

Phase Equilibria in the Carbide Region of Iron–Carbon Phase Diagram

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Abstract—The main evolution stages of the phase diagram of Fe–C in the carbide region (on the right from the cementite line) is a recently discussed theoretical topic that has been considered. It has been determined that previously isolated ϵ -Fe₂C, χ -Fe₅C₂, and g-Fe₇C₃ carbides (except for cementite Θ -Fe₃C) are nonstoichiometric compounds. Thus, they are variable composition phases containing stoichiometric composition or second-type interstitial solid solutions based on daltonides and berthollides. It has been stated that the iron–cementite phase diagram can be identified as the iron– ϵ -Fe₂C carbide phase diagram in the concentration range of 0–9.7% C. The following phase transformations are introduced to the diagram: reaction of non-variant syntectic equilibrium of cementite Θ -Fe₃C crystallization; reaction of peritectic equilibrium of carbide χ -Fe₅C₂ crystallization; low-temperature peritectoid transformation of carbide, at which solid solutions of ferrite and cementite form solid solution possessing broad homogeneity range based on ϵ -carbide Fe₂C berthollide. It has been shown that the carbide phases represent a uniform isomorphous quasi-carbide solid solution, while the carbide phase crystallizes in the form of the carbide phase mixture as quasi-eutectics.

Keywords: iron–carbon phase diagram, Θ -Fe₃C, Hägg carbide χ -Fe₅C₂, Ekström-Adcock carbide g-Fe₇C₃, ϵ -carbide Fe₂C, iron carbides, daltonide, berthollide, solid solution of cementite, isomorphous quasi-carbide solid solution

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Iron (cast iron and steel) based alloys currently represents the basic material for the production of machines, mechanisms, and contemporary industrial constructions. According to the estimation of World Steel Association (WSA), steel discharge by 64 leading manufacturing countries increased by 3.4% in 2019 up to 1.87 millions of tons, while that of cast iron increased to 1.2 millions of tons. For comparison, International Copper Study Group (ICSG) provides the data that global production of copper, which is the leader among nonferrous metals, would increase only to 250 thousands of tons in 2020.

Investigation, improvement, and formation of the characteristics of steel and cast iron as basic alloys of the Fe–C system and, consequently, experimental and theoretical description of this system is one of priority directions in the theory of alloys, which looks quite promising. Knowledge and control of phase transformations according to the Fe–C phase diagram represent the theoretical, technological, and physico-chemical foundation of metallurgy, metal science, and thermal treatment of steels and cast irons.

In spite of detailed and careful study of the Fe–C phase diagram [1–10], some structural aspects require more detailed consideration, in particular alloys and flow processes. In addition, there are large regions in

which the structure of this diagram is not totally established, in particular, temperature, composition, and pressure ranges not directly related to cast iron and steel production.

Characteristics of iron and graphite are studied in sufficient detail unlike carbide phases. Iron and carbon can form a number of carbide phases [7]: FeC, Fe₂C, Fe₃C, Fe₃C₂, Fe₄C, Fe₅C₂, Fe₆C, Fe₇C₃, Fe₈C, Fe₂₀C₉, and Fe₂₃C₆, which are considered metastable transient phases. In fact, a total of four types of carbides were so far distinguished in the Fe–C system: cementite Θ -Fe₃C, ϵ -carbide Fe₂C, Hägg carbide χ -Fe₅C₂ (further χ -Fe₃C), and Ekström-Adcock carbide g-Fe₇C₃ (further g-Fe₇C₃).

Extensive literature on carbides [11–22] described only cementite Θ -Fe₃C with poor data; only the type of crystal lattice and some thermodynamic functions were determined [4]. The melting point of cementite varies in the range from 1250°C [4, 9, 13, 15] to 1650°C [11], which is quite strange even for carbide possessing nonstoichiometric composition.

Cementite [Θ]-Fe₃C and carbides ϵ -Fe₂C, χ -Fe₅C₂, and g-Fe₇C₃ were analyzed in great detail in the monograph from [11]. It was shown that carbides undergo mutual transformation at heating. The car-

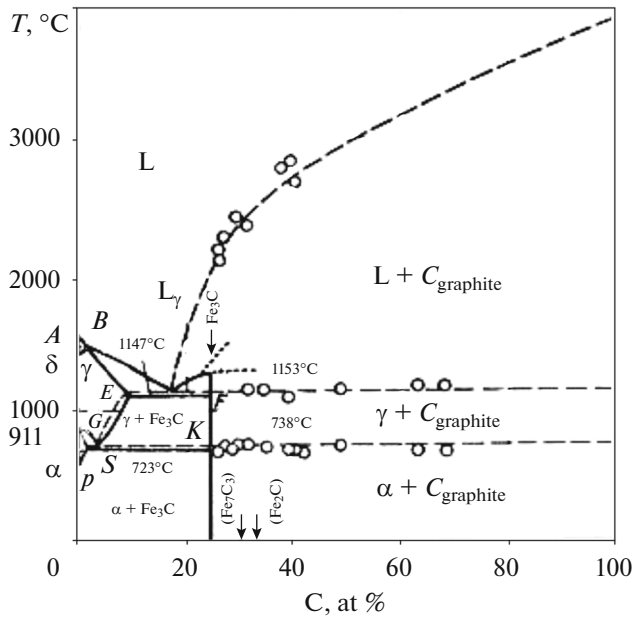


Fig. 1. Phase diagram of the Fe–100% C system [4], Fig. 71, p. 97).

bide χ -Fe₃C transforms into cementite at the temperatures higher than 360°C. In the range of 380–400°C, ϵ -carbide Fe₂C is transformed into carbide g-Fe₇C₃. At the temperatures higher than 420°C, ϵ -carbide Fe₂C does not exist. There are almost no data on other types of iron carbides. Carbide phases are not shown in the Fe–C phase diagram, because these phases are considered metastable and transient.

