SPECIFICATION OF THE FULL EQUILIBRIUM PHASE DIAGRAM OF THE IRON-CARBON SYSTEM BASED ON THE THEORETICAL AND EXPERIMENTAL INVESTIGATIONS

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Abstract

In 2018 it is 150 years since D.K. Chernov, the metallurgical science expert, made the report on the results of the research of the Fe-C alloy samples and ingots and for the first time ascertained the presence of the critical points, i.e. phase transitions. The work of D.K. Chernov served as the beginning of the construction of the iron-carbon diagram. A great amount of research on the construction and specification of the iron-carbon phase diagram has been carried out during the past period.

In the present work a critical analysis of the generally recognized combined iron-carbon and iron-cementite diagram is given, theoretical and experimental investigations by studying the microstructures of the iron-carbon alloy samples quenched from various temperatures have been carried out. Based on the research, a full equilibrium phase diagram of the iron-carbon system has been constructed, in which the non-variant three-phase equilibrium ferrite+graphite ↔ cementite at the temperature 727 °C, two-phase equilibrium ferrite+graphite in the temperature range 738 - 727 °C and two two-phase regions ferrite+cementite (up to 6.67 wt.% C) and cementite+graphite (more than 6.67 wt.% C) at the temperatures below 727 °C are present. It is shown that cementite cannot be formed in the iron-carbon alloys at the temperatures exceeding 738 °C at high cooling rates. The author considers expedient not to use the version of the metastable iron-cementite phase diagram and to exclude the designation of the alloy microstructures (perlite and ledeburite) in the phase diagram.

Keywords: Phase diagram, iron-carbon system, microstructure, equilibrium, metastable system

1. INTRODUCTION

Phase diagram of the iron-carbon system is fundamental in the metallurgical science of ferrous metals. A large number of investigations were devoted to it. Study of this diagram is bound up with great difficulties due to the iron polymorphism. In 2018 150 years have passed since D.K. Chernov, a Russian metallurgical science expert, made the report (in 1868) on his theoretical and experimental research, in which he for the first time determined the critical points of the phase transitions in the iron-carbon alloys [1]. Theoretical and experimental studies are going on at the present time as well [2, 3]. For all this practically all educational and reference literature presents combined equilibrium iron-carbon diagram and metastable iron-cementite [4 - 11]. This statement supposes that in the equilibrium system cementite (Fe_3C) cannot be present in any way, since it is a non-equilibrium phase constituent, and in the metastable system graphite must be absent. The use of the combined diagrams allows explain in a simple way the simultaneous presence of both graphite and cementite in the microstructure of the iron-carbon alloys. However, such combination just makes it difficult to explain the microstructure formation in these alloys and impedes the development of the manufacturing processes of finished products of steel and cast iron with required working parameters, which are predetermined by the phase constituents and their morphology in the alloy microstructure.

2. THEORETICAL INVESTIGATIONS

Phase constituents in the iron-carbon system are the following:

- homogeneous liquid solution of the iron and carbon atoms (*L*);

- ferrite (*Fer*) - solid solution of the carbon atoms in the bcc lattice of iron (in the present work there is no division into the high temperature (δ) and low temperature (α) phases);
- austenite (*A*) - solid solution of the carbon atoms in the fcc lattice of iron;
- graphite (*Gr*) - solid solution of the iron atoms in the hexagonal lattice of carbon;
- cementite (*Cem*) - crystal structure, formed by the iron and carbon atoms, close to the stoichiometric relation Fe_3C;
- martensite (*M*) - solid solution of the carbon atoms in the tetragonal lattice of iron.

It is common practice to consider the phases *L*, *Fer*, *A*, *Gr* equilibrium and the phases *Cem* and *M* non-equilibrium. However, in some works [4, 12] the authors consider *Cem* equilibrium phase constituent. Ledeburite, perlite, sorbite, troostite, bainite consist of several both equilibrium and non-equilibrium phases. These terms may be used to characterize the microstructures in samples, ingots and castings. In the equilibrium diagram there must be the names of only equilibrium phases. It seems incorrect to use the same term to designate structure constituents in the equilibrium (and also in the metastable) phase diagram.

