Determination of Thermodynamic Stability of FeB Monoboride

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Abstract — **The investigation was performed for Fe-B system alloys with boron content of 11.0-15.0 % (wt.), the rest is iron. We use microstructure analysis, X-ray structure analysis, differential thermal analysis and durometric one to determine physical properties of alloys. Accounting for the contribution of the first degree approximation of high-temperature expansion of the thermodynamic potential of FeB iron monoboride in a Fe-B binary alloy enables to study its thermodynamic stability. It is shown, that stability decrease of FeB iron monoboride at temperature of 1423 K allows suggesting, that at this temperature the phase transformation occurs, which correlates to differential thermal analysis results.**

Keywords — Fe-B alloys; FeB iron monoboride; thermodynamic stability

I. INTRODUCTION

It is known, that in Fe-B system alloys at a boron content of more than 8.86% (wt.) at temperature of 1882 K in the process of liquid and FeB iron monoboride interaction the peritectic transformation L+FeB↔Fe2B occurs, in consequence of which the Fe2B iron boride formation takes place [1]. The authors of [2, 3] suggested, that in Fe-B alloys the FeB iron monoboride is appeared, which can exist in two modifications: high-temperature β-FeB and low-temperature α-FeB, which are formed as a result of the polymorphic transformation β-FeB→α-FeB at the temperature of 1405 K. The Mössbauer data analysis shows, that β- and α-FeB have similar magnetization and Curie temperatures T_c=580 K [2, 3]. Moreover, the authors of these studies pointed out, that carbon, aluminum and other impurities, contained in furnace burden in the process of fabricating of alloys, have a strong influence on the formation of FeB phase. Investigations by K.I. Portnoy [4] reveal the existence of the only modification of iron monoboride with B27 structure. It is known, that carbon has a low solubility in iron monoboride [5-6]. Additionally, doping of Fe-B system alloys with carbon to 0.2% (wt.) practically does not change the alloy structure [7], and with increase of carbon content the formation of a $Fe_3(CB)$ boron cementite takes place.

There is, also, another point of view, concerned with transformation in the Fe-B system alloys at the temperature of 1400 K, namely at boron content of 11.0-15.0 % (wt.) during the isothermal holding within the temperature interval of 1400-1500 K and rapid aftercooling the formation of metastable Fe_5B_3 boride phase, possibly, takes place, but the mechanism of formation, area of the state diagram of Fe-B system and thermodynamic functions of this phase are not determined [8]. Despite the fact that structure, mechanical and chemical properties of Fe-B system alloys are under study for decades, the question of phase composition and phase transformations in these alloys remains actual.

II. MATERIALS AND METHODS

The investigation was performed on specimens with boron content of 9.0-15.0 % (wt.), the rest is iron. To obtain these alloys we used the furnace burden of such content: metal (with content of 99.99 % (wt.)), amorphous boron (with boron content of 97.5 % (wt.)). The smelting of specimens was carried out in Taman's furnace with graphite heater in alundum saggers in argon atmosphere. The cooling rate of alloys was 10 K/s. To determine the chemical composition of alloy we used the chemical and spectroscopic analysis. The microhardness of the phases we measured by means of microhardness gauge PMT-3.

The phase composition of alloys was determined by means of X-ray microanalysis on JSM–6490 microscope, as well as by means of optical microscope "Neophot-21". X-ray electron probe analysis was performed using internal standards. The X-ray structure analysis was performed on diffractometer DRON-3 in monochromated Fe-K_α radiation.

III. RESULTS AND DISCUSSIONS

The microstructure of Fe-B alloys in the as-cast condition at boron content within the range of 9.0-16.0% (wt.) contains rounded dendrites of the FeB phase located in a solid solution based on Fe_2B boride (Fig. 1). FeB iron monoboride has different coloring patterns in the process of microstructure study on optical microscope: white, shades of gray and black (Fig. 2, a).

The authors of [9] suggested, that white FeB monoborides correspond to high-temperature modification of β-FeB, and black ones – to low-temperature α-FeB modification. The authors explained their findings by incompleteness of peritectoid reaction, which results in the formation of Fe_2B boride when the liquid is interacted with iron monoboride.

