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ON OSMONDITE NATURE

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The uniqueness of iron is not only that it is one of the most common elements, and the production of its derivative (steel) «exceeds the production of other metals by 14 times», not only in its polymorphism, but also in the following: «conversion of BCC α-Fe (K = 8) into a denser FCC γ-modification (K = 12) with heating is quite unusual and along with the thermodynamic interpretation requires a special physical explanation, especially in connection with the fact that it lies at the basis of the metal science and the thermal treatment of iron alloys» (V.K.Grigorovich). «Unusual» iron is also confirmed by the fact that the hardness of Fe at 440 °C is 1.15 times higher than at 20 °C. Other metals of this unique quality do not – as the temperature rises, the hardness decreases. Only manganese with a tetragonal lattice exhibits a hardness maximum at 650-750 °C; a maximum hardness is observed near the α ⇆ β transformation of manganese. The absolute maximum of hardness at 440 °C for iron allows (by analogy) to assume a transformation in iron at this temperature. Especially note: at the temperature of unconditional α→γ → </s> transformation (910 °C) there is an absolute minimum of hardness.

A curious situation arose around the temperature interval 400-500 °C. M.V.Belous and his co-authors simply do not notice it in the classification of four transformations during drawing back process, although back in 1925 P.Oberghoffer, basing on a minimum at 400-500 °C of the thermoelectric power of the iron-platinum pair, wrote: «Whether we are here dealing with further transformations in pure iron, should be investigated in new detailed studies».

Based on the maximum etchability value, acceleration of the graphitization of steels, the maximum corrosion rate of gray cast iron, anomalies in the temperature dependences of the physical and mechanical properties, changes in the solubility of cementite, the maximum lattice parameter, the extremum on the resistance curve of the pure iron deposit, the conversion in iron at ~ 450 °C is justified.

Key words: steel, cast iron, graphite, polymorphism, hardness, heat capacity, thermoEMF, corrosion, carbide

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Introduction. The term «transformation» is explained by the example of iron. Both types of transformation with A_2 (magnetic) and A_3 (polymorphic) are thermal ones, they are accompanied by thermal effects and anomalies of properties: the peak of the specific heat, the acceleration of diffusion, the bending of the thermoelectric power curve at A_2; compression by heating, minimum thermal EMF, high impact brittleness, and creepage peak at A_3. Let us note: «There is no common opinion about the causes of polymorphism for A_3 polymorphism type» [4], and «the theoretical model of ferromagnetism ... is very approximate» [6]. Therefore, the term «transformation» implies a change in the interaction between iron atoms, which generates anomalies of properties and steels, that is processed iron.

The aim of this paper is to justify the relationship of extreme points of the curves of physical mechanical properties of iron with its transformation ~ 450 °C, which can define anomalies of the mechanical properties of the processed iron as well, i.e. steels.

Methods. The force for displacement iron samples containing 0.008 % C (⌀ 10 × 15 mm) to a half of its height was determined on the «Greeble-3800» unit, heating to deformation temperature was accomplished by passing an electric current at a rate of 5 °C/s. Deformation was then carried out at a rate of 0.5 s^{-1}, followed by an exposure of 1 min and free cooling due to the heat sink in the water-cooled copper clamps. The X-ray diffraction analysis was carried out on a general-purpose diffractometer (DRON-2) on iron samples (0.008 % C) of a cubic shape with dimensions of 10×10×10 mm.

The methodology is based on the following presuppositions. B.G.Livshits: «When studying phase equilibrium, you can use any property»; A.A.Vertman, A.M.Samarin: «As structurally sensitive properties, one can choose any of about 50 properties that are used now in physical and chemical analysis»; A.A.Bochvar: «As a measurable physical property one can take hardness ... electrical conductivity ... density, coefficient of linear expansion, etc.».

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Analysis of literature data. «When drawing back the martensitic structure, the state of maximum solubility in acids (and maximum etchability) is reached at about 400 °C; this structure was sometimes called osmondite» [4]. Thus E. Gudremon stated in 1956 that the term «osmondite» for the products of drawing back at 400 °C is obsolete now. (Unlike Roberts-Austen, Sorby and Ledebour, the surname of Floris Osmond – the pioneer of the instrumental method of polymorphism of iron – did not become a nominal word in metal science).

The maximum etchability is attributed to the «critical degree of dispersion of carbides» [4], which creates «the maximum number of working galvanic micropairs» [11].

According to K.F.Starodubov, the maximum corrosion rate is associated with the grinding of blocks *D*. The minimum *D* is possible after drawing back at ~450 °C. But the blocks at t_{drb} = 300 °C are even smaller [9] (Fig.1, curve 2), and the rate of corrosion is much lower.

