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TO QUESTION ABOUT FE_5B_3 BORIDE FORMATION IN BORON-RICH Fe–B ALLOYS

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The structure of boron-rich iron alloys in the concentration range of 9.0–15.0 wt. % B, 0.01–0.17 wt. % C, Fe – the balance (with charge impurities of Si, Al, Mn) was investigated in this work. The methods of metallographic, X-ray, stop-quenching, scanning electron microscopic, energy dispersive, and fluorescent spectral analyses were applied. The FeB- and Fe_2B-based solid solutions are proved to be the major constituents of the investigated alloys. No evidence is found for the possible formation of the Fe_5B_3 boride via peritectic reaction $L+FeB\rightarrow Fe_5B_3$ at 1650 K and its further decomposition via eutectoid reaction $Fe_5B_3\rightarrow FeB+Fe_2B$ at 1410 K. It is shown that the phase under consideration is iron hemiboride alloyed mainly by silicon which peritectically forms from primary crystals of iron monoboride and the rest of liquid at 1650 K. The thermal effect at 1410 K is assumed to be caused by a heat production connected with polymorphic transformation β-FeB$\rightarrow\alpha$-FeB in the presence of carbon.

Keywords: boron-rich iron alloys, structure, iron borides, phase transformations, solid solutions.

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1. Introduction

The boron-rich Fe–B alloys containing 9.0–15.0 wt. %B are characterized by formation of two compounds, Fe_2B and FeB respectively [1]. FeB melts congruently at 1863 K. It has a homogeneity range of about 1 at. % B. The existence of a high-temperature modification of β-FeB is confirmed by the stop-quenching technique [2,3] and the polymorphic transformation β-FeB$\rightarrow\alpha$-FeB is assumed at 1398 K in presence of up to 0.17 wt. % C. Fe_2B is formed peritectically at 1650 K via reaction $L+FeB\rightarrow Fe_2B$.

Besides, there is evidence for the existence of a Fe_5B_3 boride that forms via peritectic rection $L+FeB\rightarrow Fe_5B_3$ at 1650 K and afterwards decomposes into two phases via eutectoid reaction $Fe_5B_3\rightarrow FeB+Fe_2B$ at 1410 K [4]. Moreover, after annealing at 1473 K for 4 hours, the authors also suggested the existence of reverse reaction $FeB+Fe_2B\rightarrow Fe_5B_3$. But, the authors made all these conclusions applying only microstructural, differential thermal or X-ray analyses and showed no warranted images of reported Fe_5B_3 phase or ($FeB+Fe_2B$) eutectoid. The stoichiometric composition of Fe_5B_3 was not confirmed by energy dispersive spectroscopy as well. Therefore, considering that up to 0.1 wt. % C, 0.04 wt. % Si and traces of Al and Mn from the charge are present in the composition of the studied alloys, there is an ambiguity about the following question: Fe_5B_3 or alloyed Fe_2B form in the boron-rich Fe–B alloys. Besides, it should be taken into consideration that iron is very reactive with the said foreign atoms. The answer to this question is a matter of current investigation.

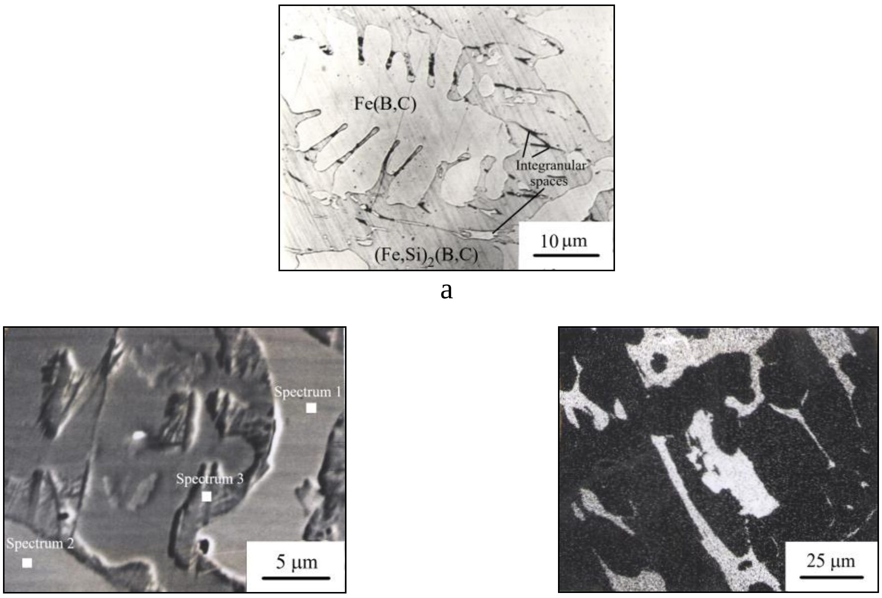
2. Experimental procedure

To carry out an investigation on the structural constituents which are present in the boron-rich alloys, 10 different alloy compositions were studied. These alloys were prepared in the following compositional range (purity 99.93–99.99 %): 9.0–15.0 % B, 0.01–0.17 % C, Fe – the balance (in wt. %). The samples were melted in alumina crucibles using arc vacuum furnace and cooled up to room temperature together with furnace. The average chemical composition was studied by fluorescent spectroscopy method using *Sprut СЕФ-01-М* device that revealed presence of impurity additions of 0.01–0.05 wt. % Si and traces of Al and Mn from the charge in the studied alloys.