In the work [13], based on the theoretical research, a complete equilibrium phase diagram of the iron-carbon system was drawn (**Figure 1**). In the proposed diagram *Cem* is considered an equilibrium phase constituent at the temperatures below 727 °C. This statement is based on the following factors:

- *Cem* is formed when pure iron is in the atmosphere of the atomic carbon at the temperature below 727 °C [14]. We observed this process at the temperature 650 °C with the treating time 12 h;
- *M* decomposes into ferrite and cementite when the samples are heated in the range 350 °C - 400 °C [9], *Gr* is not formed meanwhile.

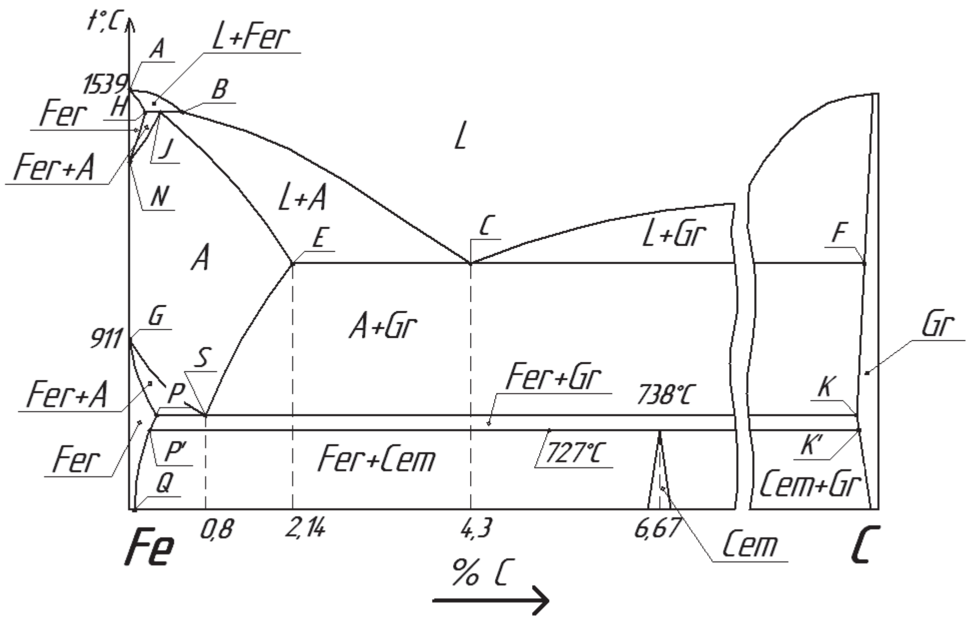

Figure 1 Complete equilibrium phase diagram of the iron-carbon system

The recognition of *Cem* as an equilibrium phase constituent at the temperature below 727 °C leads initially to a four-phase equilibrium at the eutectoid equilibrium (*Fer*, *A*, *Cem*, *Gr*), and this contradicts Gibbs phase rule, which for the systems with the elements with negligible vapor pressure is expressed by the equality $v=K-f+1$, where v is variability or the number of freedom degrees, K is the number of elements in the system, f is the number of phases in the system, *1* is one external factor - temperature. At the presence of four phases at the constant temperature the variability becomes negative, and this is impossible. This contradiction is eliminated by the necessity to acknowledge the existence of one more two-phase equilibrium *Fer* and *Gr* in the region

PSKK/P/ in the temperature range 738 °C - 727 °C. This two-phase equilibrium was experimentally determined in the low carbon alloys [4].

3. EXPERIMENT PROCEDURE

In the present work samples of the Fe - 4 wt.% C and Fe - wt.5 % C have been studied. Alloys were obtained by melting the Armco iron with the carbon breakage. Samples from these meltings with the mass 20 - 25 g were melted for the second time in the Al_2O_3 crucible in the resistance furnace (**Figure 2**) and heated to 1256 °C, treated 30 min and then cooling and quenching were performed. Initially, samples were cooled from the temperature 1256 °C at the rate 10 K/min to the temperature 1050 °C and quenched in the aluminum bath with the temperatures 700 °C and 800 °C. The treating time at these temperatures was 2 min and 40 min. After that the samples were cooled in the air.

