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The Effect of Carbon Content and Cooling Rate on the Structure of Boron-rich Fe–B–C alloys

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The structural and phase composition of boron-rich Fe–B–C alloys in the concentration range of 9.0 - 16.0 % B, 0.001 - 1.7 % C, Fe – the balance (in wt. %) was investigated in this work. The cooling rate of the alloys was from 10 to 10^3 K/s. The methods of quantitative metallographic, X-ray, energy dispersive X-ray, and differential thermal analyses were applied. It was established that the maximal solubility of carbon in Fe_2B hemiboride does not exceed 0.55 %, and that in FeB monoboride – 0.41 %. The alloys that belong to two-phase peritectic $(Fe_2(B,C) + Fe(B,C))$ region, two-phase peritectic-eutectic $(Fe_2(B,C) + Fe(B,C))$ region, and three-phase peritectic-eutectic $(Fe_2(B,C) + Fe(B,C) + C)$ region of the Fe–B–C phase diagram were distinguished depending on their structure. The appearance of an eutectic constituents in the investigated alloys was explained by transition of peritectic reaction $L + Fe(B,C) \rightarrow Fe_2(B,C)$ to eutectic reaction $L \rightarrow Fe(B,C) + Fe_2(B,C)$ within the temperature range of 1623 - 1583 K in the presence of carbon. With cooling rate increasing from 10 to 10^3 K/s, structural constituents tended to be fine, their volume fraction changed, microhardness and fracture toughness increased.

Key words: structure, cooling rate, crystallization, phase transformations, microdurometric characteristics.

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Introduction

Fe–B alloys have attracted lots of interest because they exhibit high hardness, wear resistance, oxidation and heat resistance [1-4]. In addition, these alloys require low processing cost [5]. This combination of properties may be utilized in a variety of applications like wear and corrosion resistant coatings [6-8]. However, there are still discrepancies concerning the phase and structural composition of Fe–B alloys in concentration range from 9 to 16 wt.% of boron. Thus, authors [9] and many other thought that these alloys had peritectic structure consisted of primary FeB crystals and Fe_2B phase formed by peritectic reaction $L + FeB \rightarrow Fe_2B$. Authors [10] reported that Fe_2B–FeB eutectic might exist in the structure of Fe–B alloys. They claimed that FeB phase was not observed in the structure of Fe – 9 % B alloy after quenching from melt. Therefore, they concluded that Fe_2B did not form through peritectic, but through eutectic reaction.

The described discrepancies concerning structural composition of Fe–B alloys may be attributed to the effect of additions, in the first place, carbon, on the structure formation of Fe–B alloys [11]. Iron metal is very reactive with respect to carbon. During specimen preparation this component may easily absorb from the air and, therefore, it may be considered as natural addition to Fe–B alloys. The phase composition of Fe–B–C alloys in concentration range of 9 - 16 wt. % of B was described in [12, 13]. Authors [13] considered carbon solubility of about 2 at. % in the iron borides and distinguished three three-phase equilibrium regions in the phase diagram, namely: $(FeB + Fe_2B + C)$, $(B + FeB + B_4C)$, $(B_4C + FeB + C)$. But authors [13] did not suggest possible reactions involving the revealed phases which might be responsible for structure formation of the alloys, and authors [12] did not proved the expected reactions experimentally.

Better understanding of the solidification microstructure of Fe–B–C alloy system with cooling rate is essential to support the utilization of the alloys in which a wide range of cooling rates might be encountered during metallurgical processing including

Table 1

The effect of carbon on phase and structural composition of Fe–B–C alloys

Carbon content (in wt. %)	Structure	Phase composition	Structural composition
0.01 - 0.165	Two-phase peritectic	$Fe_2(B,C)$, $Fe(B,C)$	$Fe_2(B,C)$, $Fe(B,C)$
0.17 - 0.5	Two-phase peritectic-eutectic	$Fe_2(B,C)$, $Fe(B,C)$	$Fe_2(B,C)$, $Fe(B,C)$, $Fe_2(B,C)$–$Fe(B,C)$ eutectic
0.55 - 1.7	Three-phase peritectic-eutectic	$Fe_2(B,C)$, $Fe(B,C)$, C	$Fe_2(B,C)$, $Fe(B,C)$, C globules, $Fe_2(B,C)$–C colonies, $Fe_2(B,C)$–$Fe(B,C)$–C eutectic

