

THE PECULIARITIES OF FORMATION AND THERMODYNAMIC FUNCTIONS OF τ -PHASE

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It is shown that for alloys with boron content of 0.1–6.5% (wt.) and carbon content of 0.3–4.0% (wt.) without pretreatment no formation of cubic boron carbide takes place under crystallization. The cubic boron carbide can be obtained by pre-annealing at a temperature of 1173 K for an hour and further heating to a temperature of 30 K above the liquidus and cooling of alloys with boron content of 2.5–4.0 % (wt.) and carbon content of 0.8–3.0 % (wt.). Formation of crystals of cubic boron carbide is possible as a constituent of multiphase inclusions for alloys with boron content of 0.1–0.3 % (wt.) and carbon content up to 0.4–0.5 % (wt). It should be noted that for alloys with boron content of 4.2–6.0 % (wt.) and carbon content of more than 3.0 % (wt.) the pretreatment does not result in formation of cubic boron carbide. The increase in boron content in the alloy to 0.3–0.5 % (wt.) and carbon content to 0.5–0.7 % (wt.) leads to formation of the eutectic α -Fe+Fe₂₃(CB)₆, which is arranged on the boundaries of pearlite grains.

The thermodynamic functions of Fe₂₃(CB)₆ cubic boron carbide are derived for the first time using the Hillert and Staffansson model and accounting for the first degree approximation of high-temperature expansion of the thermodynamic potential for binary alloys. We obtain temperature dependences of such thermodynamic functions for Fe₂₃(CB)₆ phase as Gibbs energy, entropy, enthalpy and heat capacity C_p , as well as calculate their values at the formation temperature of the phase. The approach used in this paper enables to give the most complete from the thermodynamic point of view description of cubic boron carbide formed from a liquid.

Keywords: Fe₂₃(CB)₆ cubic boron carbide, Gibbs energy, entropy, enthalpy, heat capacity, fluctuation process.

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1. Introduction

The study of the physical properties and thermodynamic functions of boron-bearing alloys is of theoretical and practical significance, because borides and boron carbide are formed not only in boron-bearing metal-based alloys, but also in a process of saturation of the surface of alloy with boron and have an effect on the physical properties of borated layer [1-2]. As well, it would enable to develop metal alloys containing borides and boron carbide, composite materials and coatings with predictable physical properties and phase composition. It is known that τ -phase (Fe₂₃(CB)₆) is isomorphic to Cr₂₃C₆ carbide [3] and can be formed at high cooling rates [4-5] or from the liquid state after prior thermal cycling in solid-liquid state for, at least, 5-6 cycles in the temperature range of 1123–1613 K [6-8]. Besides, in the structure of iron-based alloys with boron content of no more than 0.1 % (wt.) the cubic boron carbide is a constituent of multiphase inclusions, which are arranged on the boundaries of austenite grains [9]. In literature there is information on position of Fe₂₃(CB)₆ cubic boron carbide on the state diagram of the Fe-B-C system [10] and there are even presented the structural diagrams where the regions of Fe₂₃(CB)₆ phase and eutectics containing Fe₂₃(CB)₆ phase are outlined [5, 11]. Besides, the Gibbs energy for an equilibrium state is calculated [11-12], but there is no estimated data on the thermodynamic properties of Fe₂₃(CB)₆ with accounting for the fluctuation processes.

The purpose of this study is to determine the mechanism of formation, physical properties and thermodynamic functions of Fe₂₃(CB)₆ iron cubic boron carbide.

2. Materials and methods

Investigation was carried out for the specimens with carbon content of 0.3–4.0 % (wt.) and boron content of 0.1–6.5 % (wt.), the rest is iron. For obtaining the Fe-B-C system alloys we used the furnace charge of such composition: carbonyl iron (with iron content of 99.95 % (wt.)), amorphous boron (with boron content of 97.50 % (wt.)), electrode graphite (with carbon content of 99.96 % (wt.)). To prevent the segregation, alloys were made from pre-mixed thoroughly and pressed powder of charge materials. Smelting of specimens was performed in a Taman furnace with graphite heater in alundum crucibles in argon atmosphere. To determine the chemical composition of alloy, chemical and spectral analysis was used [13]. Microhardness was measured by PMT-3 device (according to GOST 9460-76). The phase composition of alloys was determined by X-ray microanalysis by means of JSM-6490 microscope, as well as by means of optical microscope “Neophot-21”. Local X-ray analysis was carried out using internal standards. The main results were obtained with an electron microscope JSM-6490 with ASID-4D scanning head and “Link Systems 860” software energy-dispersive X-ray microanalyser. The X-ray diffraction analysis was performed with DRON-3 diffractometer in monochromated Fe- K_{α} radiation. Sizes of coherent scattering blocks, density of dislocations and microstresses in cubic boron carbide were estimated by means of approximation method [14].

