ISSN 2616-8685. JOURNAL OF PHYSICS AND ELECTRONICS Vol. 27(2), 2019

DOI 10.15421/331927

DETERMINATION OF THERMODYNAMIC STABILITY OF FeB MONOBORIDE

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In this paper we investigate the phase composition and phase transformations in the Fe-B system alloys with boron content in the range of 9.0–15.0 wt.%. We use microstructural, X-ray diffraction, differential thermal and durometric analyzes to determine the physical properties of the alloys. The experimental findings show that in the as-cast alloy structure there is Fe_5B_3 phase in small quantities along with FeB monoboride and Fe_2B boride. The Fe_5B_3 phase is formed as a result of the peritectic reaction $L+FeB \rightarrow Fe_5B_3$ at the temperature of 1680 K. The eutectic transformation $L \rightarrow Fe_5B_3+Fe_2B$ occurs in the boron concentration range of 8.8–10.5 wt.%. After annealing of the Fe-B alloys at the temperature of 1473 K and cooling with the rate of 10^2 K/s we observe the occurring of the Fe_5B_3 phase. To spot an opportunity of the secondary monoboride formation in the alloys under consideration, we calculate the thermodynamic characteristics of stability of the system.

Accounting for the contribution of the first degree approximation of high-temperature expansion of thermodynamic potential of FeB iron monoboride in a Fe-B binary alloy enables us to study its thermodynamic stability. It is shown that stability decrease of FeB at 1423 K allows suggesting that at this temperature the phase transformation occurs and this fact correlates to the differential thermal analysis results.

Keywords: Fe-B alloys; FeB iron monoboride; thermodynamic stability.

Received 01.11.2019; Received in revised form 11.12.2019; Accepted 23.12.2019

1. Introduction

Nowadays the equilibrium state diagram of Fe-B system is available in the literature. Study of Fe-B alloys with boron content within the range from 9.0 wt.% to 16.0 wt.% conditioned by the practical use in strengthening the surface of alloys is of particular importance. Many literature sources show the state diagram of the Fe-B system, in which the FeB monoboride primary crystals are formed from the liquid, and Fe_2B iron boride appears as a result of the peritectic reaction. But there is another opinion that the formation of the eutectics $FeB+Fe_2B$ from the liquid takes place. It is known, that in the Fe-B system alloys at boron content of more than 8.86 wt.% at temperature of 1882 K in the process of liquid and iron monoboride interaction the peritectic transformation $L+FeB \leftrightarrow Fe_2B$ occurs, in consequence of which the Fe_2B iron boride formation takes place [1]. The authors of [2, 3] suggested that in Fe-B alloys FeB iron monoboride appeared; the compound can exist in two modifications: high-temperature β-FeB and low-temperature α-FeB 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 the same magnetization and Curie temperatures T_c=580 K [2, 3]. Moreover, the authors of these studies pointed out that carbon, aluminum, and other impurities, which contained in furnace charge in the process of fabricating alloys, had a strong influence on the formation of FeB phase. Investigations by K.I. Portnoy [4] revealed the existence of the only modification of iron monoboride with B27 structure. It is known, that carbon has a low solubility in iron monoboride [5-7]. Additionally, doping of Fe-B system alloys with carbon to 0.2 wt.% practically does not change the alloy structure [8], and with increase of carbon content the formation of $Fe_3(CB)$ boron cementite takes place.

The authors of Ref. [9] showed that there are no FeB phase in the alloys with boron content up to 10.9 wt.% at high cooling rate, whereas in the alloys with boron content in the interval of 8.8–10.9 wt.% the Fe_2B phase occurs in the microstructure. In [9] it is stated that in the Fe-B alloy with boron content of 8.8 wt.% Fe_2B boride melts at the temperature of

1678 K, and at 1660 K and boron content of 10.9 wt.% there is the eutectics Fe_2B+FeB. The authors of [10] carried out the comparative analysis of the transition metals diagrams and boron. For example, comparing the diagram obtained by E. Kneeller and Y. Khan [9] to the Co-B diagram [11] and to the results of studying thermodynamic functions of the phases for the Fe-B alloys, one concludes that in the Fe-B system alloys there are the eutectics $L \rightarrow FeB+Fe_2B$ at the temperature of 1657 K.

There is also another point of view concerned with transformation in Fe-B alloys at 1400 K, namely 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 at boron content of 11.0–15.0 wt.%, but the mechanism of formation, area of the state diagram of Fe-B system, and thermodynamic functions of this phase are not determined [12]. Despite the fact that structural, 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 topical.