Table 2

The effect of carbon content (in wt. %) and cooling rate on crystal lattice parameters of $Fe_2(B,C)$ and $Fe(B,C)$ phases in Fe–10.1%B–C alloy

Carbon content	Cooling rate, K/s	Fe_2B (tetragonal lattice)			FeB (rhombic lattice)		
		a, Å	c, Å	c/a	a, Å	b, Å	c, Å
0.1	10	5.1112± 0.0031	4.2442± 0.0075	0.8304	5.5057± 0.0023	4.0614± 0.0096	2.9517± 0.0042
	10^3	5.1109± 0.0038	4.2495± 0.001	0.8315	5.5041± 0.0052	4.0596± 0.0106	2.9501± 0.0037
0.7	10	5.1141± 0.0040	4.2241± 0.0137	0.8250	5.4803± 0.0115	4.0401± 0.0051	2.9579± 0.0055
	10^3	5.1121± 0.0020	4.2393± 0.0055	0.8293	5.4778± 0.0031	4.0362± 0.0021	2.9595± 0.0012
1.6	10	5.1149± 0.0019	4.2245± 0.0120	0.8259	5.4805± 0.0018	4.0397± 0.0011	2.9582± 0.0007
	10^3	5.1132± 0.0031	4.2356± 0.0059	0.8284	5.4737± 0.0046	4.0345± 0.0037	2.9614± 0.0016

solidification technology. Besides, in many potential applications Fe–B alloys can be directly in contact with a carbon-containing medium. Therefore, the purpose of the present work is to investigate the influence of carbon and cooling rate on structure formation of Fe–B–C alloys inside the Fe_2B–FeB–C compositional triangle.

I. Experimental procedure

The Fe–B–C alloys containing 9.0 - 16.0 % B, 0.001 - 1.7 % C, Fe – the balance (in wt. %) were prepared of high purity (99.93 % - 99.99 %) components and melted in alumina crucibles using Tamman furnace. The cooling rate of the alloys was $10 - 10^3$ K/s. The average chemical composition of the alloys was studied by atomic absorption spectroscopy method using *Sprut СЕФ-01-M* device. The local chemical composition of phases was determined by an energy dispersive (EDX) attachment linked to JSM-6491LV scanning electron microscope. The alloys were examined by light-optical microscope *Neophot*. Quantitative metallography was carried out with structural analyzer *Epiquant*. X-ray diffraction analysis was done to identify the existing phases in produced samples on an X-ray diffractometer *ДРОН-УМ-1* with CuK_α source. The phase transformations were investigated by means of differential thermal analysis (DTA). Cooling curves were recorded for each sample at a cooling rate of 5 K/min. The Vickers microhardness (H_μ) was measured from at least 10 different indentations, and fracture toughness

(K_{1C}) was evaluated from the crack length at the corners of the Vickers microindentation using *ПМТ-3* device.

II. Experimental results and discussion

In compositional range of 9 – 16 % of B, 0.001 - 1.7 % C, Fe – balance, the majority of the structure of the Fe–B–C alloys comprise Fe(B,C) and $Fe_2(B,C)$ solid solutions (Table 1). The maximal carbon solubility in Fe_2B iron hemiboride measured by EDX is about 0.55 %. The Fe(B,C) phase has been found to dissolve up to 0.41 %. With cooling rate increasing from 10 to 10^3 K/s, the deviations of lattice parameters from etalon values for iron borides increase (Table 2). It may be related to increasing carbon solubility in these phases. Above a critical content of carbon in FeB and Fe_2B phases, free graphite appears in the alloys structure (Table 1).

