About the concentration range of homogeneity of cementite in iron-carbon alloys

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Abstract. On the basis of X-ray analysis and quantitative metallography to determine the minimum content of carbon in cementite eutectic - coordinate of the point F of the binary phase diagram of the Fe-Fe₃C. The results are checked by calculation using data on saturation magnetization, which gave a good quantitative agreement. Given the preliminary nature of the results presented conclusions about the larger than previously estimated, the width of the field homogeneity cementite and feasibility correction on this basis of heat treatment alloys, carbide grade.

1. Introduction

Various Thermokinetic conditions of crystallization and cooling iron-carbon alloys often results in them cementite with significantly different physical and mechanical properties, such as microhardness, saturation magnetization, the effective magnetic field at the nucleus Fe57 and isomer shift at NGR [1, 2].

The nature of these differences were not sufficiently clear explanation, primarily because of the traditional notions of iron carbide as a connection with a strictly stoichiometric ratio of the components Fe₃C. In fact, the cementite has a homogeneity within which the equilibrium carbon content in it can be less than a stoichiometric and varies depending on temperature. Accordingly, in the homogeneity of the cementite will change the thermodynamic activity and chemical potential of carbon (Figure 1) [3], exerting a certain influence on the physico-mechanical and chemical properties of the compound.
Figure 1. Field homogeneity in the cementite Fe–Fe₃C [3].

The boundaries of the homogeneity region of cementite to date no generally accepted quantitative expression, including the position of point F. The carbon content of point F, many researchers have tried to determine [4-12]. In the literature data calculations and experimental studies of the provisions of this point diverge (from 5.22% to 6.3% carbon) and in need of further clarification.

In this paper we attempt to calculate using the data [2] on the saturation magnetization minimum carbon content of cement (position of the point F) and determine the effect of variable concentrations of carbon to change the physical-mechanical and chemical properties of cementite.

2. Materials and methods
We assume as a first approximation that the saturation magnetization cementite is linearly dependent on its carbon content ($\nu_x$ % m.):

$$I_5^0 = I_5^0 (1 - B \nu_x),$$

where $I_5^0$ - saturation magnetization of the iron components of cementite.

Using the data of [2], we can write the boundary conditions to determine the linear function (I):

at $\nu_x = 0$ $I_5^0 = 2,014$T; at $\nu_x = 6,67$ $I_5^0 = 1,12$T.

In light of these boundary conditions, the expression (1) takes the form:

$$I_5^0 = 2,014 - 0,134 \nu_x$$

From equation (2) for the saturation magnetization cementite composition close to the point F (1.32T according to [2]), we find the minimum carbon content of this phase, equal to 5.18 wt.%, Which practically coincides with the experimental results by A. N. Rozanov.

It should however be borne in mind that the saturation magnetization is equal to 1.12 T measured at the eutectoid cementite, the carbon content of which was assumed to be stoichiometric, i.e. 6.67% m., And in fact could be somewhat shorter, so the linear approximation $I_5^0 = f(\nu_x)$ should be carried out according to a slight shift to the right, and the concentration of carbon at the point F of this shift should though not much, but to exceed the calculated.

3. Results
Considering cementite as a chemical compound with a variable concentration of vacancies in the carbon sublattice possible carbon content within the region of homogeneity of this phase is expressed in terms of varying degrees of filling of the pores of a certain type, suppose prismatic, and quantify defects of the crystal lattice of cementite. The lattice defect free Fe₃C each unit cell 12 of the iron atoms, and 4 carbon atoms.

From simple calculations that the mass fraction of carbon, equal to 0.0518, corresponding to a ratio of iron and carbon-12: 3. Consequently, at maximum lattice defect cementite (point F) prismatic pores are filled by at least three quarters. Thus, within the region of homogeneity of the cement may vary in composition from Fe₃C to Fe₃C0,75.
Change of properties of cementite depending on the carbon content of the samples was tested for binary \( \text{Fe}-\text{C} \) (2.66\% S) and triple \( \text{Fe}-\text{S}-\text{Si} \) (2.79\% C, 0.42\% Si) alloys melted at the charge of carbonyl iron class B-3, and the reference spectral graphite chemically pure ferrosilicon containing 79.63\% Si.

The mixture was compressed into tablets weighing 40-50 g, and then fused in an atmosphere of CO at high frequency LPZ-67. By changing the conditions of crystallization and cooling metal in quartz capillary 6mm and directly obtained in a crucible furnace varying degrees nonequilibrium carbon content in cement, since the cooling rate of the metal, with the temperature range, and a eutectic eutectoid transformation differs by two orders of magnitude.

