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Thermodynamic Functions of Fe_3B Borides

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In this work we study the structural properties of hypoeutectic and hypereutectic Fe-B alloys, depending on the temperature of heating above the liquidus line and the cooling rate. Experiments were carried out for the Fe-B system alloys with boron content of 2.0 - 4.5 % (wt.), the rest is iron. To determine physical properties of the alloys microstructural and X-ray diffraction analysis were used. It is shown that overheating of the molten alloy to 150 K above the liquidus line and aftercooling leads to complete suppression of the formation of primary iron crystals in the hypoeutectic alloys and partially to suppression of Fe_2B formation in the hypereutectic alloys of the Fe-B system.

For the first time it is shown that heating of Fe-B hypoeutectic alloys to 150 K above the liquidus line and cooling with a rate of 10^3 K/s lead to formation of Fe_3B boride in as-cast state, which was present in the eutectic colony.

Taking into account the contribution of the first degree approximation of the high-temperature expansion of the thermodynamic potential for Fe_3B iron boride in the binary Fe-B alloy, we obtain for the first time temperature dependences for the thermodynamic functions such as Gibbs energy, chemical potentials of boron and iron in Fe_3B boride, entropy, enthalpy and heat capacity C_p. In addition, the method suggested enables to determine the temperature of the formation of Fe_3B iron boride, which is in agreement with the data of other authors.

Keywords: melting, alloy overheating above the liquidus line, the Fe-B system alloys, thermodynamic functions, Fe_3B iron boride.

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Introduction

Boron-bearing alloys containing boron find practical application because of a set of unique properties such as infusibility, high hardness, chemical resistance in various corrosive environments, and others [1-2]. Thus, borides and boron-bearing alloys are used in the producing of new composite materials, where borides are used as hardening phases [1-2].

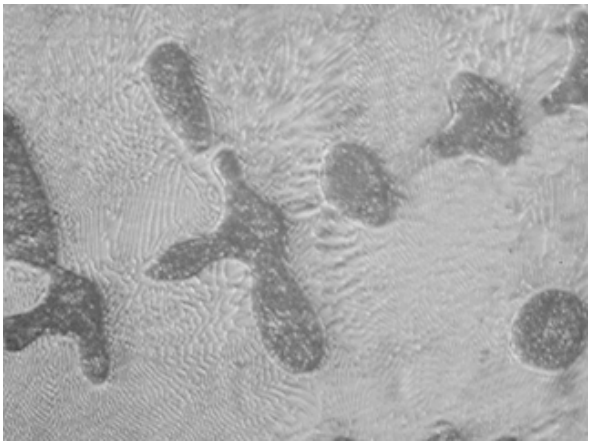
It is known that in alloys of the Fe-B system with boron content of 3.8 % (wt.) formation of the eutectics $L \to g + Fe_2B$ occurs. The structure of hypoeutectic alloys is represented by two constituents, primary α-Fe dendrites and γ-Fe + Fe_2B eutectics, and structure of hypereutectic alloys consists of Fe_2B and eutectics [1, 3-4]. The formation of Fe_3B boride in the binary Fe-B alloys was observed as a result of the annealing of amorphous films [5-7], abrasive wear of films, etc. [8]. It was found that Fe_3B boride exists in the temperature range 1423 K to 1523 K in two modifications: Fe_3B(o) orthorhombic high-temperature and Fe_3B(t) tetragonal low-temperature [9-10].

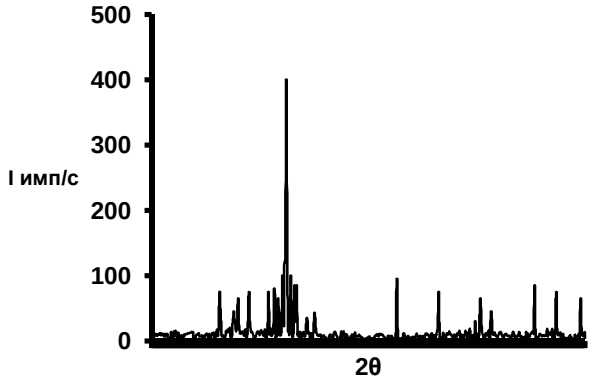
Investigation of the phase composition and thermodynamic functions of boron-bearing alloys is of theoretical and practical importance, because borides are formed in a wide concentration range, as well as a result of the process of saturation of the alloy surface with boron, and affect the physical properties of the boronated layer. In addition, it would enable to develop the metal alloys containing borides, composite materials and coatings with predictable physical properties and phase composition.

The objective of this paper is to investigate the structural state of the hypoeutectic and hypereutectic alloys in the Fe-B system in terms of the heating temperature and cooling rate, along with thermodynamic functions of the Fe_3B boride, their temperature dependences with accounting for the first degree approximation of the high-temperature expansion for the thermodynamic potential of binary alloys, describing the fluctuation processes.