Depending on carbon content in the investigated Fe–B–C alloys, the following structural changes are revealed. In the structure of two-phase peritectic Fe–B–C alloys containing 0.001 – .165 % C primary dendrites of Fe(B,C) phase are observed in the background of $Fe_2(B,C)$ solid solution formed by peritectic reaction L + Fe(B,C) → $Fe_2(B,C)$ (Table 1, Fig. 1). In the alloys with composition close to peritectic point, $Fe_2(B,C)$ phase may also crystallize directly from the liquid due to a low content of primary Fe(B,C) phase. DTA thermograms show that temperature of peritectic reaction lowers to 1653 - 1643 K when carbon is added (Fig. 2, a). The weak exothermic effect at 1398 K may be related to
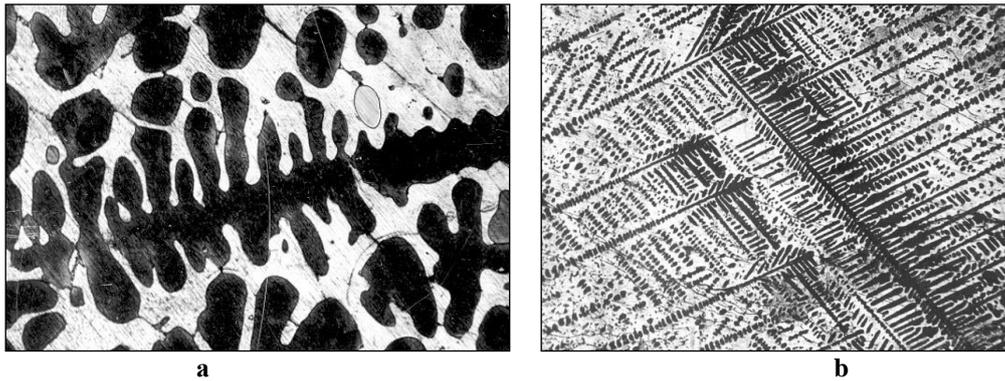
Fig. 1. Microstructure of Fe – 12.1 % B – 0.1 % C alloy (x300): a – V_{cool} = 10 K/s; b – V_{cool} = 10^3 K/s
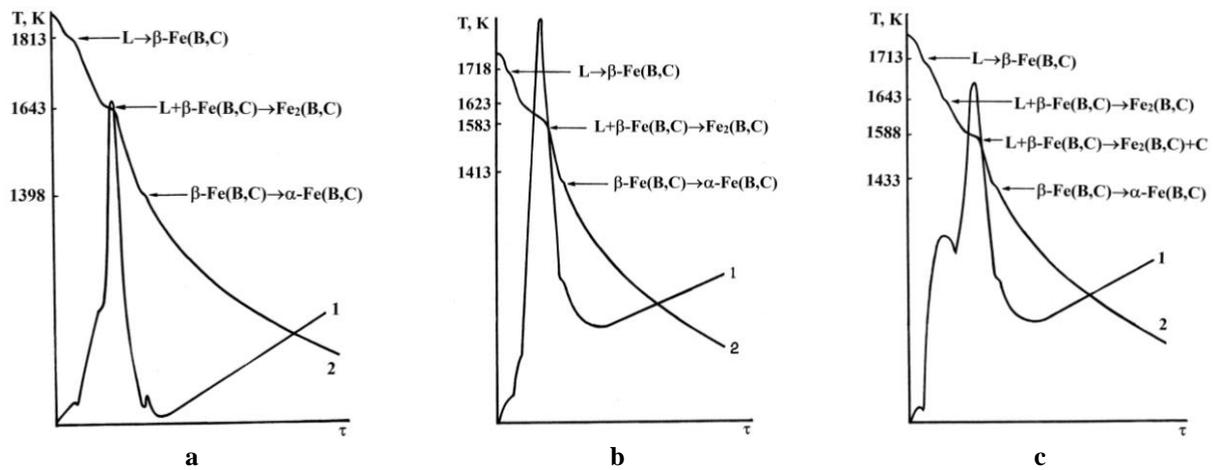

Fig. 2. Thermograms of Fe – 12.1 % B – 0.1 % C (a), Fe – 10.8 % B – 0.3 % C (b),
Fe – 11.0 % B – 1.24 % C (c) alloys: 1 – $\Delta T(\tau)$; 2 –$T(\tau)$.

the polymorphic transformation β-Fe(B,C) → α-Fe(B,C) [4]. As the carbon content increases from 0.01 % to 0.165 %, the relative amount of Fe(B,C) phase increases by 10 vol.% on average which may be explained either by the facilitation of its nucleation or by the inhibition of the peritectic reaction.

Cooling rate during solidification does not affect the phase composition of two-phase peritectic alloys. With cooling rate increasing from 10 to 10^3 K/s, the structural constituents tend to be fine (Fig. 1, b). A diameter (d) of secondary dendritic arms of Fe(B,C) crystals changes as a function of cooling rate (V_{cool}) as follows: ln d = –0.55·ln V_{cool} + 3.0. Carbon-containing Fe_2B- and FeB-based solid solutions solidified with a higher cooling rate do not practically exhibit changes in their crystal lattices parameters (Table 2). The volume fraction of Fe(B,C) phase in the rapidly cooled alloys increases by 12 vol.% on average, and that of Fe_2(B,C) phase decreases correspondingly. The increase in both carbon content and cooling rate enhances the microhardness values.