Figure 1 shows a full phase diagram of the Fe–100% C system from the diagram atlas [4] with a reference to the works of V.K. Grigorovich, which indicates only carbides γ -Fe₇C₃ and ϵ -Fe₂C by arrows without lines corresponding to phase equilibria. G.I. Sil'man specified the diagram of the Fe–C metastable system using thermodynamic analysis [2, 9] by calculating the position of cementite liquidus in the cementite range and “post-cementite” range (before carbide Fe₇C₃) and determining the conditions of thermodynamic equilibrium of carbide g-Fe₇C₃ with other phases (Fig. 2).

Let us highlight the most important statements from that work.

(1) A low-temperature modification of carbide Fe₇C₃ can be correlated with ϵ -carbide Fe₂C according to chemical composition and thermodynamic characteristics, which is precipitated upon the decomposition of martensite during tempering of quenched steel.

(2) Cementite possesses a clear homogeneity range.

(3) The structure of the phase region between cementite Fe₃C and carbide Fe₇C₃ represents a quasi-eutectics, which consists of primary crystals of Fe₇C₃

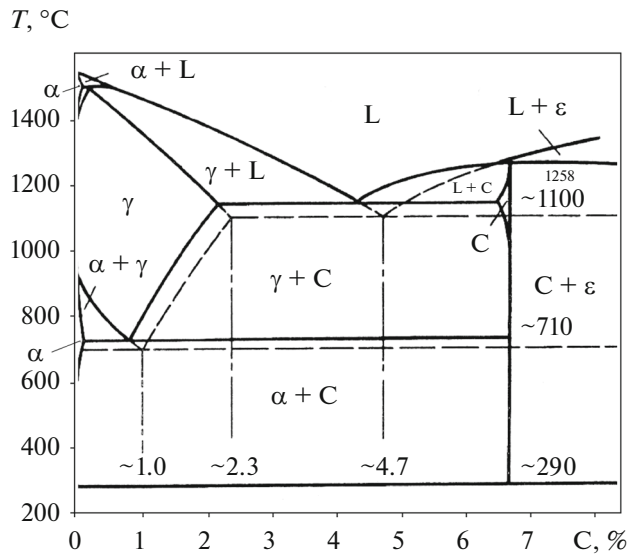


Fig. 2. Metastable equilibria diagram in the Fe–C system before carbide

(this carbide is indicated as ϵ -Fe₂C in the diagram) and finely differentiated quasi-eutectic mixture of cementite with carbides of various compositions.

(4) There is nonvariant peritectic equilibrium L + ϵ -carbide = C at 1258°C; i.e., cementite melts incongruently.

(5) There is eutectoid equilibrium C = α + ϵ -carbide at 290°C, whereas both carbide phases are characterized by a high degree of metastability below this temperature.

The most important theoretical statement of G.I. Sil'man is focused on the equivalence of carbides and their mutual co-crystallization in the form of quasi-eutectic mixture. It should be noted that his theoretical calculations were not confirmed in experimental alloys.

Alloys with 7.0–9.0% C consisting of the carbide Fe₇C₃ crystals surrounded by layered eutectics Fe₃C–Fe₇C₃, whose melting point is close to 1400°C, were prepared in [12, 13] at the temperatures of up to 1500°C and pressures up to 9.9 kPa from the mixtures of iron powder and carbon soot. X-ray diffractometric and metallographic studies showed that the alloys contain a small impurity of cementite Fe₃C and in fact represent the synthesized carbide Fe₇C₃ with a pseudo-hexagonal orthorhombic lattice; in this case, diamond lattice was not detected. Derived from the experimental studies, configuration of phase equilibria in the post-cementite range of the diagram as the initial stage of the iron–diamond diagram was plotted (Fig. 3a).

It might be argued that the configuration of the post-cementite range of the Fe–C phase diagram under excess pressure of 9.0 kPa is incompatible with

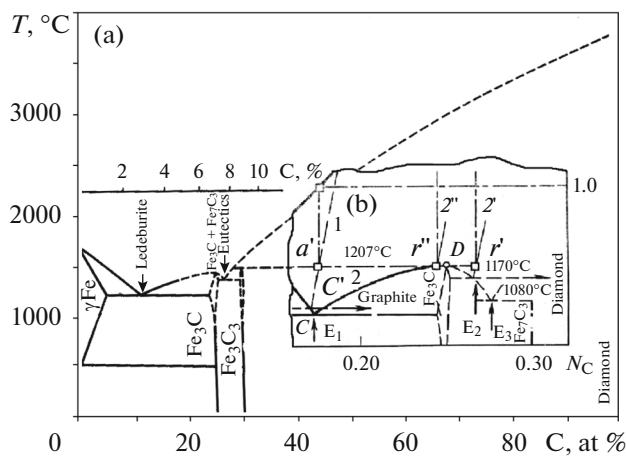


Fig. 3. Alloy phase diagram of the iron–diamond system: (a) under the pressure of 8.0 kPa ([12], Fig. 3, p. 182); (b) plotting of diamond liquidus line on the iron–carbon diagram: (1) graphite liquidus and (2) variants of diamond liquidus ([13], Fig. 4, p. 196).