3. Results and discussion

The microstructure of alloys with boron content of 2.0–4.5 % (wt.) and carbon content of 1.0–4.0 % (wt.) consists of primary crystals of $Fe_3(CB)$ boron cementite and lamellar eutectics γ -Fe+ $Fe_3(CB)$ (Fig. 1, a).

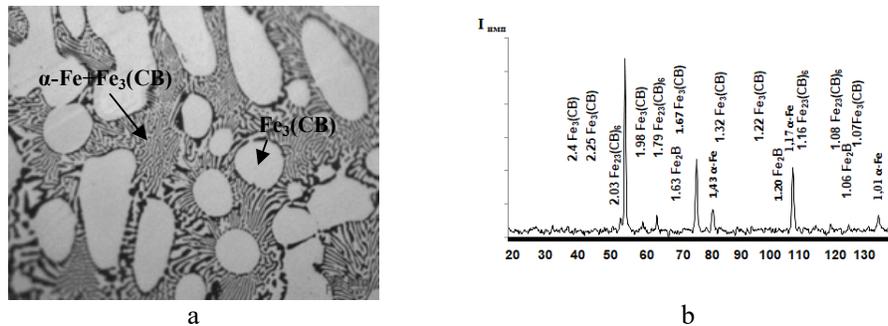


Fig. 1. Microstructure (a, $\times 500$) and diffractogram (b) of Fe-B-C alloy with boron content of 2.95 % (wt.), carbon content of 2.3 % (wt.).

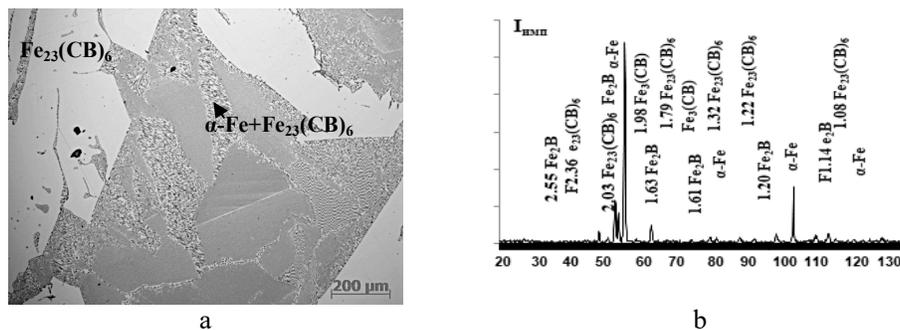


Fig. 2. Microstructure (a, $\times 500$) and diffractogram (b) of Fe-B-C alloy with boron content of 2.95 % (wt.), carbon content of 2.3 % (wt.) after pre-annealing.

The results of X-ray diffraction analysis of alloy show attendance of $\text{Fe}_{23}(\text{CB})_6$ cubic boron carbide line on diffractogram, but this phase is not observed in the microstructure (Fig. 1). Fig. 2, a shows the microstructure of alloy pre-annealed after melting at 1173 K for an hour and then heated to a temperature of 30 K above the liquidus and cooled to a room temperature with a rate of 10–100 K/s. The choice of pre-annealing temperature coincides with the temperature given in [7, 12] as the phase formation temperature of $\text{Fe}_{23}(\text{CB})_6$. As a result of the pretreatment, in the structure of the alloy Fe_2B primary borides, $\text{Fe}_{23}(\text{CB})_6$ phase and dispersed eutectics $\alpha\text{-Fe}+\text{Fe}_{23}(\text{CB})_6$ with a rod morphology were revealed (Fig. 2). The cubic boron carbide has a skeletal structure, and separate crystals of cubic boron carbide reach 150 microns. According to analysis findings, it is found that formation of $\text{Fe}_{23}(\text{CB})_6$ phase occurs at the temperature of 1400–1410 K.