The purpose of this work is to determine the phase transformations in the Fe-B alloys with boron content within the range from 9.0 wt.% to 16.0 wt.%, and examine the mechanism of the Fe_5B_3 phase formation and the thermodynamic stability of this phase.

2. 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 charge 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 Tammann furnace with graphite heater in alundum crucibles 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 was measured by means of microhardness gauge PMT-3.

The phase composition of alloys was determined by means of X-ray microanalysis with 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 with diffractometer DRON-3 in monochromated Fe-K_α radiation.

3. Results and discussion

The microstructure of Fe-B alloys in the as-cast condition at boron content within the range of 9.0–15.0 wt.% contains rounded dendrites of FeB phase located in solid solution based on Fe_2B boride (Fig. 1). FeB iron monoboride has different coloring patterns in the process of microstructure study by optical microscope: white, shades of gray and black (Fig. 2, a).

The authors of [13] suggested that white FeB monoborides corresponded to high-temperature modification of β-FeB and black ones – to low-temperature α-FeB. The authors explained their findings by incompleteness of peritectic reaction resulted in the formation of Fe_2B boride when the liquid 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 phases: FeB iron monoboride, Fe_5B_3 boride, and Fe_2B boride. The results of the durometric analysis show that the microhardness of iron monoboride takes different values depending on the color. Thus, white in color monoboride has microhardness of 24.05 GPa, and black-colored one – 21.8 GPa. The microhardness of the solid solution based on Fe_2B iron boride is 20.01 GPa. In addition, the white-colored monoboride is less fragile than the black one.

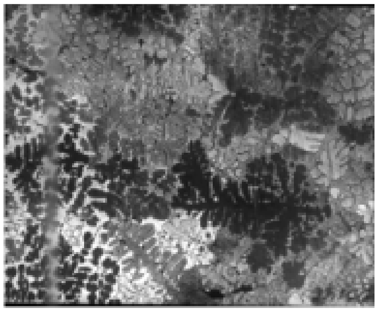
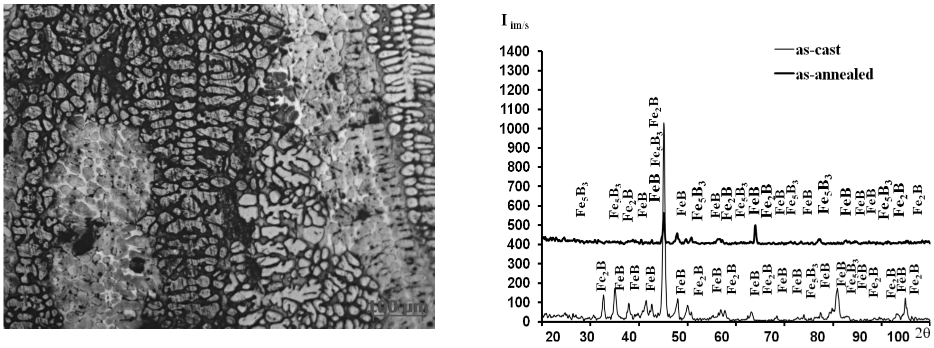


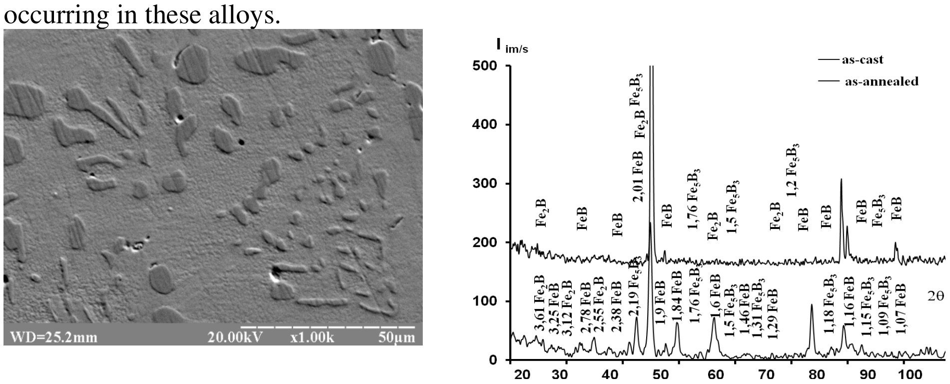
Fig. 1. Microstructure of Fe-B alloy with boron content of 13.0 wt.%.



