Research Article

Experimental Investigation of Isothermal Section of the B-Cr-Fe Phase Diagram at 1353 K

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Received 28 February 2017; Accepted 20 April 2017; Published 11 May 2017

Academic Editor: Pavel Lejcek

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The isothermal section of the B-Cr-Fe ternary system was studied experimentally at 1353 K. X-ray diffraction and scanning electron microscopy equipped with EDX analyzer were used for determination of phase equilibria and composition of the coexisting phases in the B-Cr-Fe model alloys after long-term annealing (1500–2205 h). Two iron borides FeB and Fe₂B, six chromium borides Cr₂B, Cr₅B₃, CrB, Cr₃B₄, CrB₂, and CrB₄ and also iron and chromium solid solutions (α (Fe,Cr), α (Cr,Fe), γ (Fe,Cr)) and β -rhombohedral B were observed in the alloys. High solubilities of the third element in binary borides and no ternary phase were found. Based on the experimental results, isothermal section of the B-Cr-Fe system at 1353 K was determined.

1. Introduction

The knowledge about phase equilibria of the B-Cr-Fe system is important in several fields of materials research. The system is subsystem of various complex alloys, for example, modified ferritic steels for energy industry [1–3], steels for production abrasive, and corrosion-resistant components [4]. Information about the system is also important for study of boride coatings on various alloys and metals, including iron [5, 6].

Borides of transition metals, including chromium borides, have unique combination of thermal, mechanical, magnetic, and electrophysical properties and are being widely used in atomic power and chemical industry [7, 8].

The B-Cr-Fe system has been experimentally studied by only a few authors. Gorbunov and Bodurjan [9] investigated system at 1373 K after annealing for 320 h and Chépiga and Kuzma [10] at 973 and 1173 K after annealing for 400 and 750 h, respectively. In the works [9, 10], some questionable phases were found. CrB₆ boride, found by Gorbunov and Bodurjan [9] and also by Chépiga and Kuzma [10], is not boride, but it is oxyboride as it was later clarified [11]. Besides the phase, Gorbunov and Bodurjan [9] found Cr₄B and Cr₂B₅ phases. The phase that was predicted as Cr₂B₅ was not

observed by any other investigators neither in ternary B-Cr-Fe [10] nor in binary B-Cr system [12]. Regarding the Cr₄B phase, it was shown that the phase is orthorhombic Cr₂B phase [13]. The phase constitution of the system at 1373 K was investigated also by Gianoglio et al. [14], but, however, only in region up to 50 at% boron.

The present work is focused on experimental study of phase equilibria of the B-Cr-Fe system at 1353 K in the entire composition range after long time annealing within 1500–2205 h that guarantee to achieve equilibrium state.

2. Experimental Procedure

High purity powders of Fe (99.98%), B (99.9%), and Cr (99.99%) were used as input material for the production of twenty B-Cr-Fe alloys. Powders were mixed, pressed into cylindrical pellets at a pressure of 700 MPa, and subsequently melted. The melting was carried out in an argon arc furnace on water cooled copper plate in argon atmosphere of 99.999% purity. The solidified alloys (15 g) were remelted several times in order to achieve good homogeneity. The final chemical compositions of the produced alloys were determined by atomic absorption spectroscopy; see Table 1. The alloys were

TABLE 1: Chemical compositions of model alloys, conditions of annealing, and phases identified in the alloys after annealing.

Composition [at.%]	Annealing	Identified phases
17Fe-65B-18Cr	1353 K/1848 h	CrB ₂ , CrB ₄ , FeB
33Fe-62B-5Cr	1353 K/1848 h	B, FeB, CrB ₄
8Fe-56B-36Cr	1353 K/1848 h	Cr ₃ B ₄ , CrB
50Fe-40B-10Cr	1353 K/1848 h	Fe ₂ B, FeB
32Fe-40B-28Cr	1353 K/1848 h	CrB, FeB, Cr ₂ B
15Fe-40B-45Cr	1353 K/1848 h	CrB, Cr ₂ B, Cr ₅ B ₃
15Fe-25B-60Cr	1353 K/1848 h	Cr ₂ B, α (Cr,Fe)
8Fe-10B-82Cr	1353 K/1848 h	Cr ₂ B, α (Cr,Fe)
5Fe-52B-43Cr	1353 K/1848 h	CrB, Cr ₃ B ₄
48Fe-10B-42Cr	1353 K/1848 h	Cr ₂ B, α (Fe,Cr)
70Fe-10B-20Cr	1353 K/1848 h	Cr ₂ B, α (Fe,Cr)
8Fe-62B-30Cr	1353 K/1848 h	CrB ₂ , Cr ₃ B ₄
10Fe-25B-65Cr	1353 K/1848 h	Cr ₂ B, α (Cr,Fe)
3Fe-35B-62Cr	1353 K/1848 h	Cr ₂ B, Cr ₅ B ₃
10Fe-38B-52Cr	1353 K/1848 h	CrB, Cr ₂ B, Cr ₅ B ₃
37Fe-45B-18Cr	1353 K/2205 h	Fe ₂ B, FeB, Cr ₂ B
23Fe-45B-32Cr	1353 K/1500 h	Cr ₂ B, CrB, FeB
29Fe-51B-20Cr	1353 K/1688 h	Cr ₃ B ₄ , CrB, FeB
20Fe-52B-28Cr	1353 K/1688 h	Cr ₃ B ₄ , CrB, FeB
45Fe-30B-25Cr	1353 K/2205 h	Cr ₂ B, Fe ₂ B, γ (Fe,Cr)

then sealed into evacuated silica glass tubes with titanium turnings and annealed at 1353 K within 1500–2205 h. After the annealing, the samples were quenched into cold water.