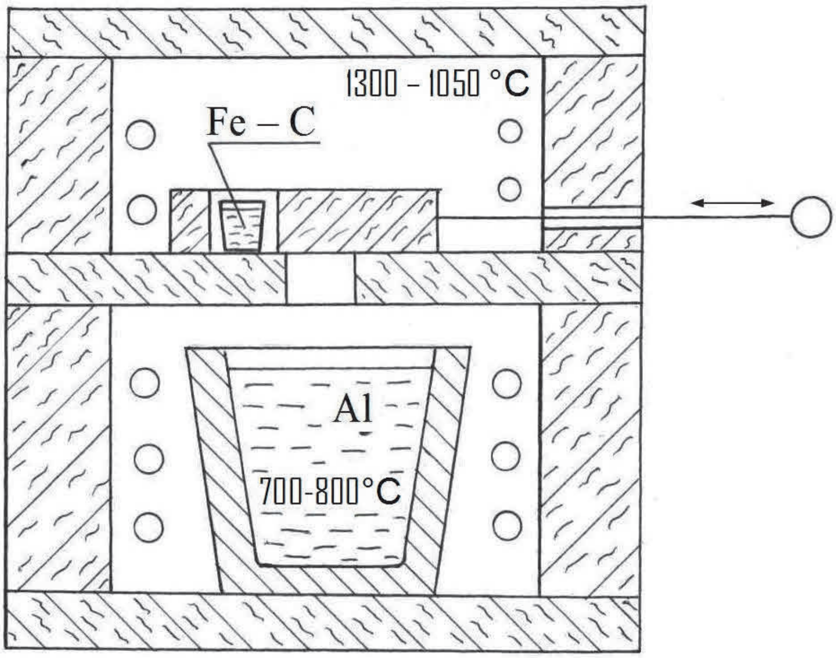

Figure 2 Layout of the facility for quenching samples from liquid and liquid - solid states in the aluminum bath

4. RESULTS AND DISCUSSION

Microstructure analysis of the Fe - 4 wt.% C and Fe - 5 wt.% C alloys cooled to 1050 °C and quenched into the bath with the temperatures 700 °C and 800 °C with the following 2 min treating showed the presence of the dendrite cell of the iron crystals with the size ~110 µm (**Figure 3**) and graphite crystals. The ferrite-cementite microstructure in the dendrite centre and periphery is 2 - 2.5 times coarser in the samples cooled in the air from the temperature 800 °C. The increase of the treating time to 40 min led to the formation of the extra graphite crystals only in the samples treated at 800 °C. At the same time it was found out that the ferrite-cementite microstructure did not depend on the treating time at the temperatures 700 °C and 800 °C.

When the samples were quenched from the temperature 1256 °C into the aluminum melt at the temperatures 700 °C and 800 °C with the treating time 2 min and 40 min and the subsequent cooled in the air, in the alloy microstructures a dendrite structure with the parameters 16 µm and 38 µm and the ferrite-cementite plates with the parameters 4 µm and 9 µm were revealed accordingly (**Figure 4**). The increase of the treating time from 2 min to 40 min did not lead to a noticeable change of the microstructure parameters.

