MELTS

STRUCTURE OF IRON-CARBON MELTS.
ABOUT STABILITY OF CEMENTITE IN MELTS

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A model of the structure of Fe – Fe₃C melts in the temperature range 1300 – 1700°C is developed on the basis of recent experimental data. In accordance with the model, the solubility of carbon in liquid iron is limited (about 2%). Stable dispersed particles of the second phase (cementite) form in the melt at a higher carbon content.

Keywords: structure of iron-carbon melts, graphite, cementite, eutectic.

INTRODUCTION

A generally accepted concept of the structure or iron-carbon melts has not been developed yet. As is noted in the textbook [1], "the form of the presence of carbon in Fe – C melts has not been determined exhaustively, though it has principal importance...".

According to the most distant and widely used concept, carbon is present in liquid iron in atomic form and forms a molecular solution with iron. This firmly established notion is hard to shake despite the appearance of a great number of other experimental data. The concept is fixed in the conventional phase diagram of Fe – C alloys in which the domain above the liquidus line is described as "a liquid solution of components." A model of the structure of Fe – C melts suggested by A. A. Vertman and A. M. Samarin [2] is also in use to some extent. Having studied the concentration dependence of some structurally sensitive properties of melts (viscosity, conductivity, magnetic susceptibility) the authors arrive at a conclusion that colloidal graphite particles form melts bearing over 2% carbon. The microheterogeneity of such melts is attributed to the special features of dissolution of graphite.

It should be noted that in the model suggested the authors treat a melt not as an equilibrium colloidal solution but rather as a system with "temporary colloidal inhomogeneity" characterized by "rather long-term residence of dispersed graphite particles that gradually dissolve in the dispersion medium" [2, p. 259]. Thus, in accordance with this model, a melt is finally represented by a molecular solution of components above the liquidus line.

In the special monograph [3] devoted to the Fe – C phase diagram we read, as in many other works, that "carbon dissolves in liquid iron in unlimited amounts." The same has been confirmed by experimental results, in particular, in diffraction studies of iron-carbon melts (in the 1960s – 1970s). By the data of [4, 5] diffractograms of liquid iron after melting exhibit lines typical for graphite, which disappear after a long enough isothermal hold. This allows the authors to assume that carbon contained in the alloy in an amount of 3, 4, or 5% passes completely to the molecular solution in iron. Similar conclusions are made in a number of other known studies. However, the results of many new studies, especially in experiments on hardening from liquid state (LSH), reject the concept of formation of molecular solution of components above the liquidus line quite convincingly. Many diffraction studies also show that the structure of iron-carbon melts is microscopically inhomogeneous and consists of steadily existing ordered regions of two types that differ substantially in the constitution and in the content of carbon. Very important data have been obtained by the method of LSH at very high rates of cooling of the melts (up to 10^7 K/sec). The results of these experiments have given accurate data on the nature and composition of phases detected in melts after hardening. Comparison of these data with the results of diffraction studies has thrown light on some unclear aspects and made it possible to amend the model of the

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structure of Fe – C melts. The possibility of judging on the structure of initial melts from data obtained after hardening has been proved by special studies. For example, in accordance with [6, 7] the structure of an alloy after LSH (at high cooling rates) gives accurate and reliable data on the structure of the initial melt.

Let us consider in brief the information obtained due to studies by the method of LSH.

1. The components in Fe – C melts do not mix fully; carbon dissolves limitedly in liquid iron; if the carbon content exceeds the ultimate solubility, a second phase forms in the melt. Hardened alloys always have a two-phase structure. These facts allow us to assume that the initial melts also consist of two phases.

2. One of the two phases detected in a hardened alloy is austenite (products of its transformation due to cooling). It has been established that the concentration of carbon in the primary solid solution in a hardened alloy does not exceed its maximum solubility in the solid state near the eutectic temperature. According to the data of most studies the content of carbon in the austenite detected in hardened specimens ranges within 1.7 – 2%. For example, the tests of alloys with 2.2 – 4% C performed by I. V. Sally [8] have shown that the concentration of iron in the austenite of hardened specimens does not exceed 1.65%. By the data of [9] the carbon content in the austenite is 1.85%. In a later study of alloys bearing up to 5% C by the method of LSH [10] (the rate of cooling in some tests exceeded 10^6 K/sec) the concentration of carbon in the austenite did not exceed 1.8% (at higher cooling rates used for the hardening a supersaturated solid solution has not been detected at all).