According to results of X-ray analysis the lattice parameter of cubic boron carbide is 10.6387 Å; 10.64 Å as follows from [6]; 10.61 Å as results of [15], 10.599 Å from [16].

The carbon content in alloy affects the physical characteristics (Table 1).

Table 1

Crystallite size, microstress degree, and density of dislocations in $\text{Fe}_{23}(\text{CB})_6$ phase

Content in alloy, % (wt.)		Crystallite size L, Å	Microstress degree	Density of dislocations, $\rho \times 10^{10}, \text{cm}^{-2}$	Microhardness $H\mu$, 10^9 Pa
Boron	Carbon				
3.2	1.4	565	$5.54 \cdot 10^{-3}$	9.654	$6.48 \pm 0,012$
3.2	2.4	631	$4.74 \cdot 10^{-3}$	9.972	$7.3 \pm 0,014$
3.3	2.8	702	$6.53 \cdot 10^{-3}$	10.456	$7.65 \pm 0,011$
3.5	3.0	752	$7.91 \cdot 10^{-3}$	11.24	$7.51 \pm 0,013$

Analysis of the obtained results enables to assume that substitution of boron atoms by carbon atoms in the crystal lattice of $\text{Fe}_{23}(\text{CB})_6$ cubic boron carbide is possible and affects the physical characteristics of the phase.

As-cast investigation of the microstructure of alloy with boron content of 4.0 % (wt.), carbon content of 0.9 % (wt.) showed that the primary phase is Fe_2B boride. Besides, two eutectics were present in the specimens: $\gamma\text{-Fe}+\text{Fe}_2\text{B}$ and $\gamma\text{-Fe}+\text{Fe}_3(\text{CB})$. The boride eutectics $\gamma\text{-Fe}+\text{Fe}_2\text{B}$ succeeded to the shape of Fe_2B boride growth and boron cementite eutectics $\gamma\text{-Fe}+\text{Fe}_3(\text{CB})$ was presented as curved plates. According to the results of differential thermal analysis, formation of Fe_2B boride primary crystals occurs at the temperature of 1452 K. Formation of boride eutectics takes place at 1425 K, and formation of the eutectics $\gamma\text{-Fe}+\text{Fe}_3(\text{CB})$ starts at the temperature of 1420 K. At the temperature of 993 K the polymorphic transformation $\gamma\text{-Fe} \leftrightarrow \alpha\text{-Fe}$ occurs (Fig. 3). The primary crystals in alloy with boron content of 4.0 % (wt.), carbon content of 1.2 % (wt.) after pretreatment are Fe_2B phase crystals, on the surface of which boride eutectics $\gamma\text{-Fe}+\text{Fe}_2\text{B}$ surrounded by $\text{Fe}_{23}(\text{CB})_6+\gamma\text{-Fe}$ eutectics is formed.

For alloys with boron content of 2.8–3.0 % (wt.) and 2.0–2.2 % (wt.) without pretreatment the formation of cubic boron carbide occurs during crystallization.

Note that for the specimens with boron content of 4.2–6.0 % (wt.) and carbon content of more than 3.0 % (wt.) the annealing at 1173 K and further heating and cooling do not lead to formation of cubic boron carbide.

The obtained results indicate that formation of cubic boron carbide is possible in the concentration range at boron content of 2.5–4.0 % and carbon content of 0.8–3.0 % (wt.).

At boron content of 0.1–0.3 % (wt.) and carbon content up to 0.4–0.5 % formation of cubic boron carbide as constituent of multiphase inclusions is observed on the boundaries of pearlite grains [9].

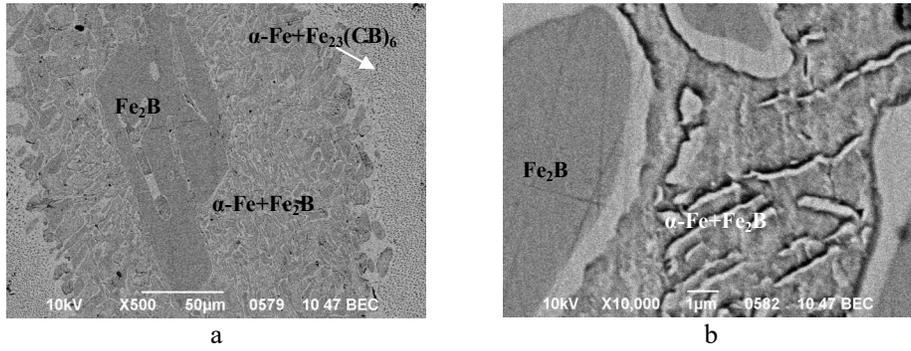


Fig. 3. Secondary electron microstructure of the Fe-B-C alloy with boron content of 4.0 %, carbon content of 0.9 % (wt.) after pre-annealing.