As carbon content increases from 0.17 to 0.5 %, binary rod-like Fe_2(B,C)–Fe(B,C) eutectic additionally appears in the structure of two-phase peritectic-eutectic Fe–B–C alloys which can be attributed to the effect of C in the alloys during solidification (Table 1, Fig. 3,a) [14]. About formation of this eutectic also reported authors [15], but they did not explain mechanism of its

crystallization in the alloys which structure should be peritectic according to the phase diagram.

The volume fraction of Fe_2(B,C)–Fe(B,C) eutectic decreases with increasing boron content in the alloys. Firstly, as the cooling rate increases over a range of 10 - 700 K/s, the eutectic volumic amount increases and its constituents exhibit more fine morphology (Fig. 3,b). As the cooling rate is further raised up to 10^3 K/c, the relative amount of the eutectic decreases. The microhardness of the eutectic increases from 17.5 ± 0.2 GPa to 19.0 ± 0.5 GPa.

In the presence of carbon, binary Fe_2(B,C)–Fe(B,C) eutectic may appear in the Fe–B–C alloys due to a continuous transition of peritectic reaction L + Fe(B,C) → Fe_2(B,C) into eutectic reaction L → Fe(B,C) + Fe_2(B,C) in a temperature range of 1623 – 1583 K (Fig. 2, b). Quenching microstructural analysis (stop-quenching) shows that at the temperatures of 1633 - 1623 K primary Fe(B,C) crystals first dissolve in the peritectic reaction forming Fe_2(B,C) phase. Then, with boron and carbon accumulating in the liquid, the dissolution slows down and in the region of peritectic-to-eutectic transition the interface of Fe(B,C) dendrites stabilizes. Dissolution is terminated and in the presence of Fe(B,C) phase Fe_2(B,C) crystals start forming in the liquid. The transition of the composition of the liquid into eutectic region is accompanied by its two-phase decomposition over a range of temperatures [16]. As a
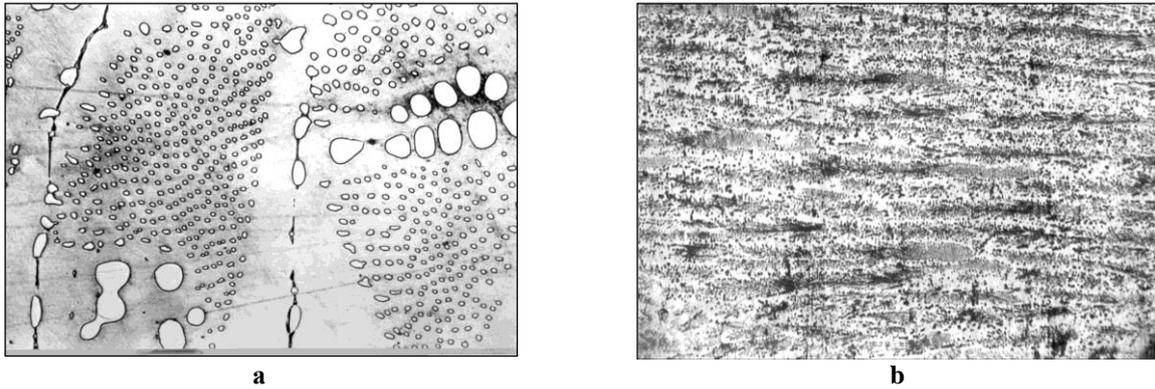
Fig. 3. Microstructure of Fe – 10.8 % B – 0.3 % C alloy (x300): a – V_{cool} = 10 K/s; b – V_{cool} = 700 K/s
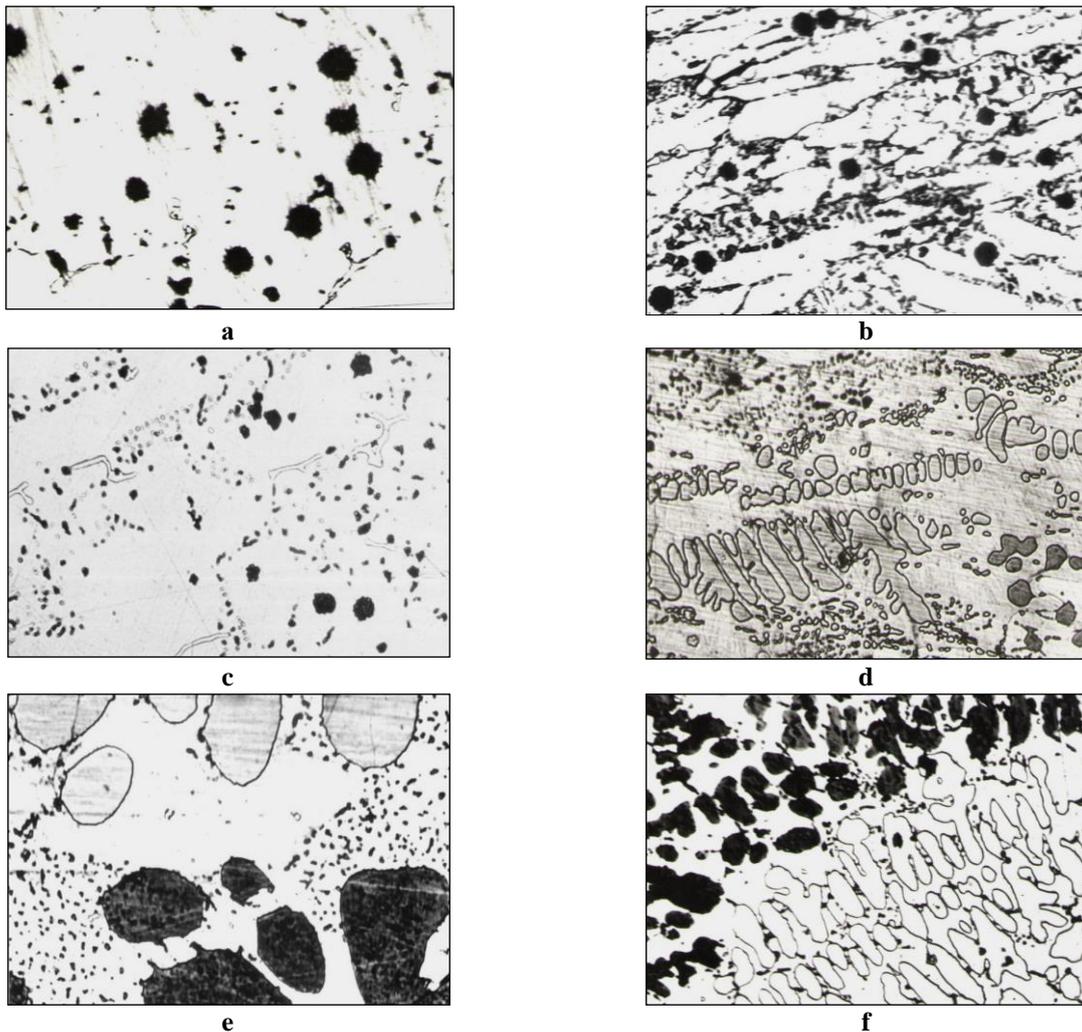