The obtained white iron samples electrochemically dissolving in 7.5\% aqueous KCl precipitate was isolated anode comprising a eutectic eutectoid cementite and research was only eutectic cement, which was separated by elutriation anode sludge in ethanol. Larger crystals of eutectic cementite after shaking the mixture deposited on the bottom and the fines eutectoid remained suspended and removed from the solution.

Electrochemical resistance eutectic cementite was studied by anodic dissolution in an aqueous solution of KCl (7.5\%) and citric acid (0.5\%) of paste electrodes made based on the spectrally pure coal - and 0.5 g of dibutylphthalate - 0.15g supplemented with 0,05g study phase \( \text{Fe}_3\text{C} \). The surface area of the electrode during dissolution remained constant. It served as a reference electrode saturated silver chloride half cell, which connects to the sample through the capillary Lugin’s anode. Offset potential occurs automatically in a positive direction at a rate of 1 mV/s. Shooting conditions provided sufficient reproducibility, the coefficient of variation did not exceed 10\%.

Potentiodynamic curves (ATSDK) taken by dissolving paste electrode with cementite of slow- and fast-cooled samples \( \text{Fe}-\text{C} \) and \( \text{Fe}-\text{C}-\text{Si} \) alloys are significantly different (Figure 2).

On ATSDK for rapid cooling are almost vertical portions of the curves when the speed of the anode electrode process depends little on the building, as determined by the rate of dissolution of the protective oxide film, which is likely due to the deficiency of the carbon lattice of the cementite.

The main parameters of the electrochemical dissolution analyzed (Table 1) show that the eutectic cementite rapidly cooled samples of both binary and ternary alloy exhibits enhanced corrosion resistance as compared with slow cooling, and hence more equilibrium (minimal shift of the equilibrium potential of the electrode in the positive direction, and a lower current density at the peak of the activation site of cementite).

| Alloy       | Standard potential dissolution, \( E_{\text{st}} \), mV | Maximum current density during dissolution of cementite, a/cm\(^2\) |
|------------|-----------------------------------------------|-----------------------------------------------|
|            | fast cooled | slow cooled | fast cooled | slow cooled |
| \( \text{Fe}-\text{C} \) | -160        | -170        | 0.12        | 0.34        |
| \( \text{Fe}-\text{C}-\text{Si} \) | -175        | -198        | 0.06        | 0.65        |

Perhaps the presence of cementite eutectic alloys rapidly cooled, then filled with carbon atoms leads to the appearance in the \( dsp \)-hybridized band electron vacancies, which contribute to the activation of chemisorptions of oxygen molecules and surface passivation cementite it. With increasing carbon content \( 2p \) - the wave functions of carbon hybridizing with \( 3d4s \)-functions of the iron atoms, reduce the number of vacancies in the \( dsp \)-hybridized valence band. As a consequence, less defective eutectic cementite slowly cooled alloys can promote the formation of an adsorbed layer of oxygen molecules with weaker likely Van-der-Waals forces bond. Create better conditions for competition on the surface of the crystals of cementite molecules of oxygen and gloryons, enhanced hydration of iron ions and their transition into the electrolyte.
Figure 2. Potentiodynamic curves of dissolution of cementite eutectic alloys crystallize by slow (1) and acceleration (2) cooling: a – Fe–2.79%C–0.42%Si; b – Fe–2.66%C.

Simultaneously with the study of the chemical properties of cementite was investigated by potentiodynamic difference physic-mechanical properties of the eutectic cementite by measuring its microhardness on a PMT-3 with a load of 50 g analysis statistically processed results of microhardness measurements (Table 2) shows that the rate of cooling alloys significantly affects the microhardness eutectic cementite. This effect is inversely proportional to the nature of.

Table 2. The microhardness of the eutectic cementite Fe–C и Fe–C–Si alloys.

| Alloy    | Cooling conditions of the cast piece | The mean value of microhardness, $H_{50}$, MPa | Standard deviation, MPa | The coefficient of variation, % | Confidence interval *, MPa |
|----------|--------------------------------------|-----------------------------------------------|-------------------------|-------------------------------|--------------------------|
| Fe–C     | slow                                 | 9000                                          | 1330                    | 14.8                          | ±590                     |
|          | accelerated                          | 7250                                          | 1410                    | 19.4                          | ±560                     |
| Fe–C–Si  | slow                                 | 9790                                          | 1670                    | 17.1                          | ±540                     |
|          | accelerated                          | 7480                                          | 1150                    | 15.4                          | ±490                     |

* at probability 95%.