I. Materials and research techniques

The research was carried out for the specimens with





a **b**

Fig. 1. Microstructure (a) and diffractogram (b) of the alloy with boron content of 2.7 % (wt.) after heating up to the temperature of 1753 K and cooling with rate of 10^4 K/s

boron content of 2.0 - 4.5 wt. % (the rest is iron), for which furnace charge consisting of carbonyl iron (with iron content of 99.99 % (wt.)), amorphous boron (with boron content of 97.5 % (wt.)) was used. To prevent the segregation, alloys were made from premixed intimately and pressed powders of charge materials. The smelting of specimens was performed in a Taman's furnace with a graphite heater in alundum crucibles in argon atmosphere with overheating of 50-200 K above the liquidus line. Then the melt was cast into a copper wedge-shaped mold. The cooling rate was 10^2 to 10^4 K/s.

To determine the chemical composition of alloy chemical and spectral analysis were used [11].

The phase composition of alloys after cooling was determined by X-ray microanalysis by means of JSM-6490 microscope, as well as by means of optical microscope "Neophot-21". The X-ray diffraction analysis was performed with DRON-3 diffractometer in the monochromated Fe-K_α radiation.

II. Results and Discussion

The microstructure of hypoeutectic Fe-B alloy with boron content of 2.7 % (wt.) after crystallization from a temperature up to 50 K above the liquidus temperature (1480 K) with cooling rate of 10^2 K/s consists of two structural components: the primary dendrites of α-Fe phase and the α-Fe + Fe_2B eutectics with a lamellar structure. With increase in the cooling rate of alloy up to 10^4 K/s, the size of the α-Fe dendrites and their volume fraction are considerably reduced, whereas degree of differentiation of the eutectic colonies grows, indicating displacement of the eutectic point to the left on the Fe-B system state diagram.

The increase in overheating of the melt up to 100 K above the liquidus line and aftercooling results in the formation of a more dispersed eutectics and further suppression of the forming of primary iron crystals.

After heating of the Fe-B alloy with boron content of 2.7 % (wt.) to 150 K (up to the temperature of 1630 K) above the liquidus line and aftercooling with rate of 10^3 K/s, in addition to α-Fe phase and α-Fe+Fe_2B eutectics, another eutectics is observed, with a differing structure, namely, disperse rod morphology, and differing coloring. As a result of X-ray diffraction analysis, in this part of the wedge the Fe_3B boride presence is detected (Fig. 1).

The availability of the Fe3B phase area on the phase diagram of Fe-B alloys is given in the Khan's article [9-10], and the state diagram of the Fe-B system alloys with Fe_3B presence can be found in several directories [12-13]; in other sources [2-4] there is no such information. This is because of the fact that Fe_3B phase is revealed only after the annealing of amorphous films, after high-temperature synthesis or mechanical processing [5-6], but not in the as-cast condition.

The analysis of the obtained results enables to assume that overheating of alloys to a temperature over than 150 K above the liquidus line and aftercooling at rate of 104 K/s makes it possible to detect for the first time the Fe_3B boride presented in the eutectic colony in the as-cast condition.

Similar results are obtained in the study of the effect of heating temperature of the hypereutectic alloy above the liquidus line and aftercooling with different rates on formation of the Fe_3B phase. For hypereutectic alloys with boron content of 3.9 - 4.5 % (wt.) which were heated to a temperature of 50 K above the liquidus line, we observe a decrease in the size and increase in the volume fraction of primary crystals of the Fe_2B phase. The eutectics inherits the shape of primary Fe_2B crystals and is lamellar, cellular and rod in morphology.

As a result of cooling with rates of 102 and 103 K/s, we observe significant decrease in the volume fraction of primary crystals of Fe_2B compared with specimens overheated to a lower temperature, and at overheating to 150 K we observe suppression of the formation process of the Fe_2B phase crystals. The eutectics has more homogeneous structure, such as rod and partially lamellar ones.

One of the key factors of the phase formation and phase transformations is thermodynamic functions of the phase. Value calculation of thermodynamic functions of

Fe3B boride from experimental data runs into certain difficulties. In this paper we consider the contributions to Gibbs free energy, which are responsible for fluctuation processes, and this enables to determine theoretically the thermodynamic functions of Fe3B boride.

2.1. Gibbs energy of Fe3B iron boride.

The Gibbs energy of the phase is known to be a function of independent variables $G = G(p,T,y)$, where p - is pressure, T -is temperature, y - is weight content of elements. For molar fractions of components in a compound or in alloy the following condition is fulfilled: $\sum_{i=1}^{2} y_i = 1$.