Fig. 4. Microstructure (x300) Fe – 9.1 % B – 1.45 % C (a, b); Fe – 12.3 % B – 0.82 % C (c, d);
Fe – 14.3 % B – 0.8 % C (e, f) alloys: a, c, e – V_{cool} = 10 K/s; b, d, f – V_{cool} = 10^3 K/s.

result, in the structure of ternary Fe–B–C alloys containing 9.0 - 16.0 % B and 0.17 - 0.5 % C, univariant Fe$_2$(B,C)–Fe(B,C) eutectic is observed. So, the formation of the eutectic is strongly influenced by the addition of carbon.

When the carbon concentration is further increased up to 0.5 - 1.7 %, the structure of three-phase peritectic-eutectic Fe–B–C alloys features the formation of structural constituents composed of graphite (Table 1, Fig. 4). Globular graphite inclusions are usually observed in the alloys containing 9.0 - 9.2% B (Fig. 4,a). Besides, in the overall concentration range, two-phase Fe$_2$(B,C)–C colonies are revealed at Fe$_2$(B,C) boundaries (Fig. 4, 2,c). They exhibit globular dispersed morphology. Their formation is related to four-phase peritectic transformation L + Fe(B,C) → Fe$_2$(B,C) + C [12]. As cooling rate is raised up to 10^3 K/s, the microstructural size and relative amount of this structural constituent decrease (Fig. 4, b, d, f). With boron concentration increasing above 12.0 %, the amount of globular graphite

inclusions decreases and ternary $Fe_2(B,C)$–$Fe(B,C)$–C eutectic appears at $Fe_2(B,C)$ boundaries (Fig. 4,c). Its eutectic origin may be concluded from the results of quenching microstructural analysis. The ternary eutectic is not revealed in the Fe–B–C alloys with boron content ranging from 14 to 16 % B (Fig. 4,e). The increase in cooling rate up to 10^3 K/c induces refinement of the structure and decrease in the volume fraction of eutectic constituents (Fig. 4, b, d, f). Wherein, a total microhardness of the alloys increases by 15 % on average, and fracture toughness – by 2.5 times.

The formation of the ternary $Fe_2(B,C)$–$Fe(B,C)$–C eutectic in the structure of three-phase peritectic-eutectic Fe–B–C alloys may be explained as follows. It is known that figurative point of the four-phase peritectic transformation $L + Fe(B,C) \rightarrow Fe_2(B,C) + C$ is the point in which intersect three univariant curves that correspond to two eutectic transformations $L \rightarrow Fe_2(B,C) + C$, $L \rightarrow Fe(B,C) + C$ and one peritectic transformation $L + Fe(B,C) \rightarrow Fe_2(B,C)$. However, considering the possibility of continuous transition of three-phase peritectic transformation $L + Fe(B,C) \rightarrow Fe_2(B,C)$ into three-phase eutectic transformation $L \rightarrow Fe(B,C) + Fe_2(B,C)$, the decomposition of the liquid by reaction $L \rightarrow Fe_2(B,C) + Fe(B,C) + C$ at 1588 K is possible when the composition of the alloy falls within the four-phase eutectic region of the phase diagram [16].

Conclusions

Depending on carbon content, the Fe–B–C alloys in the compositional range of 9.0 - 16.0 % B, 0.001 - 1.7 % C, Fe – balance cooled at rates from 10 to 10^3 K/s, exhibit two-phase peritectic (0.001 - 0.165 % C), two-phase peritectic-eutectic (0.17 - 0.5 % C) and three-phase peritectic-eutectic (0.55 - 1.7 % C) structures.

The two-phase peritectic alloys have been found to consist of primary $Fe(B,C)$ crystals and $Fe_2(B,C)$ phase forming in two ways: through the ternary peritectic reaction or directly from the melt. As cooling rate increases up to 10^3 K/s, the resultant microstructural size and volume fraction of primary $Fe(B,C)$ phase decrease, microhardness and fracture toughness increase.

The two-phase peritectic-eutectic alloys feature the formation of rod-like $Fe_2(B,C)$–$Fe(B,C)$ eutectic in addition to $Fe(B,C)$ and $Fe_2(B,C)$ phases. The eutectic appears in the Fe–B–C alloys due to a continuous transition of univariant peritectic transformation $L + Fe(B,C) \rightarrow Fe_2(B,C)$ into eutectic transformation $L \rightarrow Fe(B,C) + Fe_2(B,C)$ in a temperature range of 1623 - 1583 K. First, with cooling rate increasing from 10 to 700 K/s, a volume fraction of the eutectic increases. The further increase in a cooling rate up to 10^3 K/s gives rise to the decrease in a relative amount of the eutectic. Wherein, microhardness of the eutectic increases.

In the three-phase peritectic-eutectic alloys, the following structural constituents are present: $Fe_2(B,C)$ and $Fe(B,C)$ solid solutions, graphite, $Fe_2(B,C)$–C colonies and ternary $Fe_2(B,C)$–$Fe(B,C)$–C eutectic. Globular graphite inclusions and $Fe_2(B,C)$–C colonies form in the four-phase peritectic transformation $L + Fe(B,C) \rightarrow Fe_2(B,C) + C$. The ternary $Fe_2(B,C)$–$Fe(B,C)$–C eutectic crystallizes during the four-phase eutectic transformation $L \rightarrow Fe_2(B,C) + Fe(B,C) + C$ that undergoes instead of the peritectic transformation $L + Fe(B,C) \rightarrow Fe_2(B,C) + C$ due to the continuous transition of the univariant peritectic transformation $L + Fe(B,C) \rightarrow Fe_2(B,C)$ into the eutectic transformation $L \rightarrow Fe(B,C) + Fe_2(B,C)$ in a narrow temperature range. As a cooling rate increases from 10 to 10^3 K/s, the refinement of eutectic constituents and decrease in their amount are observed. Rapidly cooled alloys exhibit enhanced total microhardness and fracture toughness.