3. When an alloy bears more than 1.7 – 2% carbon, the latter is present in the liquid and solid (after hardening) states in the composition of another phase. Numerous studies of alloys of the Fe – C system by the method of LSH have shown that this second phase in hardened specimens, and thus in the melt, is cementite. (In our work we considered the structure of melts bearing up to 6% C in the most studied temperature range of 1300 – 1700°C; these temperatures will be amended.) In this range of temperatures and carbon concentrations graphite cannot be present in the melt whatever the initial structure of the alloy in the solid state or dissolution of graphite in liquid iron; in an isothermal hold of a melt containing over 2% C graphite does not pass to the molecular solution but forms a thermodynamically stable chemical compound with the iron, i.e., cementite. In this region of melts graphite is unsteady and unstable (this explains the "disappearance" of the line of graphite in diffractograms of melts after holding). Cementite is an endothermic compound and forms in a melt at a high temperature; when the temperature decreases, its stability drops.

The two-phase structure of Fe – Fe$_3$C melts, just as those of other eutectic systems, has a very important feature. The combination of structure and physicochemical properties of
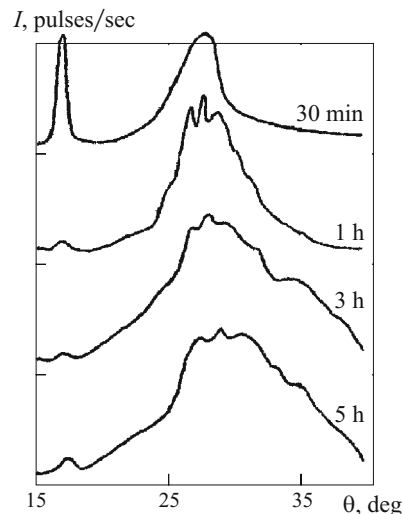

Fig. 1. Intensity curves for liquid iron after a hold at 1400°C for different times (given at the curves) [15].

the phases stimulates self-induced dispersing and yields a disperse system [14, 17, 21].

Below, we present experimental results that confirm formation (and stability) of cementite in a melt.

The presence of cementite in the structure of alloys after LSH has been detected in many experimental studies. In the mentioned work of I. V. Sally [8] an alloy with an eutectic composition had a structure of ledeburite after hardening. In accordance with [12], the structure of hardened alloys with 4.6 and 5.6% carbon contained cementite. Cementite has also been detected in specimens of cast iron (2.8% C, 2.1% Si) after LSH in [13]; with growth in the hardening temperature the amount of cementite in the structure increased from 25% at t_h = 1350°C to 30% at t_h = 1550°C. Similar results are known to have been obtained in many other works too. It should be noted that in accordance with the data of some studies performed in the 1970 – 1980s the structure of some hardened alloys contained an ε-phase, i.e., a solid solution of carbon in ε-iron. Some arguments in monograph [14] allow us to doubt the formation of such phase due to hardening. In many studies of alloys of the Fe – C system performed by the method of LSH (at various cooling rates including very high ones) such a phase has not been detected.

The absence of ε-phase and the presence of cementite is mentioned in later works [10, 11]. In these studies the content of cementite in the structure of hardened specimens increased from 0% in an alloy with 1.8% C to 80% in an alloy with 5.7% C. Note that some researchers have detected a low amount of graphite in the structure of hardened specimens containing over 4 – 4.5% C. It is possible that the impurities present in the alloy produce this effect. It is shown in [2] that the primary excess phase in alloys with over 6% C is graphite and the eutectic is austenite-cementite.

The data obtained by LSH are confirmed convincingly by results of x-ray studies of melts. A study of liquid iron

containing 3.85% C and 2.67% Si (in monochromatic K_α radiation, which gave some methodological advantages) has given a fine structure of maxima on the intensity curves and auxiliary maxima and buildups in the range of the angles corresponding to cementite lines (Fig. 1) [15]. This structure was detected only after a 1-h hold at 1400°C (after a hold of 30 min, the fine structure of a maximum is undetectable; at $\theta = 16°30'$, a narrow and intense maximum corresponding to graphite appears; after a hold of 1 h, this maximum decreases abruptly). When the hold is prolonged from 3 to 5 h, the diffraction pattern does not change substantially. These results reflect steady existence of three regions with different compositions and structures in the liquid alloy. It is inferred in [15] that the structures of these regions (with respect to the short-range ordering) correspond to a solution of carbon in ε-iron, cementite, and graphite (recall that the alloy contained an elevated amount of silicon). The stability of cementite after a 5-h hold deserves special attention. Similar regions have been detected in iron-carbon melts containing 3, 4.3 and 4.5% carbon [16]. The intensity curves for these alloys (obtained after a hold of 1 h) are presented in Fig. 2, where we compare the positions of resolved maxima and buildups on the intensity curves of the melts with the positions of the corresponding lines of the cementite, the carbon solution of ε-iron, and the graphite (the weak maximum at $\theta = 16°35'$) on the diffraction pattern of the solid alloys. It is obvious that they are related through an angular dependence. Thus, the results of diffraction studies prove the data obtained by the method of LSH.