the Fe–C diagram under atmospheric pressure. However, the studies from [12] showed that the alloy structures formed under excess pressure should decompose after its release, because they are unstable (metastable) under atmospheric pressure; however, X-ray diffractometric and metallographic analyses were carried out under atmospheric pressure and the structure did not respond to the change of environmental pressure and remained stable. This contradiction was solved in [23], which was devoted to investigation of the iron carbide stability under the pressure of the Earth’s core. Fig. 4 shows the change of the enthalpy of iron, diamond, cementite Θ - Fe_3C , and carbides g - Fe_7C_3 and ϵ - Fe_2C .

Enthalpy is the energy stored in substance during its formation for the maintenance of the stable state of its molecular structure. Enthalpy of all considered carbides is varied nearly identically up to the pressure of 300 GPa, which indicates its structural stability. This effect is proved by the retention of the main thermodynamic parameter values of carbide phases [23–31]; enthalpy $H = 0.2$ MeV/atom, energy of formation $F_{\text{form}} = 0.058$ – 0.07 eV/atom, and energy of the main state E_0 from -8.53 to -8.63 eV/atom.

The studies in [23] showed that the structure of carbides is stable up to the pressures of 200–250 GPa. Consequently, external excess pressure does not alter phase processes of structure formation and stability of the carbide phases in the Fe–C system. The system practically did not respond to the pressure of 9.0 GPa in [12], the obtained structures were in fact real carbide compounds in the Fe–C system, and external pressure nearly did not influence the form of phase transformations in the carbide range of the phase diagram. Consequently, either excess external pressure over the melt or ultrahigh overheating temperature of the melt, or both, are necessary to prepare the alloys

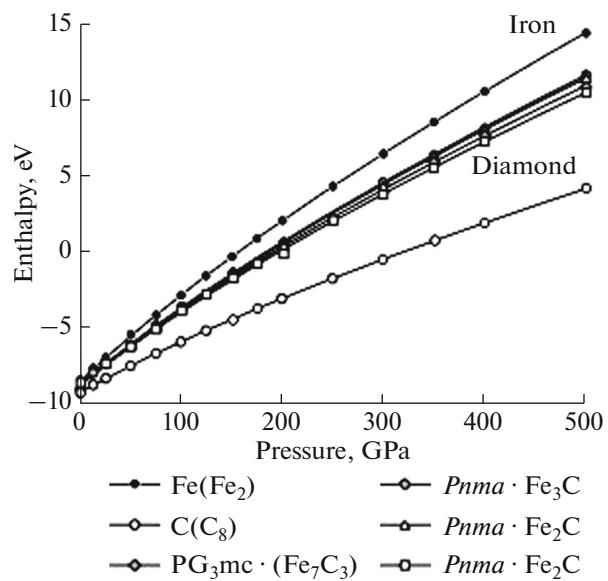


Fig. 4. Formation enthalpy per one atom of substance for the investigated iron carbides, pure iron, and diamond depending on pressure ([23], p. 216, Fig. 1).

with more than 5.0% C; in this case, the obtained structures in the alloys would not contradict to the laws of two-phase diagrams of alloys.

Density values of the carbide phases, g/cm^3 , were also determined in [23] under atmospheric pressure: cementite Θ - Fe_3C , 8.36; g - Fe_7C_3 , 8.17; and ϵ - Fe_2C , 8.10. Similar density values also indicate a homogeneous structural state of carbides or uniform isomorphous quasi-carbide solid solution in the Fe–C system.

Thus, excess external pressure does not change the structural state of carbide phases in the Fe–C system and does not alter phase transformations; it rather provides process capability of the preparation of high-carbon quasi-carbide alloys up to the concentration of 15.0% C upon electric-arc melting at the temperature of overheating of 6000°C ($N_{\text{C}_{\text{saturated}}}^{6000} = 15.0\%$ C).

In [24], formation conditions of graphite and diamond at the temperature and pressure values of the Earth mantle were investigated. The interaction of iron carbide Fe_3C and iron oxides was studied on a high-pressure multiple-blanking instrument of “dissected sphere” type at 6.3 GPa in the range of 900–1600 $^\circ\text{C}$ for 18–20 h. It was determined that graphite crystallizes along with Fe^{3+} containing wustite upon carbide–oxide interaction in the Fe_3C – Fe_2O_3 system¹. Oxidation of cohenite² by following reactions is

¹ Iron monoxide characterized by lattice defects of bcc lattice, which is described by Fe_{1-x}O formula. It represents nonstoichiometric compound with deficiency of iron atoms.)