It should be noted that in dark-colored monoborides, according to the results of microstructure analysis, there was decomposition and, according to the results of X-ray diffraction analysis, this alloy consists of such components: FeB iron monoboride, Fe_5B_3 boride, and Fe_2B boride. The results of the durometric analysis show that the microhardness of the iron monoboride takes on different values depending on the color. Thus, white in color monoboride has a microhardness of 24.05 GPa, and black-colored one – 21.8 GPa. The microhardness of solid solution based on Fe_2B iron boride has a microhardness is 20.01 GPa. In addition, white-colored monoboride is less fragile than black one.
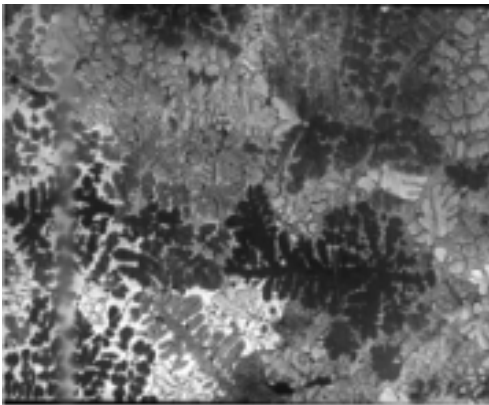

Fig. 1. Microstructure of Fe-B alloy with boron content of 13.0% (wt.)

The presence of monoborides of different colors with distinct physical properties in the structure of alloys can be explained by the fact that in the process of grinding the fracture of monoboride dendrites takes place. This phenomenon is associated with the fact that in the monoboride structure there are [001] and [100] planes, in which there are no boron atoms at all [10-11], but this explanation will not be sufficient to substantiate the processes occurring in these alloys.

In order to reveal the phase transitions in Fe-B alloy the differential thermal analysis was performed. According to its results, in the iron-based alloy with boron content of 10.0% (wt.), the phase transformation $L \rightarrow FeB$ occurs while cooling at the temperature of 1809 K. The formation of Fe_5B_3 boride is possible as a result of the peritectic reaction of $L+FeB \leftrightarrow Fe_5B_3$ at the temperature of 1680 K. At the temperature of 1411 K an insignificant thermal effect was observed on the thermogram, which may indicate the phase transformation $Fe_5B_3 \rightarrow FeB+Fe_2B$ occurring in a solid state. Thus, the formation of the Fe_5B_3 phase takes place at the temperature of 1680 K as a result of the peritectic reaction $L+FeB \rightarrow Fe_5B_3$, and the decomposition $Fe_5B_3 \rightarrow FeB+Fe_2B$ arises at 1420 K.

As shown in [12], the formation of the Fe_5B_3 boride occurs at the temperature of 1680 K, which correlates with data obtained in this paper, and at the temperature of 1420 K a phase transformation is possible, resulting in the formation of a secondary monoboride FeB.

To verify a possibility of phase transformations at the temperature of 1420 K, specimens of alloys were heated to the temperature of 1473 K for four hours and cooled at a rate of 10^2 K/s.
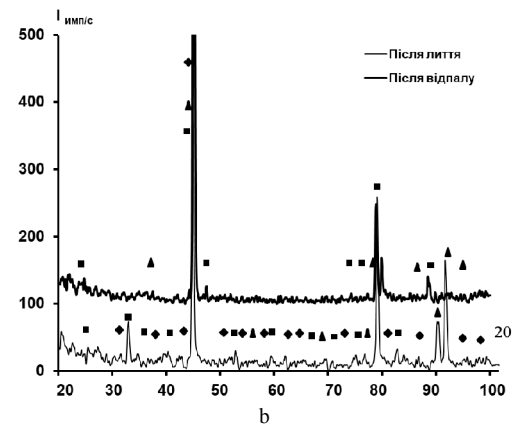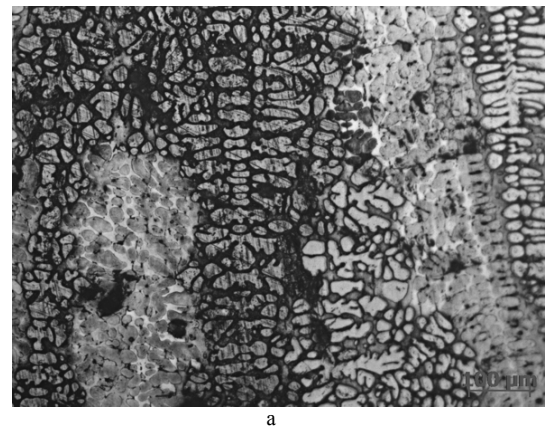