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[1]   X. Ren, H. Fu, J. Xing, Y. Yang, S. Tang, Journal of Materials Research 32(16), 1 (2017).
[2]   I.M. Spiridonova, E.V. Sukhovaya, V.F. Butenko, A.P. Zhudra, A.I. Litvinenko, A.I. Belyi, Powder Metallurgy and Metal Ceramics 32(2), 139 (1993).
[3]   O. Hesse, J. Merker, M.N. Brykov, V.G. Efremenko, Tribologie und Schmierungstechnik 60(6), 37(2013).
[4]   I.M. Spiridonova, E.V. Sukhovaya, V.P. Balakin, Metallurgia 35(2), 65 (1996).
[5]   O.V. Sukhova, Metallofizika i Noveishie Tekhnologii 31(7), 1001 (2009).
[6]   I.M. Spiridonova, O.V. Sukhova, A.P. Vashchenko, Metallofizika i Noveishie Tekhnologii 21(2), 122 (1999).
[7]   O.V. Sukhova, Y.V. Syrovatko, Metallofizika i Noveishie Tekhnologii 33 (Special Issue), 371 (2011).
[8]   E.V. Sukhovaya, Journal of Superhard Materials 35(5), 277 (2013).
[9]   K.I. Portnoi, V.M. Romashov, Powder Metallurgy and Metal Ceramics 5, 48 (1972).
[10] E. Kneller, Y. Khan, Z. Metallkunde 78(12), 825 (1987).
[11] I.M. Spyrydonova, Metallovedenie i Termicheskaya Obrabotka Metallov i Splavov 2, 58 (1984).
[12] E. Schurmann, L. Shao-Xiong, Giessereiforschung 37(4), 121 (1985).
[13] V. Homolova, L. Ciripova, A. Vyrostkova, J. Phase Equilibria and Diffusion 36(6), 599 (2015).
[14] I.M. Spyrydonova, E.V. Sukhovaya, G.A. Sergeyev, Theory and Practice of Metallurgy 4-5, 57 (2006).
[15] N.Y. Filonenko, E.Y. Beryoza, O.G. Bezrukavaya, Physics and Chemistry of Solid State 5, 168 (2013).
[16] D.A. Petrov, Binary and Ternary Systems (Metallurgy, Moscow, 1986).

O.V. Sukhova

О.В. Сухова

Вплив вмісту вуглецю та швидкості охолодження на структуру високобористих сплавів Fe–B–C

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У роботі досліджено структурний та фазовий склад високобористих сплавів Fe–B–C в області концентрацій 9,0 - 16,0 % B, 0,001 - 1,7 % C, Fe – залишок (у мас. %). Швидкість охолодження сплавів становила 10–10^3 К/с. Використано методи кількісного металографічного, рентгеноструктурного, мікрорентгеноспектрального і диференціального термічного аналізів. Встановлено, що максимальна розчинність вуглецю в гемібориді Fe_2B становить 0,55 %, а в монобориді FeB – 0,41 %. Залежно від структури можна виділити сплави, що належать до двофазної перитектичної ($Fe_2(B,C) + Fe(B,C)$), двофазної перитектико-евтектичної ($Fe_2(B,C) + Fe(B,C)$) та трифазної перитектико-евтектичної ($Fe_2(B,C) + Fe(B,C) + C$) областей діаграми стану Fe–B–C. Появу евтектичних складових у структурі досліджених сплавів пояснено переходом перитектичної реакції $L + Fe(B,C) \rightarrow Fe_2(B,C)$ в евтектичну реакцію $L \rightarrow Fe(B,C) + Fe_2(B,C)$ в інтервалі температур 1623 - 1583 К у присутності вуглецю. Збільшення швидкості охолодження з 10 до 10^3 К/с супроводжується подрібненням структурних складових, зміною їх об'ємного вмісту, збільшенням мікротвердості та коефіцієнта тріщиностійкості.

Ключові слова: структура, швидкість охолодження, кристалізація, фазові перетворення, мікро-механічні характеристики.