² Mineralogical name of cementite.

the main mechanism of formation of free graphite/diamond from carbide carbon:

(1) $\text{Fe}_3\text{C} + 3\text{Fe}_2\text{O}_3 \rightarrow 9\text{FeO} + \text{C}^0$ (graphite, diamond);

(2) $\text{FeO} + \text{Fe}_3\text{C} \rightarrow (\text{Fe}^{2+}, \text{Fe}^{3+})\text{O} + \text{C}^0$ (graphite, diamond).

At the temperatures above solidus ($\geq 1400^\circ\text{C}$), a redox mechanism of crystallization of graphite and diamond with the formation of associate of Fe^{3+} containing wustite + graphite/diamond is realized upon oxidation of metal-carbon melt with wustite. Reaction in the $\text{Fe}_3\text{C}-\text{Fe}_2\text{O}_3-\text{MgO}-\text{SiO}_2$ system results in the formation of the associate of Fe^{3+} containing magnesiowustite, olivine, and graphite. At $t \geq 1500^\circ\text{C}$, two contrast melts are generated, more specifically, metal-carbon and silicate-oxide, whose redox reaction leads to crystallization of graphite and growth of diamond.

Thus, it was experimentally proved that cementite transformation into diamond is possible only upon redox reactions based on oxides of iron and other elements under high pressure and temperature in another alloy system and there is no “diamond” phase, as well as graphite and diamond liquidus lines on the Fe-C phase diagram (Fig. 3). The hypothesis of A.A. Zhukov [3, 8, 10, 13] focused on the possible direct transformation of cementite $\Theta\text{-Fe}_3\text{C}$, carbides $g\text{-Fe}_7\text{C}_3$, and $\varepsilon\text{-Fe}_2\text{C}$ into diamond at high temperatures and pressures in iron-carbon alloys and plotting corresponding iron-diamond diagram is presently considered invalid. Results of theoretical calculations without experimental validation are usually interesting though tentative.

Consequently, full physicochemical identification of carbides (even though this problem could practically not be solved due to the absence of the studied objects represented by single phases of different composition carbides) and investigation of the alloys with the content of 6.0–10.0% C, whose phase and structural compositions should presumably consist of cementite $\Theta\text{-Fe}_3\text{C}$ and carbides $\varepsilon\text{-Fe}_2\text{C}$ and $g\text{-Fe}_7\text{C}_3$, are necessary to specify phase composition in the post-cementite region of the phase diagram. However, these supercarbon alloys are yet not prepared. In contrast to the production of other types of metal carbides [14–21], cementite as carbide is not available at industrial scale and it is produced for experimental studies at low quantities using electrolysis from steels, ferroalloys, and white cast irons [11, 22]. Absence of the cementite synthesis technology at industrial scale contradicts to its identification as a chemical compound.

Real single crystal rather than molecule inherits the properties of a substance in solid state or, in other words, appearance of any chemical compound as an individual substance. Single crystal acts as a quantum-mechanical system in chemical reactions with solid body and its thermodynamic characteristics, such as

melting, boiling, and vaporization temperature; lattice type; entropy; enthalpy; energy of formation and main state; and others do not depend on the degree of nonstoichiometry and imperfection of crystal lattice. According to a general analysis of the nonstoichiometry degree of crystals, it can be stated that cementite possessing unusual characteristics, such as broad range of melting point, significant variations of chemical composition, and its inaccessibility through direct synthesis unlike other metal carbides, is not carbide to some extent.

Development of mechanosynthesis or mechanofusion [25, 32, 33] solved the problem of full identification of physicochemical and thermodynamic properties of the carbide phases of the Fe-C system [23–33]. Single phases of cementite $\Theta\text{-Fe}_3\text{C}$ [26, 27] and carbides $\chi\text{-Fe}_5\text{C}_2$ [28], $g\text{-Fe}_7\text{C}_3$ [29], and $\varepsilon\text{-Fe}_2\text{C}$ [26–28] prepared through low-temperature ($< 100^\circ\text{C}$) mechanosynthesis of $\alpha\text{-Fe}$ powder ($< 100 \mu\text{m}$) were studied in full detail upon its dispersion in centrifugal planetary mill with balls that are 8 mm in diameter in liquid hydrocarbons (toluene C_7H_8) [26–29]. This method provides iron carbides in single-phase state within their thermal stability range. Analogous results were obtained in [25, 33]. The following was determined [24–31]:

Single-phase cementite $\Theta\text{-Fe}_3\text{C}$ and carbides $\chi\text{-Fe}_5\text{C}_2$ [28] and $g\text{-Fe}_7\text{C}_3$ are the phases with variable composition or solid solutions of carbon in cementite rather than stoichiometric compounds;

Carbon diffusion is drastically enhanced upon heating of single-phase carbides, which indicates the absence of strong valence bond of carbon with crystal lattice of iron, which is not intrinsic for single crystal;

There is unusually high concentration of vacancy-carbon atom equilibrium pairs ($V_{\text{C}}\text{-C}_{\text{gr}}$), which form graphite phase, upon heating of single-phase cementite in the range of $625\text{--}727^\circ\text{C}$; consequently, there is irreversible change of single-phase cementite with precipitation of solid solution of $\alpha\text{-Fe}$ and graphite; i.e., its thermal decomposition occurs without diffusion and ends at the temperature of 762°C ;

Single-phase ε -carbide Fe_2C is carbide and decomposes at the temperatures above 380°C with diffusion according to the scheme $\varepsilon\text{-Fe}_2\text{C} \rightarrow \chi\text{-Fe}_5\text{C}_2 \rightarrow \text{cementite } \Theta\text{-Fe}_3\text{C} + \text{graphite}$;

Single-phase carbide $\chi\text{-Fe}_5\text{C}_2$ is a structural modification of ε -carbide Fe_2C and is stable up to 600°C ;

Single-phase carbide $g\text{-Fe}_7\text{C}_3$ is stable in the range of $500\text{--}652^\circ\text{C}$.