Fig. 2. Microstructure, ×100 (a), and diffractogram (b) of alloy with boron content of 13.0% (wt.) after annealing at 1473 K for 4 hours and cooling with a rate of 10^2 K/s

The microstructure of cast alloy with boron content of 13.0% (wt.) was represented by monoboride and iron boride. After annealing at a temperature of 1473 K and cooling at a rate of 10^2 K/s, the phase composition changes. The primary crystals of FeB monoboride were observed in a matrix, which is represented by Fe_5B_3 phase and decomposition of this phase into two phases, monoboride and Fe_2B boride, which is testified by the results of X-ray diffraction analysis (Fig. 2).

According to the results of microspectral analysis, after annealing the content of boron in alloys in the FeB phase was 15.85%, and in Fe_2B boride it was 7.65%.

Investigation of microhardness of the constituents enabled to obtain the following results: after annealing white-colored monoborides has microhardness of 23.06 GPa, for dark-colored monoborides microhardness is 17.22 GPa, for decomposition it is 27.93 GPa.

So, for alloys with a boron content of 13.0% (wt.) the microstructure after casting is represented by the phases: monoboride and Fe_5B_3 and Fe_2B borides. After annealing at a temperature of 1450 K, the phase decomposition of Fe_5B_3 occurs to form monoboride and Fe_2B boride.

To determine the existence of the decomposition, the thermodynamic stability of the FeB monoboride should be examined.

One of the main factors of the control of process of the phase formation and phase transformation are the thermodynamic functions of the phase. But obtaining the values of thermodynamic functions of FeB monoboride from experimental data faces with certain difficulties. Accounting in Gibbs free energy for contributions, which are responsible for fluctuation processes, enables to determine theoretically the thermodynamic functions of FeB monoboride.

To calculate the thermodynamic stability of the monoboride, the equation of the thermodynamic potential (Gibbs energy) of FeB phase was derived and approach proposed by the authors of [12] was used. The value of the energy of pure components and the energy of interaction between boron and iron atoms from were taken from [13-14].

The Gibbs energy of FeB monoboride can be written as

$$G_m^{FeB} = x_1 G_1^0 + x_2 G_2^0 + RT (x_1 \ln x_1 + x_2 \ln x_2) +$$

$$+ x_1 x_2 L_{12} - L_{12}^2 x_1^2 x_2^2 / (2ZRT) \qquad (1)$$

where G_i^0 is Gibbs energy of pure components (J/mole), R is universal gas constant (R=8,31 J/(mole·K)), T is temperature (K), L_{12} is interaction energy of components (J/mole), Z is coordination number, which equals Z=4 for monoboride [1]. The interaction energy L_{12} of elements depends on a temperature. The temperature dependence of the interaction energy in a general form can be written as $L_{12} = a + bT + cT \ln T$. Using data for the pure components G_1^0, G_2^0 [13-14], and the energy of interaction between components in the phase from [15-17], we obtained temperature dependences of the Gibbs energy of the melt.

To determine the stability of the phase let us find a variation of Gibbs energy:

$$\delta G = \Sigma_{n=1}^{\infty} [\delta T \, \partial/\partial T + \delta x_1 \, \partial/\partial x_1 + \delta x_2 \, \partial/\partial x_2]^n \, G/n!$$

The general condition of the phase stability by Gibbs is that arbitrary variations of the internal energy and external parameters of a system should not cause in the system both reversible and irreversible processes (so that the system is not out of equilibrium). Therefore, these deviations must be with the property that

$$\delta U - T\delta S + p\delta V - \mu\delta x > 0$$

(here S is entropy, p is pressure, V is volume, μ is chemical potential), as well as accounting for the relation between the internal energy U and Gibbs free energy $U = G + TS - pV$ both with the fact, that

$$\delta S = -\delta(\partial G/\partial T)_{x_1 x_2} = -(\partial \delta G/\partial T)_{x_1 x_2},$$

$$\delta\mu_1 = -(\partial \delta G/\partial x_1)_{Tx_2}, \quad \delta\mu_2 = -(\partial \delta G/\partial x_2)_{Tx_1}.$$

Let us expand the Gibbs energy in series for small δT and δx, and then take into consideration only the first and the second degree approximation [18].

