\alpha - \epsilon$ equilibria. This is explainable by the fact that the slopes of the $\alpha - D$ and $D - \epsilon$ lines at low temperatures are so close that it is impossible to determine the point of their intersection in the extrapolation with satisfactory accuracy. The coordinates of this point can be determined much more simply when the diagram is plotted in $1/T - \ln a_C$ coordinates where T is the absolute temperature in degrees Kelvin (Fig. 4b and c). The lines of the biphasic equilibria with the ϵ -phase are plotted using the main calculated points in Fig. 4b and with allowance for the band of errors in Fig. 4c. The $\alpha - D$ equilibrium lines are plotted with the use of experimental data [15].

The coordinates of the intersection points in Fig. 4 that characterize the conditions of nonvariant three-phase equilibria in the Fe – C system with participation of the ϵ -phase are presented in Table 3 with indication of the calculation errors.

An analysis of the calculated results and the plotted values has shown that the temperatures of the first three equilibria have been determined the most accurately. The greatest error occurred in the determination of the temperature of the fourth equilibrium. If we take into account that the error due to the calculation method has been evaluated without considering the errors introduced with the initial data for the calculation (in particular, the experimentally determined coefficients of the interphase distribution of the elements), the total error can be much higher than that given in Table 3 (sometimes by a factor of 2 – 2.5). Even in this case the results remain quite reliable for the first three equilibria, but for the fourth equilibrium we can only state that the method used can

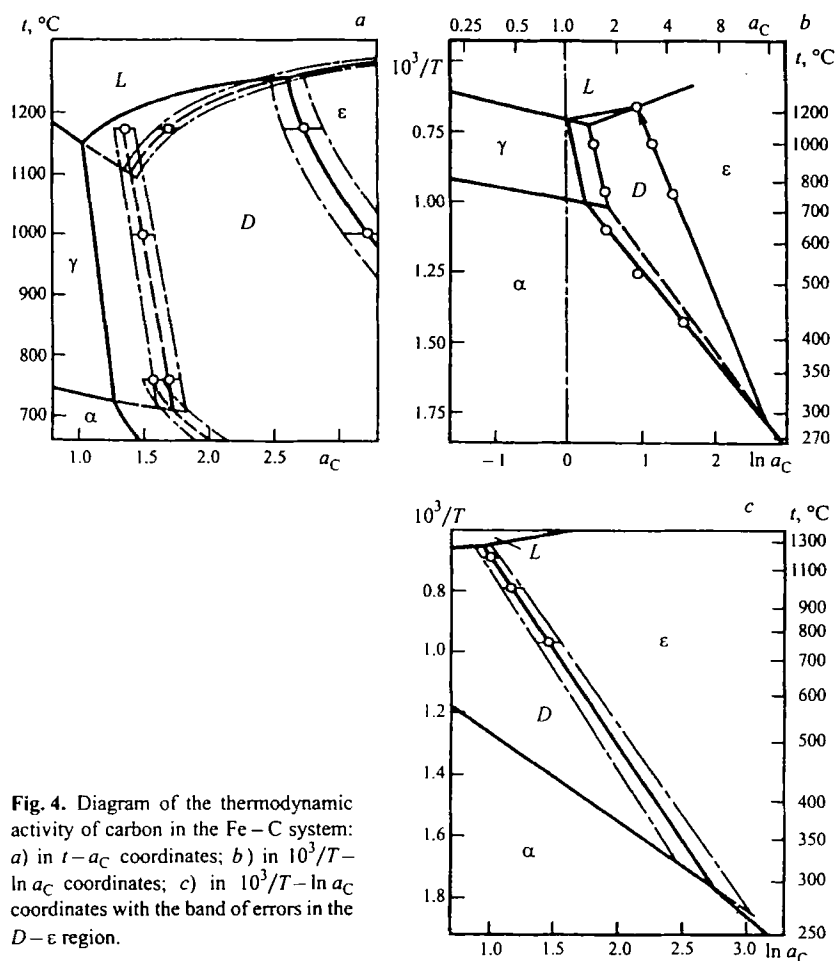


Fig. 4. Diagram of the thermodynamic activity of carbon in the Fe – C system: a) in $t - a_C$ coordinates; b) in $10^3/T - \ln a_C$ coordinates; c) in $10^3/T - \ln a_C$ coordinates with the band of errors in the $D - \epsilon$ region.

determine its existence only qualitatively. Here the mean temperature given in Table 3 and used in the subsequent plotting is only a first quantitative approximation that requires refining.

Using the calculated data, after the transition from the thermodynamic activity of carbon to its content (on the basis of the data and dependences presented in [2, 12 – 15]) we plotted a diagram of metastable equilibria in the Fe – C system (Fig. 5). This diagram differs from other known variants by the presence of regions with a Fe_7C_3 carbide (ϵ -phase), which made it possible to continue it to the carbon content corresponding to the stoichiometry of Fe_7C_3 .

TABLE 3

Equation of three-phase equilibrium	$10^3/T$	$t, ^{\circ}C$	a_C	$\ln a_C$
$L + \epsilon \rightleftharpoons D$	0.653 ± 0.001	1258 ± 3	2.62 ± 0.13	0.964 ± 0.05
$L \rightleftharpoons \gamma + \epsilon$	0.725 ± 0.002	1100 ± 10	1.40 ± 0.08	0.34 ± 0.05
$\gamma \rightleftharpoons \alpha + \epsilon$	1.017 ± 0.005	710 ± 5	1.72 ± 0.10	0.54 ± 0.06
$D \rightleftharpoons \alpha + \epsilon$	1.78 ± 0.09	290 ± 30	15.1 ± 5.0	2.72 ± 0.30

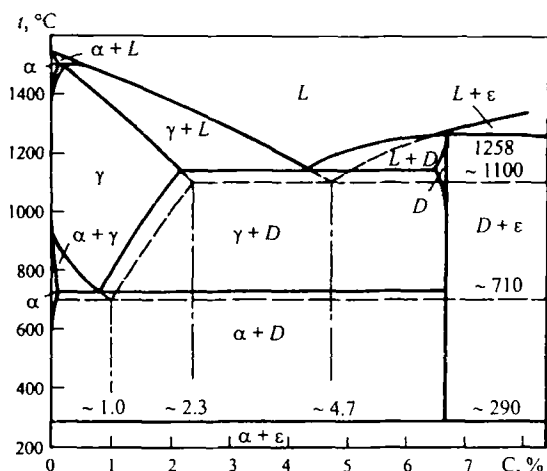


Fig. 5. Diagram of metastable equilibria in the Fe-C system (before the Fe_7C_3 carbide).

CONCLUSIONS

1. The Fe-C system includes a biphasic region of carbide equilibria (cementite Fe_3C and carbide Fe_7C_3).

2. The domain of the existence of cementite is bounded from above (1258°C) and from below (about 290°C); outside this domain another carbide phase, namely, Fe_7C_3 (or ϵ -phase), is more stable thermodynamically.

3. At 1258°C the Fe-C system possesses a nonvariant peritectic equilibrium $L + \epsilon \rightleftharpoons D$, i.e., cementite melts incongruently.

4. At about 290°C there is a eutectoid equilibrium $D \rightleftharpoons \alpha + \epsilon$; below this temperature both carbide phases are characterized by a high degree of metastability ($a_C > 15$).

5. In accordance with the stoichiometric composition and the thermodynamic characteristics the low-temperature modification of Fe_7C_3 carbide can be identified with ϵ -carbide segregated in the decomposition of martensite in tempering of hardened steel.

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