The boron-rich alloys were examined by light-optical microscope *Neophot* (OM) and scanning electron microscope *Jeol – 2010 F* (SEM) equipped with energy-dispersive spectrometer (EDS). X-ray diffraction (XRD) analysis was done on X-ray diffractometer *ДРОН-УМ-1* with CuK$_\alpha$ source. To identify the phases forming in the temperature range from 1700 to 1390 K, the stop-quenching technique was applied. The samples were heated up to 1850 K till melting, cooled up to temperatures of 1700, 1650, 1600, 1430, 1390 K with furnace, and then quenched in the water.

3. Results and discussion

The investigated boron-rich alloys exhibit two-phase structure consisting of solid solutions based on FeB and Fe_2B borides (Fig. 1). A peritectic reaction $L+FeB \rightarrow Fe_2B$ has been proved as a formation mechanism of the Fe_2B phase [3]. Carbon, silicon and traces of Al and Mn are revealed in the iron hemiboride (Table 1, Spectrums 1, 2). But preferentially these elements are present in the intergranular spaces (Table 1, Spectrum 3). It may be suggested that during solidification, mainly, excess Si atoms that are no longer soluble in the iron hemiboride are rejected into interphase gaps (Fig 1, c). Spectrums 1 and 2 in Fig. 1, b certainly correspond to the composition of $(Fe,Si)_2(B,C)$ solid solution (Table 1). In the iron monoboride silicon is found to dissolve in negligible quantities. That is why, in the SEM micrographs, FeB crystals look dark (Fig 1, c).



a

b c

Fig. 1. Structure of polished cross-section of Fe–13.8B–0.1C–0.05Si alloy: a – OM image; b – second electron image; c – elemental EDS X-ray mapping in SiK$_\alpha$ radiation

Table 1

Chemical composition of structural constituents in the investigated boron-rich alloys (in at. %)

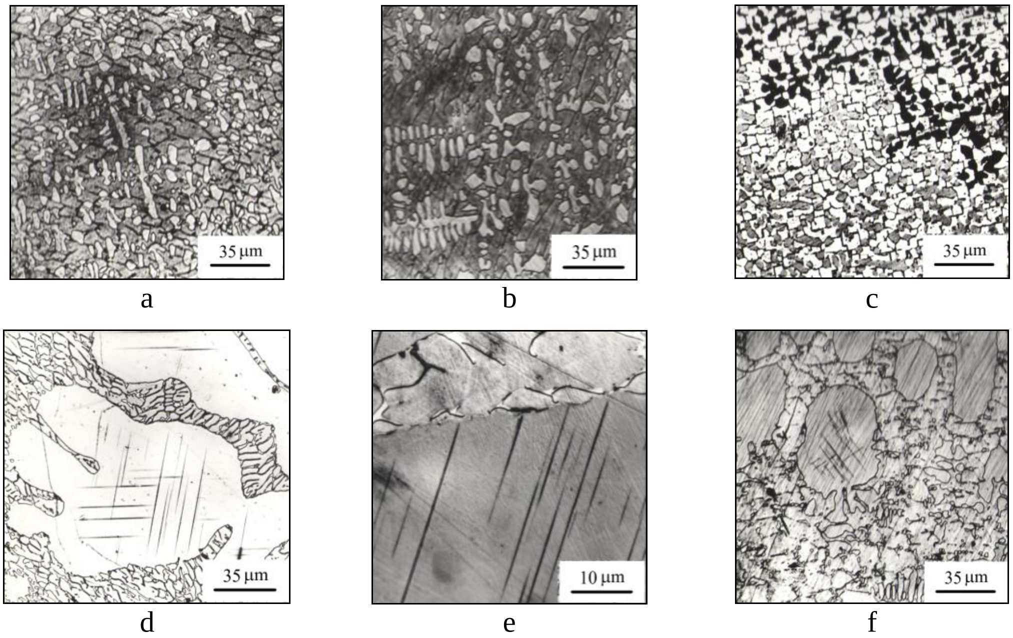
Spectrum	Fe	B	C	Si	Al	Mn
Fe_2B-based solid solution						
1	63.1	29.2	4.2	3.2	0.2	0.1
2	63.6	30.2	3.1	2.8	0.3	–
Intergranular space						
3	48.4	2.4	9.3	37.2	1.2	1.5