In [30] and the monograph from the group of authors edited by V.M. Schastlivtsev [31], upon a large experimental material, it was proved that cementite represents a solid solution of carbon in iron with variable composition (with broad homogeneity range), which is stoichiometric within this range correspond-

ing to compound Fe_3C . More generally, cementite is a solid solution with the broad homogeneity range and interstitial phase corresponding to carbide $\Theta\text{-Fe}_3\text{C}$. Interstitial phase is featured by the difference of its lattice type (orthorhombic) from the lattice type of the ferrite matrix metal (bcc). The ε -carbide Fe_2C is also related to this type of solid solution with interstitial phase.

Identification of cementite as solid solution also solves the problem of its “melting” point. Melting points of austenite and martensite are not discussed; any solid solution is characterized by the temperature range of its precipitation from solution or dissolution upon melting rather than melting point. The studies devoted to quenching or iron-carbon melts [34] established that there are austenite and cementite in the structures upon quenching of melts in the range of 1300–1700°C. In [24] devoted to the study of the formation conditions of graphite and diamond from iron carbides upon quenching of metal-carbon melts (mean C content in the melt is 5.0–6.0%), only austenite and cementite were detected in hardening structures from the temperature of 1400–1600°C. Consequently, it is reasonable to consider that the “melting” point of cementite corresponds to the range of 1600–1650°C [11, Table 2]. However, assuming the fact that “alloys” in the Fe–C system are solutions, the “melting” point of cementite at heating is in fact the temperature corresponding to its full dissolution in liquid iron. The range of its “melting” temperatures from 1250 to 1700°C is the temperature range of its dissolution as solid solution in analogy with austenite. When cooling the solution of iron with carbon, it becomes oversaturated with respect to carbon. Furthermore, the temperature of 1600–1700°C corresponds to the stable precipitation range of solid solution of cementite from the melt. From this viewpoint, the suggestion that stable precipitation of cementite from melt occurs through peritectic reaction [36] could be accepted. In particular, the melting point of sodium chloride is 800.8°C; however, the temperature of salt dissolution at 100°C in boiling water is not identical to its melting point.

Identification of cementite $\Theta\text{-Fe}_3\text{C}$ [26, 30, 31] and carbides $\chi\text{-Fe}_5\text{C}_2$ [28], $g\text{-Fe}_7\text{C}_3$ [29], and $\varepsilon\text{-Fe}_2\text{C}$ [26–29] as solid solutions is not sufficient for their full identification from the conventional viewpoint of classification of chemical substances and their accordance in phase transformations on the Fe–C diagram. According to the theory of N.S. Kurnakov on berthollides and daltonides, cementite $\Theta\text{-Fe}_3\text{C}$ and carbides $\chi\text{-Fe}_5\text{C}_2$ and $g\text{-Fe}_7\text{C}_3$ can be related to daltonides, whereas $\varepsilon\text{-Fe}_2\text{C}$ is considered berthollides. Nonstoichiometric compounds were identified as daltonides, that is, phases with transient composition containing stoichiometric composition and berthollides without stoichiometric composition. Berthollides are based on dissociated chemical compounds, whereas daltonides

are based on non-dissociated compounds. More detailed analysis of daltonides and berthollides is given in [37] with the suggestion to introduce the existing phase region of carbide $\varepsilon\text{-Fe}_2\text{C}$ and peritectoid transformation on the Fe–C diagram.

The possibility of nonstoichiometric compounds being solid solutions from excess atoms of components in the main substance allows one to consider nonstoichiometry as the ability of crystalline compounds to dissolve their own components; i.e., iron-based carbide phases could dissolve carbon. Consequently, carbon should freely distribute inside the iron sublattice forming a particular type of solid solution. Thus, the carbide phase is related to second-type interstitial solid solutions.

This fact was proved in [38–40, 41], which showed that unbound carbon in the iron sublattice of cementite is distributed along four types of pores: “normal” and “distorted” octahedral and prismatic. This results in the entropy gain and a decrease in the free energy of cementite, which is intrinsic for the behavior of carbon in solid solution.

It was determined in [25–33] that single-carbide phases possess the following type of crystal structure and space group:

- cementite $\Theta\text{-Fe}_3\text{C}$, orthorhombic, $Pnma$ (62 gr);
- carbide $g\text{-Fe}_7\text{C}_3$, orthorhombic, $Pnma$ (62 gr);
- ε -carbide Fe_2C , orthorhombic, Pnm (58 gr);
- carbide $\chi\text{-Fe}_5\text{C}_2$, monoclinic, $SG[C1\ 2/c1]$; structural modification ε -carbide Fe_2C .

