THE STRUCTURE OF ALLOYS OFBORON-RICH CORNER
OF Fe–B–C PHASE DIAGRAM

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The structure and microdurometric characteristics of the Fe–B–C alloys in the range of high
concentration of boron (>16.0 wt. % B) and low concentration of carbon (<0.1 wt. % C) were investigated
in this work. The methods of quantitative metallographic, X-ray, differential thermal, fluorescent spectral
and microdurometric analyses were applied. Carbon was established to dissolve completely in phase
constituents of the investigated alloys, forming solid solutions based on iron borides FeB, FeB₂, FeB₄ or
FeB₁₉. It was suggested the existence of one eutectic transformation between borides FeB₂ and FeB₄ as
well as two peritectic transformations between borides FeB and FeB₂ or FeB₄ and FeB₁₉ correspondingly
in the studied concentration range. The formation of boride FeB₄ was explained by its stabilization in the
presence of carbon in the alloys. After annealing in vacuum at 900 °C for 10 hours with following
quenching, the structure became coarser, but no traces of phase decomposition were revealed in the most
alloys. Microhardness of the phases observed in the structure of the investigated alloys increased in the
following sequence: FeB→FeB₂→FeB₄→FeB₁₉.

Keywords: phase diagram, structure, iron borides, phase transformations, microdurometric characteristics.

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1. Introduction

Equilibrium Fe–B diagrams are based on the studies by Hannesen, Chizhevsky, Gerdt, Wever, and Müller [1] The experimental data are mostly similar but differ in the boron
solubility in solid iron. Moreover, Hannesen discovered that Fe–B system had a stable FeB₂
boride, but Chizhevsky and Gerdt introduced the Fe₂B boride. Wever and Müller confirmed
the formation of the Fe₃B boride and explained the above discrepancies by contamination of the
studied alloys by carbon, aluminum, and silicon. In alloys with boron content higher than
8.83 wt. %, they discovered the congruently-melting FeB compound (16.23 wt. % B) that
existed in two polymorphic modifications (α-FeB and β-FeB). Later Khan, Kneller, and
Sostarich announced the existence of Fe₃B that had two stable modifications within the
temperature range of 1150 – 1250 °C [1].

In studying Fe–B system, a question arose, however, whether only three borides were
formed since the most of transition metals had more than three borides. These speculations
allowed Voroshnin et. al. [2] to assume that Fe–B system produces FeB₂ diboride that melted
congruently at the concentration of 27.9 wt. % B. The authors showed that alloys containing
more than 16 wt. % B might generate FeB–FeB₂ eutectics. Moreover, the authors suggested
that the diagram might also contain some third eutectic transformation at high boron
concentrations between FeB₂ and pure boron. Then Marder described FeB₁₉ phase with
variable boron content but did not confirmed the existence of FeB₂ diboride in boron-rich
region of Fe–B phase diagram [3]. Tylkina and Bochvar suggested eutectic reaction between
FeB and β-B [4]. They determined the solubility of iron in boron (about 2 %) that was limited
by a content of FeB₁₉. Krukovich et al. proposed equilibrium diagram of Fe–B system that
considered the existence of five experimentally defined iron borides, namely Fe₁B, Fe₂B,
FeB, FeB₂, and FeB₁₉. This diagram is based on Marder’s diagram, with two missing
borides Fe₃B and FeB₃ as well as eutectic reaction L→FeB₂+FeB₁₉ (at 34 wt. % B) and
peritectic reaction L+β-B→FeB₁₉ (at 78.6 wt. % B) added [1]. It was shown that the
solubility of iron in FeB₁₉ phase might decrease from 29 to 21.4 wt. % with temperature
lowering.

Thus, the structure of iron alloys containing more than 16.0 wt. % B is a point at issue.
Besides, it should be taken into consideration that iron is very reactive with carbon. Carbon may easily absorb from the air and, therefore, it should be considered as natural addition to Fe–B alloys. Nevertheless, the investigations of the Fe–B–C alloys are limited by a content of 18 wt. % B [5-11]. In the same time Fe–B–C alloys attract lots of interest because they exhibit high hardness, wear resistance, oxidation and heat resistance [12-14]. In this connection it seems interesting to investigate the structural composition and the mechanical properties of the alloys in the boron-rich corner of Fe–B–C diagram.

2. Experimental procedure

The Fe–B–C alloys containing 16.5–50.0 % B, 0.01–0.1 % C, Fe – the balance (in wt. %) were prepared of high purity (99.93–99.99 %) components and melted in alumina crucibles using arc vacuum furnace. The samples were cooled up to room temperature together with furnace and annealed at 900°C for 10 hours in vacuum. The average chemical composition of the alloys was studied by fluorescent spectroscopy method using Sprut CEF-01-M device. The alloys were examined by light-optical microscope Neophot. Quantitative metallography was carried out with structural analyzer Epiquant. X-ray diffraction (XRD) analysis was done to identify the existing phases in produced samples on X-ray diffractometer ДРОН-УМ-1 with CuKα source. The phase transformations were investigated by means of differential thermal analysis. Cooling curves were recorded for each sample at a cooling rate of 5 K/min. The Vickers microhardness was measured from at least 10 different indentations, and microbrittleness was evaluated from the crack length at the corners of the Vickers microindentation using ПМТ-3 device.