Comparison of the X-ray patterns reveals that the peak positions are shifted mainly towards lower angles with the introduction of silicon (Table 2). All these results support the idea that Si is soluble in the iron hemiboride, with $(Fe,Si)_2(B,C)$ solid solution forming. In the structure of the alloys, no evidence that Fe_5B_3 crystallizes peritectically or $(FeB+Fe_2B)$ eutectoid forms via the decomposition of Fe_5B_3 has been found. Therefore, stop-quenching technique has been used to investigate the phases appearing in the temperature range of Fe_5B_3 phase formation indicated in [4]. As shown in Fig. 2, only FeB and Fe_2B phases crystallize in the alloys quenched within the range from 1700 to 1390 K. This conclusion is confirmed by X-ray measurements since all peak positions unequivocally correspond to Fe_2B (Table 3). In rapidly cooled hemiboride, Si causes minor distortions of crystal lattice, as compared with the results listed in Table 2, due to a lack of time for Si to dissolve. This element is mainly pushed out into interphase gaps.

Table 2

XRD results for iron hemiboride in the investigated boron-rich alloys

Fe–13.2B–0.11C–0.01 alloy		Fe–14.1B–0.08C–0.03Si alloy		Fe–13.8B–0.1C–0.05Si alloy	
d_{hkl}, Å	I, %	d_{hkl}, Å	I, %	d_{hkl}, Å	I, %
3.625	7	3.631	8	3.634	10
2.564	20	2.250	12	2.566	25
2.130	15	2.130	7	2.132	22
2.018	100	2.010	100	2.014	100
1.833	12	1.836	12	1.806	28
1.636	17	1.637	15	1.674	27
1.287	7	1.293	8	1.292	12
1.205	27	1.208	18	1.201	10
1.192	25	1.194	20	1.192	8
1.093	8	1.096	5	1.093	5
1.048	22	1.043	12	1.051	15



a b c

d e f

Fig. 2. OM images of polished cross-sections of Fe–13.8B–0.1C–0.05Si alloy stop-quenched from temperatures: a – 1700 K; b – 1650 K; c – 1600 K; d, e – 1430 K; f – 1390 K

Table 3

XRD results for iron hemiboride in the stop-quenched Fe–13.8B–0.1C–0.05Si alloy

Quenching from 1600 K		Quenching from 1430 K		Quenching from 1390 K	
d_{hkl}, Å	I, %	d_{hkl}, Å	I, %	d_{hkl}, Å	I, %
3.625	10	3.625	25	3.624	27
2.561	37	2.561	40	2.562	35
2.128	22	2.130	52	2.130	45
2.019	100	2.020	100	2.014	100
1.834	10	1.834	15	1.830	10
1.635	20	1.636	28	1.634	30
1.287	10	1.289	18	1.288	15
1.203	20	1.206	27	1.205	22
1.189	25	1.190	30	1.191	18
1.094	7	1.096	8	1.094	8
1.048	27	1.048	32	1.047	25

According to the authors [4], Fe_5B_3 crystals peritectically form from Fe(B,C) phase and the rest of the melt at 1650 K. Quenching from this temperature shows only FeB and Fe_2B crystals in the structure (Fig. 2, b). The same structure is observed after quenching from lower temperatures (Fig. 2, c-f). Moreover, in the iron monoboride twin bands are clearly seen (Fig. 2, d-f) which indirectly confirms transformation β-FeB$\rightarrow\alpha$-FeB at 1410–1390 K in the presence of carbon [2]. So, thermal effect reported by the authors [4] may be caused not by Fe_5B_3 decomposition via eutectoid reaction at 1410 K but by a heat production related to polymorphic transformation since this effect is also seen in the thermogram of Fe–16B–0.1C alloy that forms Fe(B,C) and does not form Fe_2(B,C) phase.

Considering the results obtained, it may be assumed that no Fe_5B_3 phase forms in the structure of the investigated alloys. The shift in the peak positions reported by the authors [4] may relate to dissolution of silicon in iron hemiboride with $(Fe,Si)_2(B,C)$ phase formation. The changes in quantity or intensity of diffraction peaks after annealing at 1473 K for 4 hours may be explained by the facilitation of Si diffusion from interphase gaps to Fe_2B crystals and may not be connected with reverse reaction $FeB+Fe_2B\rightarrow Fe_5B_3$.

3. Conclusions

The investigation of boron-rich iron alloys in the same concentration range as reported in [4] indicates that the authors have made unwarranted conclusions and no Fe_5B_3 phase forms in the structure. The obtained results clearly confirm the formation of alloyed iron hemiboride via peritectic reaction $L+FeB\rightarrow Fe_2B$.

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