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Abstract

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INVESTIGATION OF THE HYPEREUTECTIC REGION OF THE IRON-CARBON SYSTEM

(FROM 2.88 TO 27 WT.% C)

The phase diagram of iron alloys with carbon has been studied in considerable detail in the region of carbon contents up to 6.67% (Fe_3C). Both the stable (Fe–graphite) and the metastable system (Fe–Fe_3C) may be regarded as having been established with sufficient accuracy. Reliable experimental data on the structure of alloys and the character of the diagram in the cementite region are lacking.

N. M. Wittorf ([1]) was the first to find the line of limiting solubility of carbon in melts containing up to 10% C, and established that cementite decomposes before melting. The existence of the carbides Fe_4C, FeC, FeC_2 assumed by him, and the variant of the diagram proposed by him in the hypereutectic region, were not subsequently confirmed. A. A. Baikov' s assumption that cementite is a solid solution led to a very interesting interpretation of the diagram of the iron-carbon system ([2]), but the existence of iron-rich solutions in carbon likewise was not confirmed.

The study of the system in the region of high carbon contents is important for elucidating the mechanism of crystallization and structure formation of cast irons ([3]), and for resolving the question of the existence of microgroupings of graphite and cementite in melts. Therefore iron alloys with 2.88–26.5 wt.% C (12.1–62.7 at.% C) were studied experimentally.

The alloys were prepared from electrolytic iron of high purity, remelted in vacuum, and spectrally pure graphite. The specified carbon content in the alloy was achieved by melting cylinders machined from pure iron in graphite crucibles tightly closed with a lid, in an induction furnace. The limiting carbon content in the melt at temperatures up to 2400° was reached in 5 min, after which the alloy was quenched from the liquid state in water.

From the carbon content in the alloys and the saturation temperature determined with an optical pyrometer, a line of limiting solubility was established, coinciding with known data ([4-6]). Alloys with 2.88–7% carbon were melted

Figure 1. Phase diagrams of iron-carbon alloys. A—in weight percent (from 2.88 to 26.5% according to the data of the present work), a and b—thermal analysis: heating (a) and cooling (b); c—solubility of C in the melt; B—complete diagram in atomic percent

Figure 1: Figure 1. Phase diagrams of iron-carbon alloys. A—in weight percent (from 2.88 to 26.5% according to the data of the present work), a and b—thermal analysis: heating (a) and cooling (b); c—solubility of C in the melt; B—complete diagram in atomic percent

from electrolytic iron and a master alloy with 7% C in an arc furnace in a helium atmosphere, remelted in the suspended state, and cast at a temperature of about 2400° into a copper mold. Alloys containing more than 6.7 wt.% carbon (25–30 at.%) were obtained by prolonged holding of melts saturated to the limit with carbon at 2400–2500° C.

Chemical analysis confirmed the homogeneity of the alloys obtained. Alloys quenched from the liquid state (at 2000–2500°) were subjected to microstructural analysis, in order to establish the phase composition, at magnifications of 200×, 500×, and 1000×, with etching in a 2% solution of HNO_3 in alcohol; the microhardness of all structural constituents was measured on a PMT-3 instrument with loads of 100–200 g (carbides, eutectic, pearlite) and 1 g (graphite). The microhardness of fine carbide precipitates, pearlite, and dendrites was measured with loads of 10–50 g. The temperature of phase transformations was determined on an apparatus for high-temperature contactless thermal analysis with a differential tungsten thermocouple co-

Fig. 1. Phase diagrams of iron-carbon alloys. **A**—in weight percent (from 2.88 to 26.5% according to the data of the present work), **a** and **b**—thermal analysis: heating (**a**) and cooling (**b**); **c**—solubility of C in the melt; **B**—complete diagram in atomic percent.

resistance thermometer calibrated against the phase-transformation temperatures of pure iron. Heating to 1500° and cooling of 1.2-1.8 g charges in BeO crucibles were carried out in an atmosphere of purified helium at a rate of 40°/min. After such slow cooling, the structure of the alloys was examined and the microhardness of all structural constituents was determined. The summarized results of the investigations are presented in Fig. 1A.