In the potentials of the most existing models the contribution of the first degree approximation of the high-temperature expansion of the thermodynamic potential for binary alloy is not taking into account.

As it is known from the theory of binary alloys, the partition function of such a system cannot be evaluated exactly, but according to the Kirkwood method it can be written as infinite series in powers of 1/T. In accordance with the Kirkwood method [14-15], the first term of the expansion take the form:

$$\Delta E = -\frac{L_{Fe;B}^2 y_{Fe}^2 y_B^2}{2ZRT},$$

where Z is coordination number, which is equal to Z = 9 for Fe_3B boride [16].

So, the Gibbs energy with accounting for the first degree approximation for the Fe3B iron boride is defined as:

$$G_m^{Fe_3B} = y_{Fe}{}^0G_{Fe} + y_B{}^0G_B + RT\left(3y_{Fe}\ln y_{Fe} + y_B \ln y_B\right) + y_{Fe}y_B L_{Fe:B} - \frac{L_{Fe;B}^2 y_{Fe}^2 y_B^2}{2ZRT} \quad (1)$$

As a result of the calculation, the following relation is obtained:

$$G_m^{Fe_3B} = -35512 + 5.25T - 10^5 T^{-1}.$$

According to the results given in [17], the heat of the phase formation is 22796.4 J/mol, and in present work – 27592.4 J/mol.

Thus, the obtained temperature dependence of the Gibbs energy for Fe_3B phase enables to determine its value in the high-temperature region, as well as the Gibbs energy of formation of this phase from the liquid.

2.2. Chemical potential of iron and boron in Fe_3B boride.

The chemical potential of boron in the boride is calculated as:

$$m_B = \left(\frac{\partial G_m^{Fe_2B}}{\partial y_B}\right)_T = {}^0G_B + RT(\ln y_B + 1) + y_{Fe}L_{Fe:B} - \frac{L_{Fe:B}^2}{ZRT} y_{Fe}^2 y_B$$

Its temperature dependence is:

$$m_B = -27834 + 4.1T + 2\cdot 10^4 T^{-1}.$$

The chemical potential of iron in the Fe3B boride is derived to be equal

$$m_{Fe} = -21563 + 2{,}4T + 6\cdot 10^6 T^{-1}.$$

As it is known from Ref. [18], to determine the temperature of formation of the Fe3B phase, one should find a solution of the equation: $\frac{\partial m}{\partial y} = 0$.

The chemical potentials of boron and iron in boride take minimum values, which correspond to the most stable state of this phase:

$$\frac{\partial m_B}{\partial y_B} = \left(\frac{\partial^2 G_m^{Fe_2B}}{\partial y_B^2}\right)_T = \frac{RT}{y_B} - \frac{L^2 y_{Fe}^2}{ZRT} = 0 \ ,$$

$$\left(\frac{\partial^2 G_m^{Fe_2B}}{\partial y_{Fe}^2}\right)_T = \frac{3RT}{y_{Fe}} - \frac{L^2 y_{Fe}^2}{ZRT} = 0 \quad (2)$$

The solution of equations (2) makes it possible to find the temperature of formation of Fe_3B boride $T = 1465{,}6K$, which agrees with the results given in papers [9, 10, 19, 20].

2.3. Entropy, enthalpy and heat capacity Cp of Fe3B boride.

One of the important thermodynamic characteristics of the phase is entropy. The entropy of the Fe_3B phase is determined as

$$S = -\left(\frac{\partial G}{\partial T}\right)_p = -R\left(3y_{Fe}\ln y_{Fe} + y_B \ln y_B\right) - \frac{L_{Fe:B}^2}{2ZRT^2} y_{Fe}^2 y_B^2$$

According to the calculation results, entropy of boride at the formation temperature is equal to 2.13 $J\cdot mol^{-1}\cdot K^{-1}$, which coincides with the results of Refs. [20-21].

Accounting in the Gibbs energy for the contribution of the first degree approximation of the high-temperature expansion of thermodynamic potential enables to determine the enthalpy of boride. To calculate the enthalpy of Fe3B phase, we use the next relationship [18]: $\Delta H = \Delta G + T\Delta S$.