In accordance with the position limit line soluble carbon in cementite slow cooling the alloy must be accompanied by an increase in concentration of carbon in cementite up to stoichiometric and increase its microhardness.

The higher the microhardness of the eutectic cementite close to the stoichiometric composition, is associated with the peculiarities of the electronic structure of carbides [8], namely to increase the number of rigid covalent bonds in the crystal Fe-C Fe3C with increasing carbon.

Thus, the distinction of physical-mechanical and chemical properties of the eutectic (and, consequently, secondary) cementite depending on thermo-kinetic conditions of crystallization and cooling alloys so significant that they can only be explained by a fairly wide homogeneity region Fe3C in the formation of the eutectic temperature.

In this regard, a good match coordinates of the point $F$, calculated from the saturation magnetization, with the results of quantitative metallography [4,10-12] provides a basis for the formulation of additional high-precision experiments designed to establish a reliable boundary of the homogeneity of cementite and revise the traditional view of the iron carbide as a compound having a very narrow homogeneity region.
4. Conclusion
In view of the large width of the homogeneity of cementite and a significant change in solubility of carbon in Fe3C fundamental importance is the correction of heat treatment of iron-carbon alloys with structural free carbides. In particular variation thermokinetic heating and cooling conditions can be widely adjusted hardness and thermodynamic stability of carbides. Theoretical aspects of the heat treatment of alloys such as white or bleached pig iron, ductile iron, steel 110G13L, chromium cast iron does not take into account the existence of the field homogeneity cementite.

References

[1] Motorin V A, Gapich D S, Borisenko I B and Kurbanov D B 2020 Simulation of the Wear of the Working Bodies of Chisel Plows Journal of Friction and Wear 41(1) 71–77
[2] Borisenko I B, Pyndak V I and Novikov A E 2012 The Development of Chisel Tillage Tools and their Theoretical Justification Machine and Technology Station 3 16-20
[3] Ovchinnikov A S, Mezhevova A S, Novikov A E, Fomin S D, Pleskachev Yu N, Borisenko I B, Zvolinsky V P, Tyutyuma N V and Vorontsova E S 2017 Energy and Agrotechnical Indicators in the Testing of Machine-tractor Units with Subsoiler ARPN Journal of Engineering and Applied Sciences 12(24) 7150-7160
[4] Kostyleva L V, Gapich D S, Motorin V A and Novikov A E 2019 Microstructure and abrasive wear resistance of heavy duty parts from high-strength cast iron in chisel plows Chernye Metally 3 37-42
[5] Makarenko K V 2010 On Obtaining from Cast State of Half-cast Irons with Ausferrite Structure Foundry 2 2-6
[6] Novikov A E, Motorin V A, Lamskova M I and Filimonov M I 2018 Composition and Tribological Properties of Cutting Blades of Tillage Machines under Abrasive Deterioration Journal of Friction and Wear 39(2) 158-163
[7] Motorin V A, Kostyleva L V and Gapich D S 2020 Increasing Wear Resistance of Chisel Tools Working Bodies Based on Improving the Metallographic Structure of Grey Cast Solid State Phenomena 299 652-657
[8] Kanatieva A V, Morozov D A and Kondrashov A V 2017 Analysis of potato cultivation technologies in difficult soil and climate conditions of the Russian Federation / A.V. Kanatieva Young scientist 11.3 10-12
[9] Maximov P L 2002 New working bodies and machines for the production of root crops: monograph Izhevsk: Publishing house Irgska 80 p.
[10] Borisenko I B, Pyndak V I and Novikov A E 2012 The Development of Chisel Tillage Tools and their Theoretical Justification Machine and Technology Station 3 16-20
[11] Motorin V A, Gapich D S and Novikov A E 2019 Improvement of wear resistance of working elements from gray iron for development of the ground IOP Conf. Series: Earth and Environmental Science 341 012138
[12] Kostyleva L V, Gapich D S, Novikov A E and Motorin V A 2020 Wear-Resistant Cast Iron Containing Spheroidal Graphite with a Two-Layer Ledeburitic–Martensitic Shell Russian Metallurgy (Metally) 3 231–237