In fact, iron-based carbide phase possesses similar chemical structure (single-type molecular composition of components and identical type of chemical bond) and forms nearly identical crystal lattices. Such phenomenon is referred to as isostructurality and its most important consequence is isomorphism. In this case, all carbides can simultaneously participate in the formation of a general crystal lattice forming mixed crystals, which represent uniform mixtures of solid substances or solid solutions.

It was shown in [29] that all structural models of the iron-based carbide phase can be generalized in the “averaged” model with the limiting number of Fe and C atoms, $n_{\text{Fe}} = 40$ and $n_{\text{C}} = 24$, which are localized in the space group $Pnma$ according to seven and five crystallographically nonequivalent positions of rhombic cell, respectively. One example is that the $\Theta\text{-Fe}_3\text{C}$ cementite phase corresponds to 25% in such universal cell, whereas the $\chi\text{-Fe}_5\text{C}_2$ carbide phase is less than 44 at % of the maximum allowable number of Fe and C atoms. Within this model, the impurity atoms (C) do not replace matrix atoms (Fe); they are rather located in the interstices. Dissolving impurity atoms (C) statistically occupy previously unoccupied interstices between matrix atoms. This type of isomorphism can be characterized as isovalent isomorphism due to the following: the same C atoms possessing the

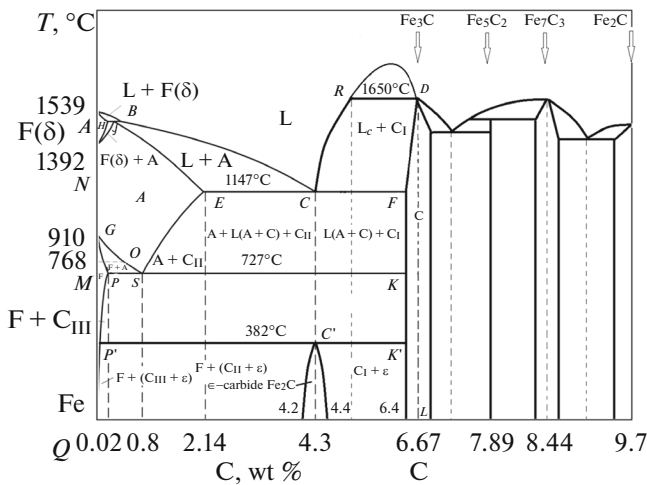


Fig. 5. Full diagram of the iron-ε-carbide Fe₂C system.

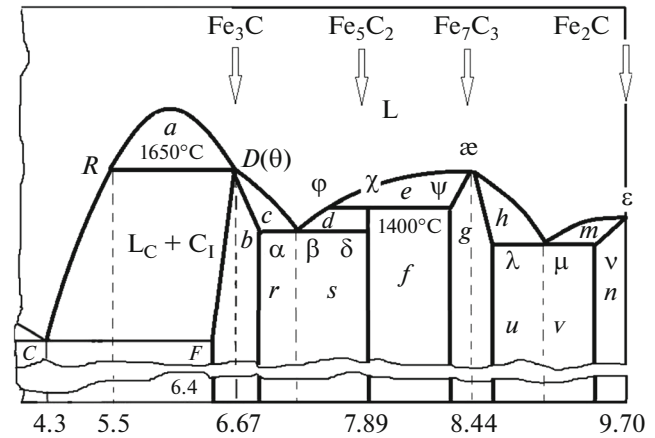


Fig. 6. Carbide region of phase equilibria in the iron-ε-carbide Fe₂C system.

same ionic radius and the same valence state are added to the Fe sublattice as a solvent with an increase in the carbon concentration in the alloy, as well as the electroneutrality of the solid solution's crystal lattice is not altered.

The consequence of isomorphism is nearly identical thermodynamic parameters of carbide phases [23–31]: enthalpy $H = 0.2$ MeV/atom, energy of formation $F_{\text{form}} = 0.058\text{--}0.07$ eV/atom, energy of the main state E_0 from -8.53 to -8.63 eV/atom. Consequently, the entire combination of the structural organization of phases (alloys) on the Fe–C diagram from the concentration of 6.67% C (cementite Θ -Fe₃C) to 9.7% C (ϵ -carbide Fe₂C) can be characterized as a general isomorphous quasi-carbide solid solution containing interstitial phases of stoichiometric compositions of cementite Θ -Fe₃C and carbides χ -Fe₅C₂, g -Fe₇C₃, and ϵ -Fe₂C. This statement is confirmed by theoretical calculations of G.I. Sil'man (Fig. 2) and experimental data by A.A. Zhukov (Fig. 3).

Because the solid solution of cementite cannot represent the component of the phase diagram of alloys, the component of the diagram is represented by chemical compound berthollide ϵ -Fe₂C and the iron–cementite phase diagram in the concentration range from 0 to 9.7% C can be renamed to the iron–carbide ϵ -Fe₂C phase diagram of alloys. In [37], the carbide transformation of peritectoid type in Fe–C alloys based on ϵ -Fe₂C was considered for the first time.