For alloys with boron content of 0.3–0.5 % (wt.) and carbon content of 0.5–0.7 % (wt.), no formation of separate crystals of cubic boron carbide occurs. The microstructure of alloy consists of pearlite and eutectics $\alpha\text{-Fe}+\text{Fe}_{23}(\text{CB})_6$ (Fig. 4). The eutectics $\alpha\text{-Fe}+\text{Fe}_{23}(\text{CB})_6$ is arranged on the boundaries of pearlite grains.

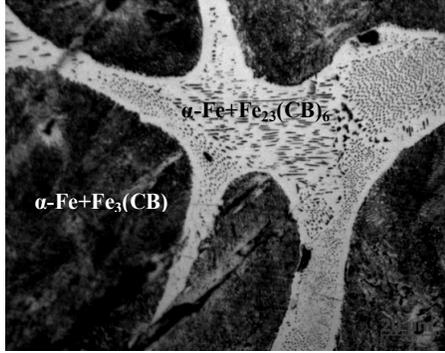


Fig. 4. Microstructure (a, $\times 500$) and diffractogram (b) of Fe-B-C alloy with boron content of 0.3 %, carbon content of 0.5 % (wt.)

One of the key factors affecting the phase formation and phase transformations are thermodynamic functions of the phase. Obtaining of the values of thermodynamic functions for $\text{Fe}_{23}(\text{CB})_6$ cubic boron carbide from the experimental data run into certain difficulties. So, accounting in this paper for the fluctuation processes made it possible to determine theoretically the thermodynamic functions of $\text{Fe}_{23}(\text{CB})_6$ cubic boron carbide.

Let us denote mole fraction of a component in alloy as x_i . In Fe-B-C system the number of components equals $i = 3$. For mole fraction of the components in a compound, the condition is fulfilled:

$$\sum_{i=1}^3 x_i = 1.$$

The Gibbs energy of cubic boron carbide $\text{Fe}_{23}(\text{CB})_6$ is defined as

$$G_m^{\text{Fe}_{23}(\text{CB})_6} = \sum_{i=1}^3 x_i G_i^0 + RT \sum_{i=1}^3 x_i \ln x_i + \frac{1}{2} \sum_i \sum_{i \neq j} x_i x_j L_{ij} - \frac{1}{2} \sum_i \sum_{i \neq j} \frac{L_{ij}^2 x_i^2 x_j^2}{2ZTR}, \quad (1)$$

where G_i^0 is the Gibbs energy of pure components (J/mol), R is universal gas constant ($R=8.31 \text{ J}/(\text{mol} \cdot \text{K})$), T is temperature (K), L_{ij} is the energy of interaction between the components (J/mol), Z is a coordination number, that for cubic boron carbide equals $Z=116$ [17]. The sum is evaluated for all i and j on the assumption that $i \neq j$.

It should be noted that the mixing energy depends on the temperature as follows: for the interaction of the first and the second elements it is $L_{12} = a + bT + cT \ln T$, for the second and the third ones $L_{23} = d + eT + fT \ln T$, and for the first and the third $L_{13} = k + lT + mT \ln T$, respectively.

To calculate the Gibbs energy of $\text{Fe}_{23}(\text{CB})_6$ phase, we used values of the energy of pure components and interaction energy from the data [18-22]. The calculations give us the following expression for the Gibbs energy of cubic boron carbide $\text{Fe}_{23}(\text{CB})_6$:

$$G_m^{\text{Fe}_{23}(\text{CB})_6} = -34520.3 + 6.3T - 10^5 T^{-1}. \quad (2)$$

According to the results of [11], the Gibbs energy of $\text{Fe}_{23}(\text{CB})_6$ phase is $G_m^{\text{Fe}_{23}(\text{CB})_6} = -13500 + 0.6T$ and, according to [12], $G_m^{\text{Fe}_{23}(\text{CB})_6} = -19276 - 1.05T$.

Thus, the obtained temperature dependence of the Gibbs energy for cubic boron carbide $\text{Fe}_{23}(\text{CB})_6$ (2) determines its value in the high-temperature region, where this phase is forming from the liquid.