The annealed material was studied by X-ray diffraction (Philips X'Pert Pro) and scanning electron microscopy (JEOL JSM-7000F) equipped with "Thermal FEG" and INCA EDX analyzer. The analyzer enables quantitative analysis for elements above and including atomic number 5 (boron). Backscattered electron image mode of scanning electron microscopy was used to study the alloy microstructure.

3. Results and Discussion

All phases identified by experimental method in alloys are given in Table 1. Two iron borides FeB and Fe₂B, six chromium borides Cr₂B, Cr₅B₃, CrB, Cr₃B₄, CrB₂, and CrB₄, and also iron and chromium solid solutions (α (Fe,Cr), α (Cr,Fe), γ (Fe,Cr)) and β -rhombohedral B were found in alloys. The borides in the system form at high temperatures. Most of them form from the liquid during production process of the alloys. Following long-term isothermal annealing leads to achievement of equilibrium chemical compositions of the phases. Crystallographic phase data of observed borides are given in Table 2. The CrB₄ boride was found in 17Fe-65B-18Cr and 33Fe-62B-5Cr alloys. This phase, known from binary B-Cr system [12], has not been observed in ternary B-Cr-Fe system till now [9, 10]. The Cr₂B₅ boride that was found by Gorbunov and Bodurjan at 1373 K after annealing for 320 h was not found. No ternary phase was found in the B-Cr-Fe system. It is in accordance with the mentioned literature [9, 10, 14].

TABLE 2: Crystal structure data of borides.

Phase	Pearson symbol	Space group	Reference
FeB	oP8	Pbmn	[15]
Fe ₂ B	tI12	I4/mcm	[15]
CrB ₄	oI10	Immm	[12]
CrB ₂	hP3	P6/mmm	[12]
Cr ₃ B ₄	oI14	Immm	[12]
CrB	oC8	Cmcm	[12]
Cr ₅ B ₃	tI32	I4/mcm	[12]
Cr ₂ B	oF40	Fddd	[12]

TABLE 3: Three-phase fields in experimentally determined B-Cr-Fe phase diagram at 1373 K according to the literature [9, 14].

[9]	[14]
FeB B CrB ₆	
FeB CrB ₆ Cr ₂ B ₅	
FeB Cr ₂ B ₅ CrB ₂	
FeB CrB ₂ Cr ₃ B ₄	
FeB CrB Cr ₃ B ₄	
FeB Fe ₂ B Cr ₂ B	FeB Fe ₂ B Cr ₂ B
FeB Cr ₂ B CrB	FeB Cr ₂ B CrB
Cr ₂ B Cr ₅ B ₃ CrB	Cr ₂ B Cr ₅ B ₃ CrB
Fe ₂ B α (Fe,Cr) γ (Fe,Cr)	Fe ₂ B α (Fe,Cr) γ (Fe,Cr)
Fe ₂ B α (Fe,Cr) Cr ₂ B	Fe ₂ B α (Fe,Cr) Cr ₂ B
Cr ₂ B Cr ₄ B α (Cr,Fe)	

Figure 1 shows SEM microstructure of the selected alloys. EDX-spectra of the borides in alloys are illustrated on Figure 2. X-ray diffraction patterns of the selected alloys are shown on Figure 3.

Four three-phase equilibria FeB+CrB₄+B (Figure 1(d)), FeB+CrB₄+CrB₂, FeB+CrB₂+Cr₃B₄, and FeB+Cr₃B₄+CrB (Figure 3(a)) were found in the part of phase diagram with boron content up to 50 at.% (Figure 4). There are some differences between phase equilibria presented in this paper and equilibria at 1373 K from work [9], as shown in Table 3. The differences in this part of the phase diagram are connected with the CrB₆ and Cr₂B₅ phases [9]. However, the CrB₆ phase, as was mentioned in introduction, is not right determined. The existence of Cr₂B₅ boride was not confirmed by present experimental results.

A part of the isothermal section of the phase diagram with boron range 33–50 at.% contains three three-phase equilibria CrB+Cr₅B₃+Cr₂B (Figure 3(c)), FeB+Cr₂B+Fe₂B, and FeB+CrB+Cr₂B (Figure 4). The same three-phase equilibria were found also at 1373 K in the works [9, 14].