A significant advance recently achieved in the study of iron carbides and behavior of iron–carbon alloys under critical parameters allows one to update the Fe–C diagram primarily in the range of phase transformations of iron carbides up to the concentration of 9.7% C corresponding to the chemical composition of ϵ -carbide Fe₂C. Fig. 5 shows the suggested full diagram of the iron–ε-carbide Fe₂C system in the concentration range of 0–9.7% C. A low-temperature

carbide transformation of peritectoid type is given on the diagram on the left from the line of cementite, at which solid solutions of ferrite and cementite form a solid solution with a broad homogeneity range based on berthollide ϵ -Fe₂C. This part of the diagram was analyzed in detail using experimental data in [37]. In the diagram, on the left from the cementite line, the lines of phase equilibria in the carbide region are given in general form, whereas Fig. 6 shows full details of this region. Only two temperatures corresponding to full dissolution of cementite as solid solution, point $D(\Theta)$, and isotherm of eutectic transformation were experimentally determined [12]. Other temperature lines are conditionally derived from nearly the total identity of carbide phases as a general isomorphous quasi-carbide solid solution in the range of 1400–1650°C and obviously require further experimental validation.

The CR line is the part of liquidus line coinciding with the carbon isoactivity line $a_C = 1.0$ according to the data from [3, 10]. The point R corresponds to the limiting solubility of carbon in liquid iron $N_{C_{\text{sat}}} = 5.5\%$ C at 1650°C.

Calculation was carried out as follows [3, p. 44, Eq. (65)]:

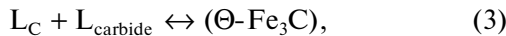
$$N_{C_{\text{sat}}} = a + bT, \quad (2)$$

where $a = 0.047$, $b = 0.873 \times 10^{-4}$ K, and T is temperature, K.

At present, it is considered that both carbides Fe₃C and Fe₇C₃ are formed from melt as a result of peritectic reactions [42, 43] (A.P. Gulyaev in 1990 suggested [36] that stable precipitation of cementite from melt proceeds according to this reaction; however, this suggestion was not accepted).

As mentioned above, there are austenite and cementite in the structures upon quenching iron–carbon melts (up to 6.0% C) in the range of 1300–

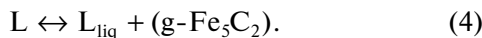
1700°C; consequently, the onset of cementite precipitation from solution as the crystal phase was recorded in the range of 1600–1700°C [24, 34, 35]. These studies stated that the liquid phase at the pre-crystallization stage consists of two phases, such as high-carbon and low-carbon; i.e., the delayered melt and is transformed into two coexisting liquid solutions. Such delayering is described in the theory of alloy phase diagrams as the peritectic-type transformation according to the reaction of nonvariant three-phase syntactic equilibrium by *RD* isotherm:



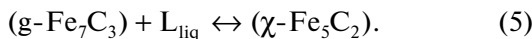
where L_C is high-carbon (“graphite”) liquid, L_{carb} is low-carbon (“carbide”) liquid, and Fe_3C is cementite as solid solution.

Consequently, the line *RD*(Θ) in Fig. 6 describes the isotherm of syntactic reaction (3), whereas the dome section over it corresponds to syntactic binodal. The melt decomposes along binodal via the reaction $L \leftrightarrow L_C + L_{\text{carbide}}$. In the region *a* below binodal, the system consists of $L_C + L_{\text{carbide}}$. After $L_{\text{carbide}} \leftrightarrow \text{Fe}_3\text{C}_{\text{s.s.}}$ transformation below *RD* isotherm, the system consists of $L_C + C_1$.

In the region *b*, there is daltonide represented by cementite $\Theta\text{-Fe}_3\text{C}$ as a solid solution of carbon in cementite with the broad homogeneity range. The region *e* is $L_\Theta + (\Theta\text{-Fe}_3\text{C}_{\text{s.s.}})$. The liquidus line $\phi[\alpha]$ is the line of crystallization of carbide $g\text{-Fe}_7\text{C}_3$ with the temperature $t(\alpha)$ of its full dissolution:



Crystallization of carbide $\chi\text{-Fe}_5\text{C}_2$ is described within peritectic-type transformation according to the reaction of nonvariant three-phase peritectic equilibrium along $\phi\chi\psi$ isotherm:



Carbide $\chi\text{-Fe}_5\text{C}_2$ is intermediate and is easily transformed into carbide $g\text{-Fe}_7\text{C}_3$ or cementite $\Theta\text{-Fe}_3\text{C}$; it represents a counterpart of ε -carbide Fe_2C [25–31]. Therefore, the carbide $\chi\text{-Fe}_5\text{C}_2$ is given by line as a chemical compound with a stoichiometric composition in order to not complicate this variant of the diagram (Fig. 6).

Regions *d*, $L\chi + (\chi\text{-Fe}_5\text{C}_2)$; *e*, $L_{\text{liq}} + (g\text{-Fe}_7\text{C}_3)$; *f*, $(\chi\text{-Fe}_5\text{C}_2) + (g\text{-Fe}_7\text{C}_3)$; and *g* is the existence range of daltonide carbide $g\text{-Fe}_7\text{C}_3$ as solid solution of carbon with the broad homogeneity range. Eutectics $E_{\chi-\varepsilon} = (\chi\text{-Fe}_5\text{C}_2) + (\Theta\text{-Fe}_3\text{C})$ could be observed on the $\alpha\beta\delta$ isotherm. Consequently, the region *r* consists of $E_{\chi-\varepsilon} + (\Theta\text{-Fe}_3\text{C})$; and region *s*, $E_{\chi-\varepsilon} + (\chi\text{-Fe}_5\text{C}_2)$. Eutectics $E_{g-\varepsilon} = (g\text{-Fe}_7\text{C}_3) + (\varepsilon\text{-Fe}_2\text{C})$ could be observed on the $\lambda\mu\nu$ isotherm; region *u* consists of $E_{g-\varepsilon} + (g\text{-Fe}_7\text{C}_3)$ and region *v* consists of $E_{g-\varepsilon} + (\varepsilon\text{-Fe}_2\text{C})$. There is berthollide represented by ε -carbide Fe_2C as a solid solution of carbon with the broad

homogeneity range including stoichiometric composition of carbide $\varepsilon\text{-Fe}_2\text{C}$ in the region *n*.