The chemical potential of the boron in cubic boron carbide is calculated as

$$\begin{aligned} \mu_B = & \left(\frac{\partial G_m^{\text{Fe}_{23}(\text{CB})_6}}{\partial x_B} \right)_T = {}^0G_B + RT(\ln x_B + 1) + x_{\text{Fe}}(cT \ln T + bT + a) + \\ & + x_C(mT \ln T + lT + k) - \frac{(cT \ln T + bT + a)^2 x_B x_{\text{Fe}}^2}{ZRT} - \frac{(mT \ln T + lT + k)^2 x_B x_C^2}{ZRT}. \end{aligned}$$

The temperature dependence of the chemical potential of boron in $\text{Fe}_{23}(\text{CB})_6$ is

$$\mu_B = -27231 + 3.4T + 10^4 T^{-1}.$$

The chemical potential of carbon and iron in cubic boron carbide takes the form:

$$\mu_C = -29566.2 + 4.7T + 10^4 T^{-1},$$

$$\mu_{\text{Fe}} = -23621 + 3.1T + 10^5 T^{-1}.$$

If we compare the values of chemical potentials for boron and for carbon in $\text{Fe}_{23}(\text{CB})_6$ phase, we can see that chemical potential of boron is greater than that of carbon. This suggests that in cubic boron carbide $\text{Fe}_{23}(\text{CB})_6$ the substitution of boron atoms by carbon atoms is possible, as it was indicated by the authors of [12].

As we know [23], to determine the formation temperature of $\text{Fe}_{23}(\text{CB})_6$ phase we have to solve an equation $\partial \mu / \partial y = 0$.

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

$$\frac{\partial \mu_B}{\partial y_B} = \left(\frac{\partial^2 G_m^{\text{Fe}_{23}(\text{CB})_6}}{\partial x_B^2} \right)_T = 0, \quad \frac{\partial \mu_C}{\partial y_C} = \left(\frac{\partial^2 G_m^{\text{Fe}_{23}(\text{CB})_6}}{\partial x_C^2} \right)_T = 0, \quad \frac{\partial \mu_{\text{Fe}}}{\partial y_{\text{Fe}}} = \left(\frac{\partial^2 G_m^{\text{Fe}_{23}(\text{CB})_6}}{\partial x_{\text{Fe}}^2} \right)_T = 0. \quad (3)$$

The solution of equations (3) enables to find the formation temperature of cubic boron carbide $\text{Fe}_{23}(\text{CB})_6$, that turns out to be equal to $T = 1400.006$ K. This is in a good agreement with experimental data.

Let us find entropy, enthalpy and heat capacity C_p of cubic boron carbide $\text{Fe}_{23}(\text{CB})_6$.

The entropy of $\text{Fe}_{23}(\text{CB})_6$ phase is determined as

$$\begin{aligned}
 S = - \left(\frac{\partial G}{\partial T} \right)_x &= -R(x_B \ln x_B + x_{Fe} \ln x_{Fe} + x_C \ln x_C) - x_B x_{Fe} (c \ln T + b) - x_C x_{Fe} (f \ln T + e) - \\
 &- x_B x_C (m \ln T + l) - \frac{(cT \ln T + bT + a)^2 x_B^2 x_{Fe}^2}{2ZRT^2} + \frac{(cT \ln T + bT + a) x_B^2 x_{Fe}^2 (c \ln T + b)}{ZRT} \\
 &+ \frac{(fT \ln T + eT + d) x_C^2 x_{Fe}^2 (f \ln T + e)}{ZRT} - \frac{(fT \ln T + eT + d)^2 x_C^2 x_{Fe}^2}{2ZRT^2} + \\
 &+ \frac{(mT \ln T + lT + k) x_B^2 x_C^2 (m \ln T + l)}{ZRT} - \frac{(mT \ln T + lT + k) x_B^2 x_C^2}{2ZRT^2}.
 \end{aligned}$$

Taking into account the contribution of the first degree approximation in the high-temperature expansion for the thermodynamic potential of binary alloys in the Gibbs energy makes it possible to derive the enthalpy of cubic boron carbide. To calculate the enthalpy of $Fe_{23}(CB)_6$, we use relationship [21]: $\Delta H = \Delta G + T\Delta S$.