The determinant of stability matrix for FeB monoboride with accounting for (1) takes the form:

$$D = (\partial S/\partial T)_{x_1 x_2} \{(\partial\mu_2/\partial x_2)_{Tx_1}(\partial\mu_1/\partial x_1)_{Tx_2} - (\partial\mu_2/\partial x_1)_{Tx_2}(\partial\mu_1/\partial x_2)_{Tx_1}\} -$$

$$- (\partial\mu_2/\partial T)_{x_1 x_2} \{(\partial\mu_2/\partial T)_{x_1 x_2} (\partial\mu_1/\partial x_1)_{Tx_2} - (\partial\mu_2/\partial x_1)_{Tx_2}(\partial\mu_1/\partial T)_{x_1 x_2}\} +$$

$$+ (\partial\mu_1/\partial T)_{x_1 x_2} \{(\partial\mu_2/\partial T)_{x_1 x_2}(\partial\mu_1/\partial x_2)_{Tx_1} -$$

$$- (\partial\mu_2/\partial x_2)_{Tx_1}(\partial\mu_1/\partial T)_{x_1 x_2}\}. \qquad (2)$$

In order for the phase to be in a state of stable equilibrium, it is necessary that D and all the leading subdeterminants of the matrix of stability are non-negative [18].

Since the determinant (3) of the matrix of stability is greater than zero and the principal minors of the matrix of stability are greater than zero, the iron monoboride within the temperature interval of 1273-1873 K is thermodynamically stable.

As we can see it from Fig. 3, the curve of the determinant of thermodynamic stability at 1423 K passes through an indistinct minimum. Stability drop with temperature decrease means that at the microscopic level the formation of a new phase begins. However, the structural changes in monoboride may not be detected: forming nuclei may differ from the initial phase only by the magnetic moment, which was observed by the authors of [2].
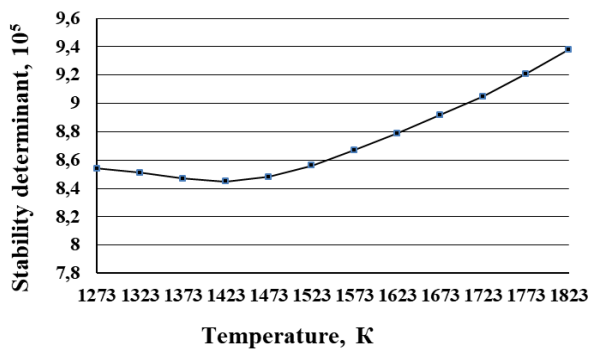
Fig. 3. Temperature dependence of the determinant of thermodynamic stability for FeB monoboride

IV. Conclusions

In the paper there were investigated the structural properties of the FeB monoboride in Fe-B alloy with weight boron content of 11.0-15.0 % (wt.), the rest is iron.

It is shown that after the casting in the alloy structure, along with FeB monoboride and Fe_2B boride, there is a Fe_5B_3 phase. After annealing of alloys of FeB system at a temperature of 1450 K and rapid cooling, the phase decomposition of Fe_5B_3 phase into two phases, monoboride and Fe_2B boride, occurs.

Accounting for the first degree approximation of high-temperature expansion of the thermodynamic potential of the FeB iron monoboride in a binary Fe-B alloy give a possibility to calculate the temperature dependence of main thermodynamic quantities and to study the thermodynamic stability of the phase. It is shown, that stability drop of the FeB monoboride at the temperature of 1423 K allow assuming that at the microlevel the formation of a new phase begins.

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