If we proceed from the definition of carbide phases as a single isomorphous quasi-carbide solid solution, the carbide phase crystallizes in the form of the carbide phase mixture as quasi-eutectics, in which the individual analytical determination of the carbide in an isolated phase is quite a difficult problem, according to the suggested diagram variant. In experimental studies from [12] (Fig. 3) and [2, 9] (Fig. 2), the possible structural type of carbide phases was also identified as quasi-eutectics.

The suggested variant of the iron–carbide $\varepsilon\text{-Fe}_2\text{C}$ phase diagram allows one to develop the construction and tailored materials of a new class, more specifically, carbide alloys. They can be conditionally divided into two groups: graphite-carbide and carbide types. Graphite carbide alloys can be prepared through partial graphitization of carbides forming a unique composition structure: disperse phases carbide + graphite possessing high wear resistance and antifriction behavior. In particular, in the range of co-crystallization of carbides $g\text{-Fe}_7\text{C}_3$ and $\chi\text{-Fe}_5\text{C}_2$ (Fig. 5, region *f*), one can suggest the formation of layered carbides, which are structurally similar to ledeburite or can form a gradient structure. These would provide significant composition strengthening of the carbide alloy, due to the high isomorphism of carbide crystal lattices. Carbide alloys need to be additionally alloyed with carbide-stabilizing elements, such as chromium, titanium, molybdenum, vanadium, manganese, and others. Stabilization of the carbide phase would provide such characteristics as heat resistance, acid resistance, and wear resistance.

Formation of the high-carbon (superhigh-carbon 15–50% C) liquid phase allows one to develop the technology for liquid-phase high-temperature preparation of new-generation construction composition materials such as: alloys reinforced with intermetallics along with fullerene-based carbon nanoparticles, or composition alloys structured by nanoparticles of different origin in the liquid-phase high-temperature process possessing unique characteristics, primarily high heat resistance and acid resistance. One example is FeBe_2 (25% Be), FeBe_3 (45% Be), and FeBe_{12} (70% Be) in the Fe–B system; Nb_3Fe_2 (30% Nb, $t_m = 1800^\circ\text{C}$), $\text{Nb}_{19}\text{Fe}_{21}$ (40% Nb, $t_{\text{decomp}} = 1500^\circ\text{C}$), and NbFe_2 (55% Nb, $t_m = 1655^\circ\text{C}$) are formed in the solid state by niobium and iron in the Nb–Fe system. Carbon exists in the nanophase in these alloys consisting of carbon interstices of different morphology, such as fullerenes, endohedrals, graphite aggregates, carbyne-type chain structures, and others.

Intermetallics and graphite phase may exist both in the form of high-disperse particles and nano-inclusions. Morphology regarding the state of the mentioned phases is governed by the phase transformation types in the alloy, precipitation age hardening

(decomposition of oversaturated solid solution) or spinodal delayering of the liquid phase as a result of high-speed cooling into nanostructures of different origin. Consequently, liquid-phase technology of alloying and modification of high-carbon carbide alloys can form the main design of a new class of construction composites, more specifically, metal-ceramic cast materials (ingots and moldings) structured and strengthened by nanoparticles of different origin. At present, these alloys are prepared in technologically complex and expensive solid-phase processes of powder metallurgy.

CONCLUSIONS

(1) Full diagram of the iron-carbide ϵ -Fe₂C system in the concentration range of 0–9.7% C without “graphite” and “diamond” liquidus lines has been suggested.

(2) Following phase transformations are added to the diagram:

crystallization of cementite Θ -Fe₃C according to the peritectic reaction of nonvariant three-phase syntactic equilibrium;

crystallization of carbide χ -Fe₅C₂ according to the reaction of nonvariant three-phase peritectic equilibrium;

low-temperature carbide transformation of peritectoid type, at which solid solutions of ferrite and cementite form a solution with the broad homogeneity range based on berthollide ϵ -carbide Fe₂C.

(3) It has been shown that the carbide phases represent a single isomorphous quasi-carbide solid solution and the carbide phase crystallizes in the form of the carbide phase mixture as quasi-eutectics according to the suggested variant of diagram.

(4) As a result of nonvariant three-phase syntactic equilibrium, excess C is precipitated from the liquid oversaturated with carbon in the form of interstices of crystalline graphite as inactive phase (precipitate) of solution.

(5) Ledeburite represents the mutual crystallization product of two solid solutions, more specifically, cementite and austenite.

(6) Iron-graphite and iron-diamond phase diagrams joined with Fe-C diagram should be scientifically reviewed due to its invalidity.

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