Table 1

Structural constituent	C content in the alloy, wt.%	Microhardness, kg/mm^2
Primary cementite	4.7–6.5	925–1150
Ledeburitic eutectic (quenching in a copper mold)	4.7–12.0	750–880

Structural constituent	C content in the alloy, wt.%	Microhardness, kg/mm^2
Ledeburitic eutectic (quenching of the alloy in a graphite crucible in water)	7.1–26.5	600–880
Graphite	4.7–26.5	3–7

As a result of studying the microstructure and determining the microhardness of the structural constituents, it was established that quenching from the liquid-state region (from 2000–2400°) in water of alloys containing more than 5.5–6.0% C does not lead to the separation of primary cementite crystals; the primary phase is graphite. All alloys from 6.5 to 26.5 wt.% C (from 24.5 to 62.7 at.% C) are a cementite eutectic with excess separations of primary graphite, the amount of which increased with increasing carbon content (Fig. 2, see insert p. 114). It was established that no carbides other than cementite are formed in the alloys.

The microhardness of the structural constituents in quenched alloys with different carbon contents, as shown in Table 1, is constant.

X-ray structural analysis revealed the presence in the quenched alloys only of cementite, graphite, and α-Fe. Carbides richer in carbon than Fe_3C were not detected. Thermal analysis showed that the eutectoid and eutectic transformations of alloys in the beyond-cementite region (7.0–26.5% C) occur at the same temperatures as in alloys containing 2.88–6.5% carbon, both in the stable and in the metastable systems. The liquidus line of the Fe–Fe_3C system could be determined only for alloys in the range from 2.88 to 4.7% C. At higher carbon contents, the primary cementite decomposes on heating without reaching melting. There is reason to suppose that at high pressures the Fe_3C content will correspond not to a maximum, but to incongruent decomposition. The liquidus of the Fe–graphite system was determined from the carbon content in the melt saturated at the given temperature and, for alloys containing up to 5.28% C, by thermal analysis. The limiting-solubility curve obtained coincides with the available data ([4–6]). Experimental points for contents above 8% C fall, with some scatter, on the isotherm 2380°.

The experimental data obtained made it possible to construct the complete phase diagram of the iron–carbon system up to 100% carbon with the vapor phase (Fig. 1B).

Proceeding from the fact that the solubility of iron in graphite does not exceed 1 at.% at 2000°, the eutectic and eutectoid horizontal may be extended from the alloy with 62.7 at.% C (26.5 wt.% C) to graphite. Above the boiling temperatures of iron (2880°) and sublimation of graphite (3870°) there exists a vapor phase. This region must be separated from the region of liquid melts and the

region liquid + graphite by two two-phase regions liquid + graphite + vapor. Thus, the horizontal at 2380° may be interpreted as the boiling temperature of an iron melt maximally saturated with carbon.

With increasing carbon content to 6–6.7% and with increasing temperature, in connection with the decrease in the stability of cementite, a transition occurs from the metastable Fe–Fe_3C system to the stable Fe–graphite system. At low con-

at carbon contents of 4.3-5.5%, quenching fixes primary cementite, whereas at higher contents it does not form and primary graphite appears. At the same time, eutectic and eutectoid cementite exists in all quenched alloys. After slow cooling (40°/min), the eutectic proves to be not cementitic but graphitic; however, eutectoid cementite continues to be sufficiently stable. The decomposition of cementite upon heating already in the solid state indicates the low stability, in hypereutectic melts, of microgroupings corresponding to the formula Fe_3C, especially in alloys containing more than 5.5-6% C; this testifies to the high stability, in high-carbon melts of iron, of graphite microgroupings.

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Note: Figure translations are in progress. See original paper for figures.