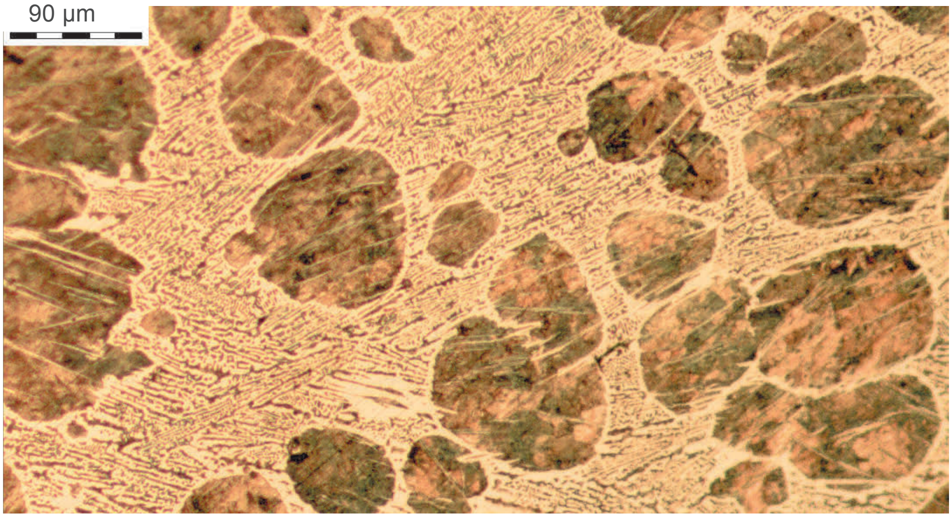

Figure 3 Microstructure of the Fe - 4 wt.% C alloy cooled from the temperature 1256 °C to 1050 °C at the rate 10 K/min and quenched at 800 °C with the treating time 2 min and cooled to the room temperature

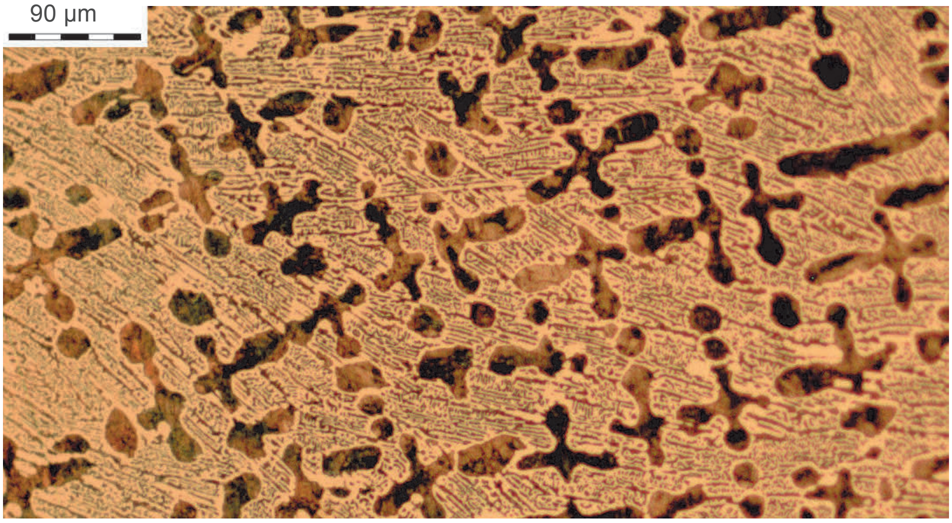

Figure 4 Microstructure of the Fe - 4 % C alloy quenched from the temperature 1256 °C into the bath with the temperature 800 °C and cooled to room temperature

The obtained experimental data show that the “primary” cementite does not form in the temperature range from liquidus to 727 °C at any cooling rates. Cementite undoubtedly is formed from the austenite crystals at the temperature below 727 °C and it is accordingly the equilibrium phase constituent below this temperature. Therefore the presence of the cementite above 738 °C in the temperature-concentration region *SECFK* is possible during some time only after the samples are heated into this region, when cementite is already present in the microstructure and further on it decomposes into austenite and graphite. Subsequent cooling leads to a very long term retaining of the graphite crystals at low temperatures, this by mistake allows to consider graphite the equilibrium phase constituent below 727 °C.

5. CONCLUSION

- A new version of the full equilibrium phase diagram of the iron-carbon system has been proposed, in which the presence of the non-variant ternary *Fer-Gr-Cem* phase equilibrium at the temperature 727 °C, binary *Fer+Gr* phase equilibrium in the temperature range 738 °C - 727 °C and two two-phase regions *Fer+Cem* (up to 6.67 wt.% C) and *Cem+Gr* (above 6.67 wt.% C) at the temperatures below 727 °C is being acknowledged.

- Theoretical and experimental results of the present work are explained in full logic in the frame of the proposed new version of the complete equilibrium phase diagram of the iron-carbon system.
- It is expedient to refuse using the combined version of the iron-graphite and iron-cementite diagram.

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