The minimum block size at t_{drb} = 450 °C is explained either by loss of coherence between carbide and solid solution [10], or by «plastic shifts in microregions at the interphase boundaries» [5].

The version of the «critical dispersion of carbides» is questionable. This is proved by the maximum corrosion rate *V* (curve 1 in Fig.1) of four gray cast iron with 3.1 % C in a 5 % solution of HNO_3 and 5 % NaCl solution after not only heat treatment and drawing back at 450 °C, but also after «isothermal treatment» at 450 °C [11]. Temperatures of drawing back and isothermal treatment were the same: 200, 350, 450, 600 and 700 °C. Since for all cast iron the dependence of the corrosion rate *V* on the drawing back temperature or isothermal processing is qualitatively the same, they are shown in Fig.1 in one curve 1.

After both types of processing, the structure is fundamentally different, and the maximum corrosion rate after the stay of cast iron at 450 °C is qualitatively the same. It has no relation to the carbide phase at all, since the metal base before heat treatment and isothermal treatment of four cast irons was very different: perlite, perlite and 8 % ferrite, ferrite and 6 % perlite, ferrite. Consequently, the amount of carbides and the distance between them after the release are different, and the maximum corrosion rate is always observed after drawing back at 450 °C, as in steels [4].

The maximums are not related to the «metallographic» structure, since unlike globular carbides, after the drawing back of martensite under isothermal treatment, they are lamellar or spiky [11].

The shape of graphite does not influence corrosion [11].

Let us make a cautious assumption about the nature of the extrema *D* and *V*, which corresponds to the maximum of the coercive force H_c [9] (Fig.1) after drawing back at ~ 450 °C.

According to M.P.Arbuzov [5, 11], the size of carbides in carbon steels is almost unchanged to t_{drb} = 400 °C, and then their rapid growth begins (Fig.1, curve 5). For a sharp increase, a distinct change in the diffusion rate of carbon is necessary. Such an acceleration is possible in transformations, for example, near the Curie point of iron [2].

With reference to M.P.Arbuzov [1, 14], almost complete dissolution of carbides in carbon steel during the drawing back process at 400 °C is shown (Fig.1, curve 4). (It is interesting that there is no comment in [7] on the almost complete dissolution of carbides).

For example, in steel with 0.33 % C and 4.05 % Cr after 2 h of drawing back at 600 °C completely disappears Fe_3C and reappears after 4 hours of drawing back, but already together with the special type of carbide Cr_7C_3 [1]. (It's like a process of jam sugaring, then dissolving of sugar crystals, and after one more sugaring without changing the temperature).

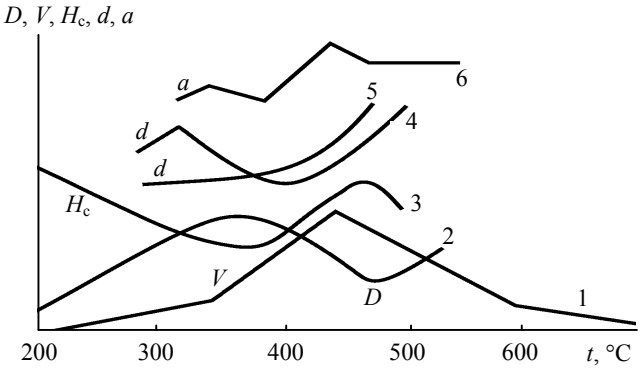


Fig.1. Diagrammatic dependency of corrosion rate *V* of four gray cast iron with different patterns of metal matrix from drawing back temperature or isothermal processing (1), block sizes *D* (2), coercitive force H_c (3) of steel 70, cementite particle sizes *d* (4, 5 according to different data), lattice parameter *a* (hardened iron at 1050 °C) (6) and drawing back temperature

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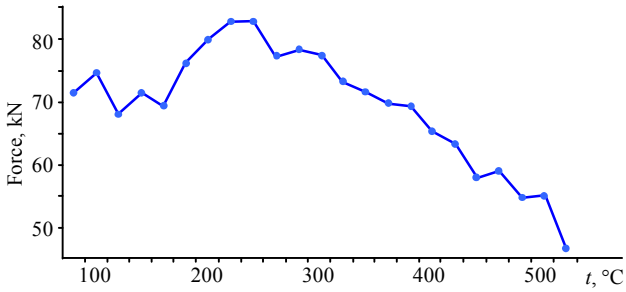


Fig.2. Dependency of force during deformation to a half of an iron sample size height at a temperature from 80 to 520 °C

Yu.I.Ustinovshchikov repeatedly asks the question: «Why does cementite dissolve?» [12], stating, on the basis of Mossbauer spectroscopy, «the unambiguous ... dissolution of cementite in a solid solution» [12]. The increase in free energy in this incredible event – just by heating for heat treatment, it is possible to «entrap» the carbon atoms into a solid solution (austenite), and then fix it in martensite – the dissolution of cementite Y.I.Ustinovshchikov explains by the subsequent after dissolution stage, when carbon atoms diffuse to «clusters of atoms of the carbide-forming element, which leads to a decrease in the free energy of the system» [12].