3. Results and discussion

The Fe–B–C alloys in the range of 16.5–17.5 wt. % B exhibit two-phase structure consisting of FeB and FeB₂ borides alloyed with carbon (Fig. 1). A peritectic reaction L+FeB → FeB₂ has been suggested as a formation mechanism of the FeB₂ phase. The FeB monoboride grows in the form of rounded dendrite with branches developed from the peaks of hexagons, and the FeB₂ diboride grows as anisotropic prism (Table 1). The microhardness and microbrittleness of FeB₂ phase are higher than those of FeB.

![Fig. 1. Isoconcentration section (at 0.1 wt. % C) of Fe–B–C phase diagram.](image-url)
The properties of iron borides in Fe–B–C alloys

| Boride     | Growth form | Microhardness, GPa | Microbrittleness, units |
|------------|-------------|---------------------|-------------------------|
| FeB        | Dendrite    | 19.29±0.4           | 2.5±0.3                 |
| FeB₂       | Prism       | 21.15±0.6           | 6.0±0.2                 |
| FeB₁₉      | Plate       | 27.76±0.5           | 7.6±0.6                 |
| FeB₁₉      | Prism       | 53.04±0.8           | 1.2±0.8                 |

As boron content further increases up to 22.7 wt. %, primary crystals of unknown phase embedded in the eutectic are formed. The X-ray diffraction analysis reveals the presence of lines that are not attributable to the known borides. This phase may be identified as FeB₄ boride that has hexagonal crystal lattice belonging to structural type MoB₄ (Table 2). The growth form of FeB₄ boride is found to be a plate. Sometimes, plates nucleate one on another which makes it difficult to distinguish their form and dimensions. This phase has high microhardness and microbrittleness (Table 1).

Table 2

| d_{hkl}, Å | I, % | hkl |
|------------|------|-----|
| calculated* | experimental | calculated* | experimental |
| 4.52       | 4.64 | 10  | 5 | 100 |
| 3.68       | 3.74 | 100 | 100 | 101 |
| 3.18       | 3.18 | 60  | 25 | 002 |
| 2.61       | 2.60 | 80  | 30 | 101 |
| 2.02       | 2.01 | 100 | 80 | 201 |
| 1.59       | 1.60 | 30  | 10 | 112 |
| 1.55       | 1.56 | 30  | 15 | 004 |
| 1.51       | 1.50 | 60  | 20 | 203 |
| 1.33       | 1.36 | 30  | 10 | 300 |
| 1.21       | 1.20 | 40  | 30 | 213 |

* - the values are determined from the XRD pattern of MoB₄ boride.

Considering the existence of FeB₄ boride, it may be concluded that the eutectic observed in the structure of the alloys containing 18–25.5 wt. % B is formed by the reaction L→FeB₂+FeB₄. It has irregular morphology and microhardness of 21.8–23.5 GPa.

As boron content exceeds 25.5 wt. %, primary crystals of FeB₁₉ boride are revealed in the structure. They are arranged in the background of FeB₄ crystals formed via peritectic reaction L+FeB₁₉→FeB₄ (Fig. 1). XRD results confirm that FeB₁₉ phase is a solid solution of iron in β-rhombohedral boron [2, 3]. It has a trigonal crystal lattice and belongs to R3m space group. The parameters of elementary cell of FeB₁₉ boride are as follows: a=10.2470 Å, α=70.5°. Metallographic analysis reveals prismatic zonal structure of this boride, the edge branches of prisms control crystallization process. The FeB₁₉ boride exhibits the highest microhardness and lowest microbrittleness (Table 1).

After annealing in vacuum at 900 ºC for 10 hours with following quenching, the coarsening of the structural constituents is observed due to the boron redistribution, but no traces of phase decomposition are revealed in the most alloys. An only exception is the alloy containing 18 wt. % B in which FeB₂ precipitates inside FeB crystals increasing the microhardness of FeB monoboride up to 20.5 GPa.
4. Conclusions

The metallographic and thermo-analytic investigation of ternary Fe–B–C alloys containing 16.5–50.0 wt. % B, 0.01–0.1 wt. % C indicates that borides previously reported as FeB, FeB₂, and FeB₁₉ are formed in the structure. Carbon added to Fe–B alloys completely dissolves in these phase constituents. Differences against earlier reports are found in the suggested existence of peritectic reactions L+FeB→FeB₃, L+FeB₁₉→FeB₄ and eutectic reaction L→FeB₂+FeB₄. The phase identified as FeB₄ is most likely stabilized by carbon.

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