a b

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

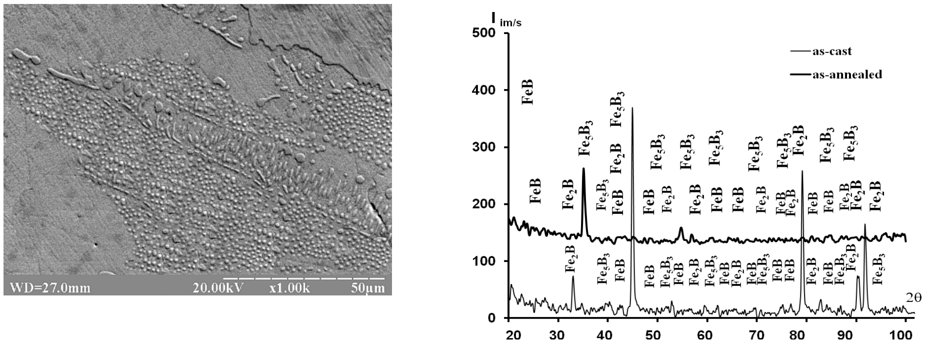
The presence of monoborides of different colors with distinct physical properties in the structure of alloys can be explained by the fact that in the process of grinding the fracture of monoboride dendrites takes place. This phenomenon is associated with the fact that in monoboride structure there are [001] and [100] planes, in which there are no boron atoms at all [14-15], but this explanation is not sufficient to substantiate the processes occurring in these alloys.



a b

Fig. 3. As-cast microstructure (a), and as-cast and as-annealed diffractograms (b) of Fe-B alloy with boron content of 10.0 wt.%.

In order to reveal the phase transitions in Fe-B alloy, the differential thermal analysis was performed. According to its results, in iron-based alloy with boron content of 10.0 wt.%, the phase transformation L→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↔Fe_5B_3 at the temperature of 1680 K. At the temperature of 1411 K an insignificant thermal effect was observed in the thermogram, that may indicate the phase transformation Fe_5B_3→FeB+Fe_2B occurring in solid state. Thus, the formation of Fe_5B_3 phase takes place at the temperature of 1680 K as a result of the peritectic reaction L+FeB→Fe_5B_3, and the decomposition Fe_5B_3→FeB+Fe_2B arises at 1420 K.



a b

Fig. 4. Fe-B alloy with boron content of 9.3 wt.%: microstructure (a) after annealing at 1473 K for 4 hours and after cooling with the rate of 10^2 K/s; as-cast and as-annealed diffractograms (b).

As it is shown in [16], the formation of 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 the phase transformation resulting in the formation of secondary monoboride FeB is possible. To verify the possibility of phase transformations at the temperature of 1420 K, the specimens of alloys with boron content of 9.0–16.0 wt.% were heated to the temperature of 1473 K for four hours and cooled with the rate of 10^2 K/s.

The microstructure of as-cast alloy with boron content of 13.0 wt.% was represented by monoboride and iron boride. The microstructure of alloy with boron content of 13.0 wt.% after annealing and further cooling represented by two phases, iron monoboride and Fe_2B boride, was, at first glance, in agreement with common point of view. After annealing at 1473 K and cooling at the rate of 10^2 K/s, the phase composition changes. The primary crystals of FeB monoboride observed in a matrix, which was represented by Fe_5B_3, and decomposition of this phase into two phases, monoboride and Fe_2B boride, were 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 FeB phase was 15.85 wt.% and in Fe_2B boride it was 7.65 wt.%.

Our investigation of microhardness of the constituents enabled us to obtain the following results: after annealing the microhardness of white-colored monoborides was 23.06 GPa, and that of dark-colored monoborides was 17.22 GPa, for phase decomposition it was 27.93 GPa. So, for alloys with boron content of 13.0 wt.% the microstructure after casting is represented by the phases: monoboride, as well as Fe_5B_3 and Fe_2B borides. After annealing at 1450 K, the phase decomposition of Fe_5B_3 occurs to form monoboride and Fe_2B boride.

