TO QUESTION ABOUT Fe₃B₃ BORIDE FORMATION IN BORON-RICH Fe–B ALLOYS

O.V. Sukhova

Oles’ Honchar Dnipro National University, Dnipro, Ukraine
e-mail: sukhovaya@ukr.net

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 Fe₂B-based solid solutions are proved to be the major constituents of the investigated alloys. No evidence is found for the possible formation of the Fe₃B₃ boride via peritectic reaction L+FeB→Fe₂B at 1650 K and its further decomposition via eutectoid reaction FeB→FeB+FeB 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→α–FeB in the presence of carbon.

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

Received 25.09.2020; Received in revised form 28.11.2020; Accepted 02.12.2020

1. Introduction

The boron-rich Fe–B alloys containing 9.0–15.0 wt. % B are characterized by formation of two compounds, Fe₂B 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→α–FeB is assumed at 1398 K in presence of up to 0.17 wt. % C. Fe₂B is formed peritectically at 1650 K via reaction L+FeB→Fe₂B.

Besides, there is evidence for the existence of a Fe₃B₃ boride that forms via peritectic reaction L+FeB→Fe₃B₃ at 1650 K and afterwards decomposes into two phases via eutectoid reaction Fe₂B→FeB+FeB at 1410 K [4]. Moreover, after annealing at 1473 K for 4 hours, the authors also suggested the existence of reverse reaction FeB+FeB→Fe₃B₃. But, the authors made all these conclusions applying only microstructural, differential thermal or X-ray analyses and showed no warranted images of reported Fe₃B₃ phase or (FeB+Fe₂B) eutectoid. The stoichiometric composition of Fe₃B₃ 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: Fe₃B₃ or alloyed Fe₂B₃ 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 CEP-01-M 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 CuKα 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 Fe₂B borides (Fig. 1). A peritectic reaction L+FeB→Fe₂B has been proved as a formation mechanism of the Fe₂B 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).

![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 SiKα radiation](image)

| Spectrum | Fe  | B   | C | Si | Al | Mn |
|----------|-----|-----|---|----|----|----|
| 1        | 63.1| 29.2| 4.2| 3.2| 0.2| 0.1|
| 2        | 63.6| 30.2| 3.1| 2.8| 0.3| 0.1|
| 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 \((\text{Fe,Si})_x\text{(B,C)}\) solid solution forming. In the structure of the alloys, no evidence that \(\text{Fe}_3\text{B}_3\) crystallizes peritectically or \((\text{FeB}+\text{Fe}_2\text{B})\) eutectoid forms via the decomposition of \(\text{Fe}_3\text{B}_3\) has been found. Therefore, stop-quenching technique has been used to investigate the phases appearing in the temperature range of \(\text{Fe}_3\text{B}_3\) phase formation indicated in [4]. As shown in Fig. 2, only \(\text{FeB}\) and \(\text{Fe}_2\text{B}\) 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 \(\text{Fe}_2\text{B}\) (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**

| Cr–13.2B–0.11C–0.01 alloy | Cr–14.1B–0.08C–0.03Si alloy | Cr–13.8B–0.1C–0.05Si alloy |
|---------------------------|-----------------------------|-----------------------------|
| \(d_{hkli}, \text{Å}\)     | \(I, \%\)                  | \(d_{hkli}, \text{Å}\)     | \(I, \%\)                  | \(d_{hkli}, \text{Å}\)     | \(I, \%\)                  |
| 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                           |

**Fig. 2.** OM images of polished cross-sections of Cr–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

81
According to the authors [4], Fe₅B₃ 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 Fe₂B 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 → α-FeB at 1410–1390 K in the presence of carbon [2]. So, thermal effect reported by the authors [4] may be caused not by Fe₅B₃ 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 Fe₅(B,C) phase.

Considering the results obtained, it may be assumed that no Fe₅B₃ 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 Fe₂B crystals and may not be connected with reverse reaction FeB+Fe₂B → Fe₅B₃.

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 Fe₅B₃ phase forms in the structure. The obtained results clearly confirm the formation of alloyed iron hemiboride via peritectic reaction L+FeB → Fe₂B.

References

1. Marder, A.R. B–Fe (Boron-Iron) / A.R. Marder // Metal Handbook. Metallography, Structures and Phase Diagrams. – 1973 – v. 8 – P. 270–347.
2. Spiridonova, I.M. Structure and deformation peculiarities of Fe(B,C) crystals / I.M. Spiridonova, E.V. Sukhovaya, V.P. Balakin // Metallurgia. – 1996. – v. 35. – No. 2. – P. 65–68.
3. Sukhova, O.V. The effect of carbon content and cooling rate on the structure of boron-rich Fe–B–C alloys / O.V. Sukhova // Physics and Chemistry of Solid State. – 2020. – v. 21. – No. 2. – P. 355–360.
4. Filonenko, N.Yu. Structural state and phase transformations in Fe-B system alloys / N.Yu. Filonenko, A.I. Babachenko, G.A. Kononenko // Metallofiz. Noveishie Tekhnol. – 2020. – v. 42. – No. 11. – P. 1559–1572.