But for this it is necessary that the «capacitance» of the lattice of the α-solid solution at a certain stage of the release noticeably changes, that is there would be «the process of returning to the previous state with greater free energy, to the state of heat treatment», which is fixed by «increasing the lattice parameter of α-iron» [12].

Research results. We have carried out a research of temperature influence on the resistance of the *P* samples drawing back process made of iron (0.008% C) at a temperature of 80-520 °C (Fig.2).

The local maximum *P* at ~ 450 °C (Fig.2) corresponds to the curve of the magnetic permeability curve, that is the maximum hardness. At ~ 450 °C, the solubility of hydrogen and carbon in the iron varies appreciably, which is an indicator of the binding forces in the lattice, which "allows" to dissolve up to ~ 5 at. % of carbon in it [3].

In this paper, in order to exclude the effect of carbon and carbides influence, the X-ray diffraction analysis was performed on samples of pure iron (0.008% C), treated in water from 1050 °C and drawn back at temperature from 300 to 600 °C in every ~ 40 ° C.

After drawing back at 430 °C, the maximum of the lattice parameter is observed (see curve 6 in Fig.1, Fig.3, *a*). Consequently, the dissolution of cementite is due to the specific behavior of iron at ~ 450 ° C. Then the nature of the osmondite can be related to this specificity – the transformation occurring in it, since neither the amount nor the shape of the carbide phase can be explained by the increased etchability after the cast irons stay at 450 °C [11].

It was not possible to establish any regularity in changing the width of the lines (Fig.3, *b*, *c*). The absence of a correlation between the hardness and the width of the line follows from the processing of data from papers of G.V.Kurdyumov and N.Oslon [15]: for $t_{drb} \approx 430$ °C there is a distinct curve *B* – HRC in tempered steels with 0.1, 0.4 and 1.0 % C. The absence of a correlation between *B* and HB after drawing back below 380 °C is noted in [13], for products of the isothermal transformation of austenite at 420 °C in [8]. The absence of correlation may indicate a significant change in the ensembles of iron atoms at ~ 450 °C.

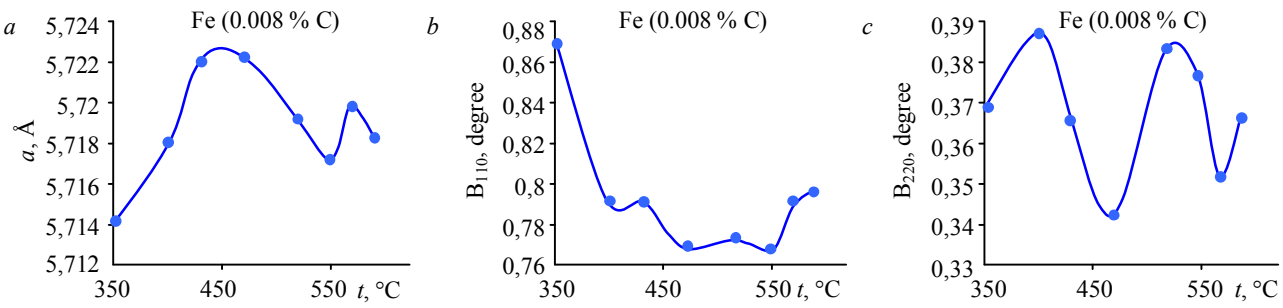


Fig.3. Dependency of crystal lattice parameter (*a*), broadening of the diffraction maximum of the line 110 (B_{110}) (*b*), 220 (B_{220}) (*c*) from pure iron drawing back process temperature

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The residence effect at ~ 450 °C is very stable. For example, if the steel 50C3 before graphitizing annealing at 700 °C is drawn back at 50-500 °C, then the graphitization time after drawing back at 450 °C will be minimal [1]. However, the mechanism of information transfer from 450 to 700 °C is not clear.

The acceleration of graphitization is explained by the increase in structural defects [1], after drawing back at 450 °C, it is maximal. The defect is created by phase hardening. Therefore, at ~450 °C, one can assume a transformation occurring in iron.

Conclusion. Anomalies in the temperature dependences of mechanical and physical properties can be a consequence of the transformation occurring in the iron at ~ 450 °C, which, possibly, determines the anomalies of the mechanical behavior of steels [16]. Recognition of transformations at these temperatures makes it possible to explain the extreme values of the properties of the products of the isothermal transformation of austenite, the products of martensite release after hardening and subcritical heat treatment, the disappearance of iron carbide, the nature of osmondite, and others.

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