Two three-phase equilibria Fe₂B+Cr₂B+ γ (Fe,Cr) (Figure 3(f)) and Cr₂B+ γ (Fe,Cr)+ α (Fe,Cr) are in the iron rich corner of the phase diagram at the temperature 1353 K (Figure 4). About 9 at.% of chromium was found in the γ (Fe,Cr)-phase in 45Fe-30B-25Cr alloy with phase equilibria

FIGURE 1: Microstructure of investigated B-Cr-Fe alloys after annealing at 1353 K for 1848 h: 50Fe-40B-10Cr (a); 15Fe-25B-60Cr (b); 8Fe-10B-82Cr (c); 33Fe-62B-5Cr (d); 8Fe-62B-30Cr (e).

$\text{Fe}_2\text{B} + \text{Cr}_2\text{B} + \gamma(\text{Fe}, \text{Cr})$. Both Gorbunov and Bodurjan [9] and Gianoglio et al. [14] found $\text{Fe}_2\text{B} + \text{Cr}_2\text{B} + \alpha(\text{Fe}, \text{Cr})$ and $\text{Fe}_2\text{B} + \gamma(\text{Fe}, \text{Cr}) + \alpha(\text{Fe}, \text{Cr})$ equilibria at 1373 K (Table 3), however, with different amount of chromium in the $\alpha(\text{Fe}, \text{Cr})$ -phase in $\text{Fe}_2\text{B} + \text{Cr}_2\text{B} + \alpha(\text{Fe}, \text{Cr})$ equilibrium, about 35 at.% of Cr according to [9] and 18 at.% according to [14]. The differences between observed phase fields of the part of isothermal section in the present work at 1353 K and in works [9, 14] at 1373 K indicate that the equilibrium phase fields are changed at temperature from temperature range 1353–1373 K.

All found borides dissolve third element. It is illustrated by EDX-spectra on Figure 2. Cr_2B phase has the highest solubility of the third element among all borides in the system.

The boride dissolves up to 39 at.% of Fe. The solubility is high also in CrB , FeB , and Fe_2B phases. It was found that Fe_2B contains up to 15 at.% of chromium and FeB dissolves up to 16 at.% of Cr. The CrB phase dissolves up to 15 at.% of Fe. Besides them, high solubility of iron is observed also in Cr_3B_4 boride, Figure 2(c), that contains up to 15 at.% of Fe. Various amounts of dissolved iron were measured also in other chromium borides. In particular, Cr_5B_3 contains up to 6 at.% of Fe, CrB_2 dissolves up to 2 at.% of Fe, Figure 2(b), and CrB_4 contains up to 7 at.% of Fe, Figure 2(a).

All the mentioned experimental results, that is, equilibrium phase compositions and composition of phases, were used to determine the isothermal section of B-Cr-Fe phase diagram at 1353 K that is shown in Figure 4.

FIGURE 2: EDX spectrum of the CrB_4 in 33Fe-62B-5Cr alloy (a); CrB_2 in 17Fe-65B-18Cr alloy (b); Cr_3B_4 in 8Fe-62B-30Cr alloy (c); CrB boride in 15Fe-40B-45Cr alloy (d); FeB boride in 50Fe-40B-10Cr alloy (e); Cr_2B boride in 15Fe-40B-45Cr alloy (f); Fe_2B boride in 50Fe-40B-10Cr alloy (g).

FIGURE 3: X-ray spectrum of the investigated B-Cr-Fe alloys after annealing at 1353 K: 20Fe-52B-28Cr alloy (a); 50Fe-40B-10Cr alloy (b); 10Fe-38B-52Cr alloy (c); 3Fe-35B-62Cr alloy (d); 15Fe-25B-60Cr alloy (e); 45Fe-30B-25Cr alloy (f).

FIGURE 4: The experimentally determined isothermal section of the B-Cr-Fe phase diagram at 1353 K. Compositions of model alloys are marked by *.

4. Conclusions

In the work, phase equilibria of the B-Cr-Fe model alloys at 1353 K were studied experimentally. The achieved results can be summarized as follows:

- (i) Two iron borides FeB and Fe_2B , six chromium borides Cr_2B , Cr_5B_3 , CrB , Cr_3B_4 , CrB_2 , and CrB_4 , and also iron and chromium solid solutions ($\alpha(\text{Fe,Cr})$, $\alpha(\text{Cr,Fe})$, $\gamma(\text{Fe,Cr})$) and β -rhombohedral B are equilibrium phases in the system at 1353 K.
- (ii) 8 three-phase equilibria were found in the phase diagram at the temperature.
- (iii) Solubilities of the third element in all binary borides were determined. High solubilities were found in Cr_2B , CrB , Cr_3B_4 , FeB , and Fe_2B phases.
- (iv) No ternary phase was found.

Based on the experimental results, isothermal section of the B-Cr-Fe system at 1353 K was established.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

The present work was supported by Slovak Grant Agency (VEGA) under Grant no. 2/0153/15. Thanks are also due to Dr. P. Repovský for help at production of alloys.

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