Study of microstructure of the alloy with boron content of 10.0 wt.% shows that the phase composition is represented by FeB monoboride and Fe_5B_3 and Fe_2B borides (Fig. 3, a). Annealing of this alloy at 1473 K for four hours and further cooling with the rate of 10^2 K/s lead to volume fraction decrease of two-phase regions containing monoborides in Fe_2B boride matrix (Fig. 3, a). After annealing, the volume fraction of Fe_5B_3 boride increases due to $FeB + Fe_2B \rightarrow Fe_5B_3$ transformation in the solid state. In the as-annealed condition diffractogram we observe a considerably declining number of lines corresponding to FeB phase. The as-cast microstructure of alloy with boron content of 9.3 wt.% consists of FeB monoboride as well as of Fe_2B and Fe_5B_3 borides. The occurrence of FeB monoboride lines in the alloy diffractogram can be explained by Fe_5B_3 phase decomposition with forming FeB monoboride and Fe_2B boride.

Annealing of the alloy with boron content of 9.3 wt.% leads to the increase in the number of Fe_5B_3 lines in the alloy diffractogram (Fig. 4, b). In addition to this phase, Fe_2B boride lines and FeB monoboride lines are detected. In the as-annealed condition the lines of monoboride phase appear in the diffractogram in a very small quantity. Findings on phase composition of the Fe-B alloy at boron content of 9.0–15.0 wt.% differ from currently available conceptions mapped in the state diagram of the system [17-18].

The analysis of obtained results reveals that at boron content of 9.0–15.0 wt.% under crystallization the formation of Fe_5B_3 boride occurs at 1680 K, and at 1420 K its decomposition into two phase, Fe_2B boride and FeB monoboride, takes place. This is in agreement with the results of previous studies [12, 16]. Thus, it is shown experimentally that in the Fe-B system alloys in the boron concentration range of 8.8–10.5 wt.% the eutectic transformation $L \rightarrow Fe_5B_3 + Fe_2B$ occurs. The silicon impurities from amorphous boron are likely to have a very significant effect on the Fe_5B_3 formation. To determine the existence of decomposition, the thermodynamic stability of FeB should be examined.

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

To calculate the thermodynamic stability of monoboride, the expression of thermodynamic potential (Gibbs energy) of FeB phase is derived and approach proposed in [16] is used. The Gibbs energy value for pure components and energy of interaction between boron and iron atoms are taken from [19-20]. Then we can write

$$G_{\mathrm{m}}^{\mathrm{FeB}} = x_1 G_1^0 + x_2 G_2^0 + RT\left(x_1 \ln x_1 + x_2 \ln x_2\right) + x_1 x_2 L_{12} - \frac{L_{12}^2 x_1^2 x_2^2}{2ZTR}. \qquad (1)$$

Here G_i^0 is Gibbs energies of pure components (J/mol), R is the universal gas constant (R=8.31 J/(mol·K)), T is temperature (K), L_{12} is an interaction energy of components (J/mol), Z is a coordination number, Z=4 for monoboride [1]. The interaction energy L_{12} of elements depends on temperature as $L_{12} = a + bT + cT \ln T$. Using data for the pure components G_1^0, G_2^0 [19-20] and the energy of interaction between components in the phase from [21-23], we obtain the temperature dependence of Gibbs energy of the melt.

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

$$\delta G = \sum_{n=1}^{\infty} \frac{1}{n!}\left[\delta T \frac{\partial}{\partial T} + \delta x_1 \frac{\partial}{\partial x_1} + \delta x_2 \frac{\partial}{\partial x_2}\right]^n G.$$

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 both reversible and irreversible processes in the system (so that the system is not out of equilibrium). Therefore, these deviations must be with the property that

$$\delta U - T\delta S + p\delta V - \mu_1 \delta x_1 - \mu_2 \delta x_2 > 0$$

(here S is entropy, p is pressure, V is volume, μ is chemical potential).

Let us expand the Gibbs energy in series for small δT and δx_i, taking into account the relation between the internal energy U and Gibbs free energy $U = G + TS - pV$, and then take into consideration only the first and the second degree approximation [24]. Then the condition of thermodynamic stability can be written in the form:

$$\left(\frac{\partial S}{\partial T}\right)_{x_1x_2}\delta T^2+\left(\frac{\partial \mu_1}{\partial x_1}\right)_{Tx_2}\delta x_1^2+\left(\frac{\partial \mu_2}{\partial x_2}\right)_{Tx_1}\delta x_2^2+2\left(\frac{\partial \mu_1}{\partial T}\right)_{x_1x_2}\delta x_1\delta T+$$
$$+2\left(\frac{\partial \mu_2}{\partial T}\right)_{x_1x_2}\delta x_2\delta T+2\left(\frac{\partial \mu_2}{\partial x_1}\right)_{Tx_2}\delta x_1\delta x_2\geq 0.$$