The enthalpy's dependence on temperature for this phase has the form:

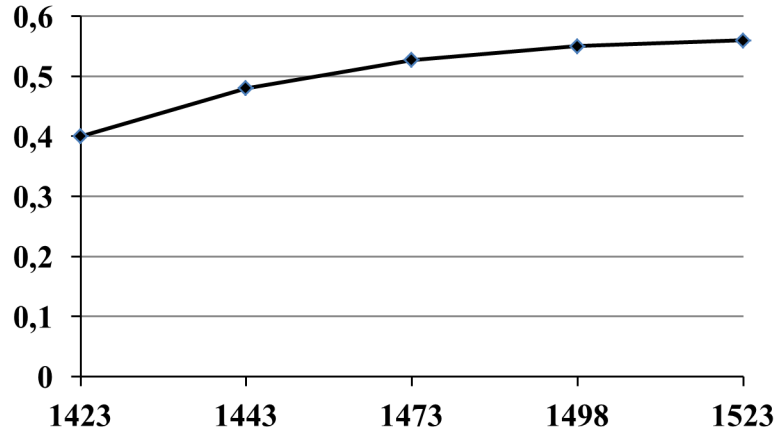


Fig. 2. Temperature dependence of heat capacity C_p of Fe_3B boride.

$$H = -32527 + 0{,}5T + 10^5 T^{-1}.$$

The enthalpy at the temperature of boride formation is -27673.6 J/mol, and -22796.4 J/mol, according to the results of [22], and -1800 J g-1atom-1 by [23], correspondingly.

Consequently, the results obtained in this paper for the values of the Fe3B phase enthalpy are consistent with the results of other authors.

For the Fe_3B phase the heat capacity is determined as:

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = \frac{L^2_{Fe:B}}{RZT^2} \cdot y^2_{Fe} y^2_B .$$

Analysis of the obtained results enables to conclude that accounting for the contribution of the first degree approximation of the high-temperature expansion of the thermodynamic potential for Fe-B binary alloy makes it possible to calculate such thermodynamic quantities of Fe_3B iron boride as entropy, enthalpy, heat capacity, and to determine their temperature dependence. Besides, it enables to describe boride the most completely from thermodynamic point of view, taking into account fluctuation processes.

Conclusions

It is shown that overheating of the melt over than 150 K above the liquidus line and rapid aftercooling leads to complete suppression of the formation of primary iron crystals in the hypoeutectic alloys and partially to suppression of Fe_2B boride in the hypereutectic alloys of the Fe-B system.

It is established experimentally that at overheating of the Fe-B hypoeutectic alloys to 150 K above the liquidus line and at cooling rate of 10^3 K/s, the formation of the Fe_3B boride presented in the eutectic colony in the as-cast condition occurs.

It should be noted that thermodynamic functions of the phases make it possible to predict the physical and chemical properties of alloys under alternate external conditions such as temperature, pressure, etc. Known methods for calculations of thermodynamic phase functions can be used only under equilibrium conditions and do not take into account the fluctuation processes.

Therefore, taking into account the contribution of the first degree approximation of the high-temperature expansion of thermodynamic potential for the Fe_3B iron boride in the binary Fe-B alloy, we obtaine for the first time temperature dependences of such thermodynamic functions as Gibbs energy, chemical potentials of boron and iron in Fe_3B boride, entropy, enthalpy and heat capacity C_p. In addition, proposed method makes it possible to determine temperature of the formation of the Fe_3B iron boride, which coincides with the data of other authors.

The advantages of the applied method are that it can be used to calculate the thermodynamic phase functions of any systems, in which fluctuation processes should be taken into account.

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Термодинамічні функції бориду Fe_3B

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В роботі було досліджено структурні властивості доевтектичних та заевтектичних сплавів системи Fe-B в залежності від температури нагріву вище лінії ліквідусу та швидкості охолодження. Дослідження проводили на сплавах системи Fe-B з вмістом бору 2,0 - 4,5 % (мас.), інше – залізо. Для визначення фізичних властивостей сплавів використовували мікроструктурний та рентгеноструктурний аналізи. В роботі показано, що перегрів розплаву від 150 К вище лінії ліквідусу та наступне швидке охолодження призводить до повного пригнічення процесу утворення первинних кристалів заліза в доевтектичних сплавах та частково - бориду Fe_2B в заевтектичних сплавах системи Fe-B.

Вперше показано, що при нагріві доевтектичних сплавів системи Fe-B вище лінії ліквідусу на 150 К та при швидкості охолодження 10^3 К/с відбувається утворення бориду Fe_3B в литому стані, який був присутній в евтектичній колонії.

Вперше з урахуванням внеску першого ступеня наближення високотемпературного розвинення термодинамічного потенціалу бориду заліза Fe_3B у бінарному сплаві Fe-B були отримані залежності від температури таких термодинамічних функцій, як енергія Гіббса, хімічні потенціали бору та заліза в бориді Fe_3B, ентропія, ентальпія і теплоємність Ср. Крім того, запропонований метод дав можливість визначити температуру утворення бориду заліза Fe_3B, яка корелює з даними інших авторів.

Ключові слова: розплав, перегрів сплаву вище лінії ліквідусу, сплави системи Fe-B, термодинамічні функції, борид заліза Fe_3B.