The structure of liquid Fe-Fe$_3$C alloys agrees fully with the general laws for other eutectic systems (metals, semiconductors, salts, other chemical compounds). These laws representing a new concept of the nature of eutectics have been published in several works [e.g. 17 – 21]. Facts of limited miscibility of components of eutectic systems in melts and the fact that the solubility of components in a melt does not exceed the maximum solubility in solid state have been confirmed in recent studies by an advanced method [22, 23]. We should also mention many works that report that melts contain particles close in the structure (short range ordering) and composition to the chemical compounds of the components existing in these systems in solid state. These are works [24] for the Tl – Te system, [25] for the Mg – Sn system, [26] for the Fe – Si system, [27] for the Cu – Sb system, etc. After LSH of aluminum alloys with REM (in a wide range of REM concentrations) the structure of the hardened alloys was represented by a matrix of virtually pure aluminum and dispersed particles of the corresponding intermetallic [28]. Similar results have been obtained in other studies.

Thus, formation of regions (particles) with structure (short-range ordering) of a chemical compound in a melt is no special property of the system but fully matches the general laws determined for the structures of melts of other similar eutectic systems. The system in question is distinguished by the fact that cementite is an endothermic chemi-
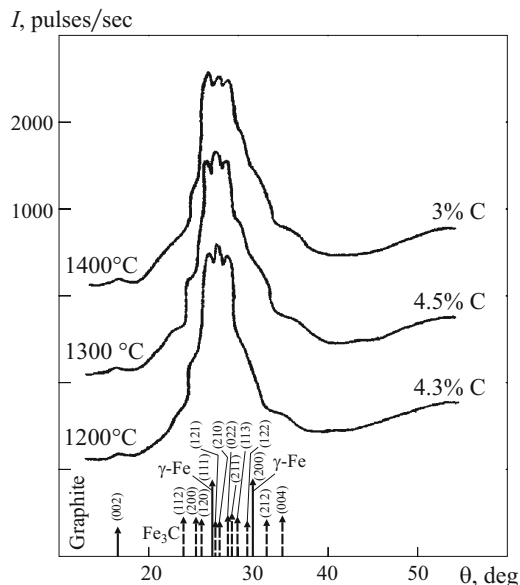

Fig. 2. Intensity curves for liquid Fe – C alloys. The temperature of the test and the carbon content are given at the curves. The lines (with arrows) at the axis of abscissas indicate the location of maxima on the lines of the corresponding phases in the diffractograms of solid alloys [16].

cal compound and forms in the melt at a high temperature; when the temperature decreases so does its stability.

It is known that cementite cannot be heated to melting because of its decomposition. This has given rise to an erroneous concept that preservation of inherited short-range ordering typical for cementite is little probable in a melt, because cementite melts incongruently. However, formation of cementite in a melt at a high temperature does not depend on the initial structure of the alloy in solid state (recall the formation of cementite upon dissolution of graphite in liquid iron).

In conclusion, we will give a short description of the structure of liquid Fe – Fe$_3$C alloys and of the state of carbon in them. The solubility of carbon in liquid iron is 1.7 – 2%; at 2 – 6% carbon in the alloy in the range of 1300 – 1700°C the melts are represented by a two-phase dispersion, i.e., a solution of carbon in liquid iron (with a structure of a γ-modification) with 2% C and cementite. In the range in question cementite is a thermodynamically equilibrium stable phase, while graphite is an unsteady unstable state. In an isothermal hold of the melt, carbon (graphite) interacts with iron, yielding cementite. The presence and contact of the two eutectic phases already in the melt, which determines the effect of the atomic interaction on the interphase on the temperature of the phase transformations, allows us to explain the virtual coincidence of the melting and crystallization temperatures (in slow cooling) of the austenite – cementite eutectic.

The aspects of application of the phase rule to thermodynamically equilibrium two-phase dispersions formed sponta-

neously in a melt are considered in detail in the literature (training and scientific) on colloidal chemistry.

The presented model of the structure of Fe – Fe$_3$C melts agrees with the special features of the crystal chemistry of the two kinds of short-range-ordered regions present in a melt and with the possible geometric mechanism of formation of cementite from austenite [29]. The topic of structural correspondence of austenite and cementite in liquid state will be considered additionally.

CONCLUSIONS

The new concept of the nature of eutectics [14, 21] based on generalization of the results of studies of hundreds of eutectic systems by three methods (diffraction, sedimentation, and LSH) and on the experimental data obtained for the Fe – C system have allowed us to answer the question on the form of the presence of carbon in melts of this system.

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