Then we obtain the determinant of stability for FeB monoboride in the form:

$$D=\begin{vmatrix}\left(\frac{\partial S}{\partial T}\right)_{x_1x_2} & \left(\frac{\partial \mu_1}{\partial T}\right)_{x_1x_2} & \left(\frac{\partial \mu_2}{\partial T}\right)_{x_1x_2}\\ \left(\frac{\partial \mu_1}{\partial T}\right)_{x_1x_2} & \left(\frac{\partial \mu_1}{\partial x_1}\right)_{Tx_2} & \left(\frac{\partial \mu_2}{\partial x_1}\right)_{Tx_2}\\ \left(\frac{\partial \mu_2}{\partial T}\right)_{x_1x_2} & \left(\frac{\partial \mu_1}{\partial x_2}\right)_{Tx_1} & \left(\frac{\partial \mu_2}{\partial x_2}\right)_{Tx_1}\end{vmatrix} \qquad (2)$$

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 [20]. Since the determinant (2) 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 from Fig. 5, the curve of thermodynamic stability at 1423 K passes through an indistinct minimum. Stability drop with the temperature decrease means that at the microscopic level the formation of a new phase begins. However, the structural changes in monoboride cannot be detected: forming nuclei may differ from the initial phase only by the magnetic moment, which was observed by the authors of [2]. The obtained results enable us to propose a new approach to constructing the state diagram for the Fe-B system and the phase transformations occurring in these alloys.

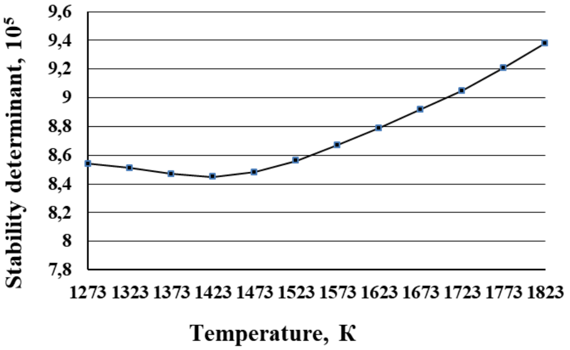


Fig. 5. Temperature dependence of the determinant of thermodynamic stability for FeB monoboride.

According to the findings, in the Fe-B system at 1680 K and boron concentration of 10.5 wt.% the formation of Fe_5B_3 occurs as a result of peritectic reaction $L+FeB \rightarrow Fe_5B_3$. In the boron concentration range of 8.8–10.5 wt.% the eutectic transformation $L \rightarrow Fe_5B_3+Fe_2B$ takes place. This fact is proved by the experimental results given in this paper and is in a good agreement with data of Refs. [9-10].

Thus, the phase transformation represented in many state diagrams of the Fe-B system alloys at the temperature of 1420 K and associated with the polymorphic transformation of the high-temperature β-FeB monoboride into the low-temperature α-FeB phase can be explained by the phase decomposition of Fe_5B_3 with the formation of FeB monoboride and borides of Fe_2B: $Fe_2B – Fe_5B_3 \rightarrow FeB+Fe_2B$.

4. Conclusions

In this work it is shown that after the casting, in the alloy structure there is Fe_5B_3 phase, as well as FeB monoboride and Fe_2B boride. It is shown experimentally that at 1680 K the formation of Fe_5B_3 occurs as a result of peritectic reaction $L+FeB \rightarrow Fe_5B_3$. At the boron content of 8.8–10.5 wt.% in the Fe-B alloys the eutectic transformation $L \rightarrow Fe_5B_3+Fe_2B$ is likely to take place. At 1420 K there is the phase decomposition of Fe_5B_3 boride with the formation of FeB monoboride and Fe_2B boride: $Fe_5B_3 \rightarrow FeB+Fe_2B$.

Accounting for the first degree approximation of high-temperature expansion of thermodynamic potential for FeB iron monoboride in a binary Fe-B alloy enables 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 FeB monoboride at 1423 K allows assuming that at the microlevel the formation of a new phase begins.

Therefore, the obtained results allows to suggest a new approach to the constructing the state diagrams and the phase transformations occurring in the Fe-B alloys.

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