DISCUSSION ON THE PROBLEM OF SYNTHESIS OF DIAMONDS IN Fe – C ALLOYS

The problem of synthesis of diamond in hard Fe – C alloys has been discussed many times in scientific publications, our journal inclusive. Today we turn to it once again because the problem of synthesis of diamond, for example, in cast iron at various acceptable temperatures and normal pressure, presents obvious scientific and practical interest. Despite the optimistic character of some publications we can state that the problem of such synthesis of diamond still remains disputable. The paper presented below describes a standpoint according to which most of the experimental data confirming the creation of diamond under such conditions are erroneous and stem from the imperfection of the methods of experiment. The editorial board does not approve the too categorical manner of the authors in their estimation of the positions of the opponents and hopes that the reader will treat this position with understanding. The aim of the paper consists in presenting one of the opinions on the essence of the problem. We assume that the opinion of the authors on a wide circle of problems, including the criticism of some works, presents interest from the standpoint of comprehending the complexity of the problem of the creation of diamonds in Fe – C alloys. The position of the authors generalized in the suggested dependence of the activity of carbon on the temperature in the temperature range of the existence of diamond under normal pressure presents much interest. We would like to think that we are approaching the solution of the riddle of A. Moissan step by step.

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ON THE FORMATION OF CARBYN (CYANOPOLYYNE) AND DIAMOND IN Fe – C ALLOYS[1]

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The Problem of Carbyn

Carbyn as a "linear" allotropic modification of crystalline carbon has not yet been obtained in Fe – C alloys despite the erroneous statements of the converse.

The first mentioning of carbyn as a possible phase in graphitized iron alloys can be found in [1]. Carbyn can have two allotropic forms, namely, cyanopolyyne –C≡C–C≡C– and polycumulene =C=C=C=C=; the former is more stable. The reaction of transformation of carbyn into graphite can be explosive.

The data of [2] are assumed to prove the formation of carbyn in steel U8 (0.8% C) after quenching from 780°C. However, the study was performed under an electron microscope UÉMV-100 (erroneously called ÉVM-100 in the paper), which is not suitable for identification of phases by the method of electron diffraction.

Steel U8 has a single-phase structure at 780°C. Under these conditions austenite is not supersaturated with carbon and the possibility of the growth of graphite, diamond, or carbyn in it is out of the question. In a quenched state steel U8 contains only martensite and retained austenite. The latter possesses a hexagonal crystal system in planes {111}, which differ from other planes by the maximum reticular density in the f.c.c. lattice. The inaccurate measurement of the parameter *a* of the hexagonal close-packed A–B–C–A–B–C system of the packing of hexahedral cellular layers combined with the absence of a rotating stand in the UÉMV-100 microscope has led to the following result: the reflections from those sur-

[1] Authorized translation from the English (with some abbreviations and editor's corrections) of the paper "Formation of carbyn (cyanopolyyne) and of diamond in Fe – C alloys" published in the book "Modeling and Optimization in the Machines Building Field" (MOCM-5), Romanian Academy, Bacau (1999), pp. 1 – 4.

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faces of the metal at which planes {111} of austenite were positioned in parallel to them were erroneously ascribed to reflections of a simple hexagonal pencil-like lattice of carbyn.

At the same time, the authors of [4, 5], despite the criticism, proclaimed that they have discovered carbyn in austenitic alloy cast iron too. The circumstance that they insisted on their discovery of carbyn in alloys bearing much austenite and not in ferritic and pearlitic ones, where the b.c.c.-iron and cementite do not have the hexagonal crystal system possessed by f.c.c.-iron, is very symptomatic.

We assume that a low amount of carbyn can be present in cast iron in principle, but not in the austenite phase. Carbyn should be sought in the axial zone of branches of coral graphite [1, 6, 7].

Problem of Diamond Cast Iron

Small crystals of diamond have been obtained in "diamond cast iron" experimentally, but the statements about their formation inside graphite globules of high-strength cast iron with globular graphite under atmospheric pressure are erroneous [8]. They require an experimental check [9]. Researchers of the Institute of Superhard Materials of the National Academy of Sciences of Ukraine studied the case of a "discovery" of diamond cast iron when they established that graphite inclusions in the surface layer of a microscopic polished specimen were simply charged with fine diamond particles, possibly, arriving from the diamond abrasive and the paste used for grinding and polishing of the specimens [10]. In our opinion, [8] contains many erroneous statements concerning the synthesis of diamond in cast iron.

The first paragraph of [8] is incorrect, which has been proved earlier in [6]. Further, we find in [8] a description of synthesis of diamond from graphite with the use of Fe – C cast iron as a liquid-metal catalyst without references to the ample available literature. Instead of them we find references to the deposited works of the author not read by specialists in diamond synthesis.

It is stated in [8]: "It was established that the realization of the mechanism of formation of diamond in Fe – C alloys is not limited by two cases of purposeful synthesis. Diamond formation is observed due to hardening of cast iron treated with elements that spheroidize the graphite phase, i.e., Mg, Y, Ce, etc." The author of [8] does not say anything on the application of pressure to this cast iron. Instead we read an indefinite phrase: "... the mentioned ideas have been confirmed experimentally; under some conditions of hardening of modified cast iron we managed to obtain a primary structure of diamond in inclusions of free carbon." But what kind of free carbon is it? In [8] it is globular graphite. And what is meant under "some conditions"? Two phrases of work [8] presented below were intended to convince the reader and the critics that the author had obtained diamond in modified cast iron without applying pressure, namely, "They (conditions) can be created under conventional pressures too, kinetically, as in Moissan's experiment, or 'chemically,' as in hardening of modified cast iron," and later: "... Our computations have shown that in modified cast iron these changes are equivalent to application of additional pressure on the order of 10 kbar to the melt."