The temperature dependence of the enthalpy for this phase is

$$H^{Fe_{23}(CB)_6} = -37056 + 5.1T + 10^5 T^{-1}.$$

The enthalpy, which corresponds to the formation of $Fe_{23}(CB)_6$ phase is $H_{Fe_{23}(CB)_6} = -29611.59$ J/mol. The enthalpy of the formation of $Fe_{23}B_6$ phase is -11 kJ \cdot mol $^{-1}$ K $^{-1}$ according to the results of [24] and for $Fe_{23}C_6$ phase equals -17.39 kJ \cdot mol $^{-1}$ K $^{-1}$ [25].

The heat capacity for $Fe_{23}(CB)_6$ phase is calculated as

$$\begin{aligned}
 C_p = T \left(\frac{\partial S}{\partial T} \right)_p &= \frac{(c \ln T + b)^2 x_B^2 x_{Fe}^2}{ZR} - \frac{2(cT \ln T + bT + a) x_B^2 x_{Fe}^2 (c \ln T + b)}{ZRT} + \\
 &+ \frac{(cT \ln T + bT + a)^2 x_B^2 x_{Fe}^2}{ZRT^2} + \frac{(f \ln T + e)^2 x_C^2 x_{Fe}^2}{ZR} - \frac{2(fT \ln T + eT + d) x_C^2 x_{Fe}^2 (f \ln T + e)}{ZRT} + \\
 &+ \frac{(fT \ln T + eT + d)^2 x_C^2 x_{Fe}^2}{ZRT^2} + \frac{(m \ln T + l)^2 x_B^2 x_C^2}{ZR} - \frac{2(mT \ln T + lT + k) x_B^2 x_C^2 (m \ln T + l)}{ZRT} + \\
 &+ \frac{(mT \ln T + lT + k)^2 x_B^2 x_C^2}{ZRT^2}.
 \end{aligned}$$

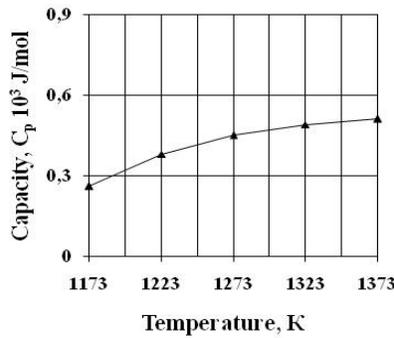


Fig. 5. Temperature dependence of heat capacity C_p of cubic boron carbide $Fe_{23}(CB)_6$.

Analysis of the results leads to the conclusion that accounting for the first degree approximation in the high-temperature expansion of the thermodynamic potential makes it possible to obtain the thermodynamic quantities such as entropy, enthalpy, heat capacity, and their temperature dependences for cubic boron carbide $\text{Fe}_{23}(\text{CB})_6$. Besides, it gives an opportunity to describe the cubic boron carbide $\text{Fe}_{23}(\text{CB})_6$ formed from a liquid in the most complete way from the thermodynamic point of view.

4. Conclusions

To obtain cubic boron carbide of iron $\text{Fe}_{23}(\text{CB})$ in Fe-B-C alloys with carbon content of 0.3–4.0 % (wt.) and boron content of 0.1–6.5 % (wt.), the rest is iron, one should perform pretreatment of alloy, such as annealing at 1173 K, further heating to a temperature of 30 K above the liquidus and then cooling with a rate of 10–100 K/s to a room temperature. At boron content of 4.2–6.0 % (wt.) and carbon content of more than 3.0 % there no formation of cubic boron carbide occurs after pretreatment.

It is shown that for alloys with boron content of 2.8–3.0 % (wt.) and 2.0–2.2 % (wt.) without pretreatment the formation of cubic boron carbide $\text{Fe}_{23}(\text{CB})_6$ takes place under crystallization. For the first time we obtain temperature dependences of entropy, enthalpy and heat capacity for cubic boron carbide $\text{Fe}_{23}(\text{CB})_6$ using the model with accounting for the first degree approximation of high-temperature expansion of the thermodynamic potential. The temperature of formation of $\text{Fe}_{23}(\text{CB})_6$ phase is calculated.

The obtained results are important and actual, because they allow to perform calculations of three-component phases taking into account fluctuation processes. In prospect, the thermodynamic functions of multicomponent phases will be studied, which would enable to explain the mechanisms of their formation and phase transformations occurring in multicomponent systems.

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