When the author of [5] defended his doctoral thesis, he admitted that all the cases of diamond synthesis considered in it involved the application of very high pressures. Then, what is the difference between his results and the data obtained earlier by D. S. Kamenetskaya, I. A. Korsunskaya, Yu. A. Litvin, and many other researchers [11, 12]? Until the results of diamond synthesis upon hardening of cast iron with globular graphite (inside the globules and at atmospheric pressure) are reproducible, the problem cannot be considered to have been solved successfully. Years pass, but this elementary requirement remains unsatisfied [13].

The same can be said about checking the formation of carbyn in steel U8 and austenitic cast iron. Is it not a systematic mistake?

As for the development of the theory in works [5, 8, etc.] and other publications, most of them deserve criticism too.

Errors in the Field of Metal Physics

It is not the concentration of π- and σ-bonds in Fe – C alloys that dictates the type of structure formation in them (crystallization of cementite or graphite, or diamond), but, on the contrary, the formation of the structure determines the proportion of the C–C and C–Fe bonds hybridized according to sp^2- or sp^3-type. In this respect the mentioned texts are obviously erroneous.

When we read in [5] that "... the rate of the relaxation processes determined by the transformations in the d-band of iron and, consequently, of the 'release' of the valence electrons of carbon, turns out to be lower than the rate of crystallization of cast iron ...," we can see that the author does not understand that electron transitions occur immeasurably faster than phase transformations. The author of [5] is not original when he writes: "In the region of low carbon concentrations, when the Fe – C interactions are the strongest, the conditions are favorable for the full disintegration of the C–C bond, and therefore carbon is dissolved in the melt in the form of C^{n+} ions. With the growth of carbon concentration the energy gain due to the formation of Fe – C bonds decreases. Consequently, beginning with some carbon content, the full disintegration of the C–C bonds becomes impossible, and the melt dissolves more and more complex radicals of graphite macromolecules, starting with the chain compounds ..., as well as the compounds of an arene type with various numbers of rings of carbon atoms (... The formation of arene complexes in Fe – C melts was established by Professor A. A. Zhukov) ...".

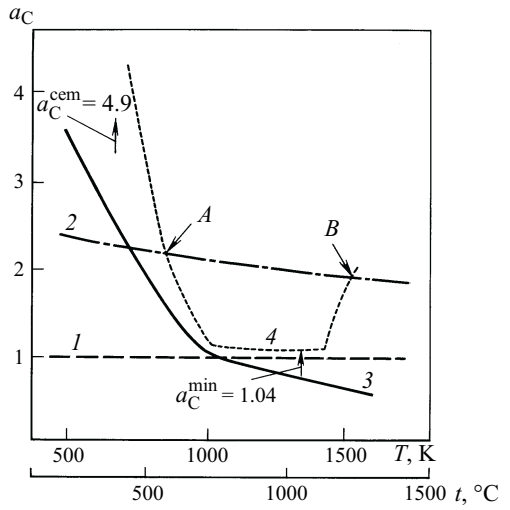

Fig. 1. Temperature dependence of the carbon activity: *1*) in graphite (chosen as a standard state of carbon); *2*) in diamond; *3*) in cementite (according to [5, 25]); *4*) in cementite (according to [17, 19]); *AB*) temperature range in which diamond cannot be obtained from cementite at atmospheric pressure.

Here not only the complexes, but also the entire concept of formation of single-phase (but quasi-colloidal) liquid solutions of "polymer" carbon are borrowed from [14 – 16].

Moissan's Riddle

Despite the great progress in the science of alloys of the Fe – C system, the riddle of the creation of synthetic diamond from cast iron by the Nobel Prize winner A. Moissan remains unanswered [9]. Even in France there is enough pessimism about the reliability of his results. However, a certain shift has been outlined [16 – 21]. Researchers from Dnepropetrovsk obtained small crystallites of diamond in cast iron by a burst followed by thermocycling under atmospheric pressure [22 – 24].

Activity of Carbon in Graphite, Diamond, and Cementite

If we choose graphite as a standard state of carbon, the activity of carbon in graphite $a_C^{gr} = 1.0$. Then in diamond at atmospheric pressure $a_C^{d} = 2$ (a bit lower than 2.0 at a high temperature and a bit higher than 2.0 at lower temperatures [14, 17, 19, 20]). In this respect the plots presented in Fig. 2 of [5, 25] are more or less accurate. The inaccuracy is found in the profile of the curve a_C^{cem} (the activity of carbon in cementite). At a high temperature a_C^{cem} is much higher than it is shown in [5, 25]. By the data of [5, 25] at $T > Ac_1$ the value of a_C^{cem} is less than unity, which cannot be, because then we would have dealt with carbidization at $T > 1000$ K (over 727°C) instead of graphitization [26]. Curve *4* in Fig. 1 does not descend below the level $a_C = 1.0$ (in contrast to the incorrect curve *3*). The commentary in [27] is not able to break the second law of thermodynamics by the word of the author or his publishers. The last points above *i* in letters [13, 27] have not been placed yet. It is impermissible to break this law ...

CONCLUSIONS

1. The authors of [2, 4] have not obtained carbyn. The published point electron patterns belong to austenite.

2. By the data of the Institute of Superhard Materials (Kiev) diamond inside graphite globules of high-strength cast iron has been introduced there mechanically [10] in the thin surface layer.

3. "The diamondization" of metastable Fe – Fe_3C alloys by the reaction $Fe_3C \rightarrow 3Fe + C$ (diamond) is possible in principle at atmospheric pressure [28] (or at other subcritical pressures) only in a specific temperature range where $a_C^{cem} > a_C^{d}$.

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