Phase analysis of Fe-B-V system

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Received 5 March 2012, received in revised form 8 October 2012, accepted 8 October 2012

Abstract

The paper deals with the study of the phases and phase composition of model alloys in Fe-B-V ternary system at 1353 K and 903 K. The experimental results were compared with calculated isothermal sections of the system. A ternary boride was found in a few alloys. Also micro-hardness of identified phases has been determined.

Key words: ternary system, phase composition, phase diagram, micro-hardness, boron

1. Introduction

The knowledge about phases in the Fe-B-V system is important in several fields of materials research. The elements as vanadium and boron are added into various complex alloys, e.g., modified ferritic and austenitic steels for energy industry. At present, boron is attracting a special attention in the production of creep resistant steels to suppress so-called type IV cracking and extend the creep life [1]. Vanadium is strong boride-forming element forming stable borides with high melting temperature, hardness and wear resistance.

The Fe-B-V system was investigated by Kuzma and Starodub [2] more than thirty years ago. They studied experimentally phase equilibria of the system at 1073 K after 300 h of annealing by X-ray diffraction on a series of alloys covering most of the phase diagram. Since then no new experimental or theoretical information about the system has been found.

The results described in the paper represent a part of the experimental results of a project dealing with the modelling of phase diagram of the mentioned ternary system. The paper describes our new experimental results about the phases and phase composition of the Fe-B-V system at 1353 K and 903 K. Besides, microhardness of the phases found has been evaluated. The first experimental results and detailed description of modelling phase diagram were published in [3].

2. Experimental procedure

Elements of high purity Fe (99.98 %), V (99.8 %) and B (99.9 %) were used for the preparation of model alloys in argon arc furnace. Their composition is given in Table 1. The batches (10–20 g) were remelted several times to achieve proper homogeneity. Then the samples were sealed in silica glass and annealed at 1353 K for 60 days and at 903 K for 190 days, with cooling in water after annealing.

The experimental material was studied using scanning electron microscopy (JEOL JSM-7000F "Thermal FEG") equipped with EDXS. The analyzer enables quantitative element analysis for elements from atomic number 5 (boron). The structure of alloys was identified by X-ray diffraction (Philips X'Pert Pro). Micro-hardness tester LECO LM 700-AT was used for the determination of micro-hardness of phases. Microhardness HV was evaluated using 100 g load and was measured on the samples annealed at 1353 K.

3. Results

Experimentally determined phase compositions of model alloys at given temperatures are shown in Table 1. Phases marked as BCC and FCC are solid solutions of iron and vanadium with bcc or fcc lattice. Examples of the microstructures of the investigated alloys are given in Fig. 1. EDX spectra of found bor-

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Fig. 1. Microstructure of Fe-B-V alloys (chemical composition of alloys is in at.%) after annealing at 1353 K for 60 days: a) 45Fe-34B-21V, b) 57Fe-20B-23V, c) 67Fe-18B-15V, and at 903 K for 190 days: d) 73Fe-25B-2V, e) 50Fe-45B-5V, f) 16Fe-60B-24V.

ides are shown in Fig. 2. Figure 3 shows an example of X-ray diffraction pattern.

All borides exhibit solubility of the third element. Up to 7 at.% of vanadium was found in Fe₂B, and up to 9 at.% in FeB. Similarly, various amounts of iron were measured in vanadium borides. In particular: up to 7 at.% Fe in VB, up to 22 at.% Fe in V₃B₄, and up to 3 at.% of Fe in VB₂.

Experimental alloys are marked in calculated isothermal sections of the phase diagram of the system at given temperatures (Fig. 4a,b). For calculations, software Thermo-Calc was used. Parameters needed for calculations and detailed description of the modelling were published in [3].

The results of measurements of identified phases are presented in Table 2.

Composition (at.%)	Annealing	Identified phases	
		1353 K	903 K
57Fe-20B-23V	$1353 \mathrm{~K}/60 \mathrm{~days}$	BCC, VB	
10Fe- 60 B- 30 V	1353 K/60 days	V_3B_4 , VB_2	
19Fe- 51 B- 30 V	1353 K/60 days	V_3B_4 , Fe_2B	
50Fe- 45 B- 5 V	903 K/190 days		V_3B_4 , FeB, Fe ₂ B
98Fe-0.7B-1.3V	1353 K/60 days, 903 K/190 days	FCC, Fe_2B	BCC
16Fe- 60 B- 24 V	903 K/190 days		V_3B_4 , FeB, VB_2
2Fe- $61B-37V$	1353 K/60 days	VB_2, V_3B_4, V_2B_3	
64Fe- 22 B- $17V$	903 K/190 days, 1353 K/60 days	BCC, Fe_2B , T	BCC, VB, T
73Fe-25B-2V	903 K/190 days, 1353 K/60 days	FCC, Fe_2B	Fe_2B , BCC
45Fe- 34 B- 21 V	1353 K/60 days	BCC, Fe_2B , T	

Table 1. Chemical composition of alloys, their heat treatment and experimentally found phases





Fig. 2. EDX spectrum of borides: a) T-phase in 45Fe-34B-21V alloy, b) Fe₂B in 73Fe-25B-2V alloy, c) FeB in 50Fe-45B-5V alloy, d) VB in 57Fe-20B-23V alloy, e) V₃B₄ in 50Fe-45B-5V alloy, f) V₂B₃ in 2Fe-61B-37V alloy, g) VB₂ in 5Fe-60B-35V alloy.



Fig. 3. X-ray diffraction pattern of 73Fe-25B-2V alloy after annealing at 903 K.

4. Discussion

4.1. Phases: binary borides, BCC, FCC, sigma, liquid, and rhombohedral B, ternary phase T

In the ternary system, there are two stable iron binary borides FeB and Fe₂B that are known in Fe-B system [4, 5], and six vanadium binary borides V_3B_2 , VB, V_5B_6 , V_3B_4 , V_2B_3 , and VB₂ in V-B system. In the investigated alloys most of the mentioned phases have been found in dependence on an alloy composition (Table 1).

Borides in the ternary system dissolve some amount of the third element. High solubility of iron in V_3B_4 boride (up to 22 at.% Fe) was found in agreement with the paper [2]. Similarly, the values of solubility of the third element in the other borides according Kuzma and Starodub [2] are comparable with our results.

Solubility of boron in BCC and FCC has not been observed in our experimental measurements. However,

Table 2. Micro-hardness of identified phases after isothermal annealing at 1353 K

Phase	$\mathrm{HV}_{0.1}$	Structure
Fe_2B	1600 - 1900	Tetragonal
V_3B_2	2200 - 2400	Tetragonal
VB	2300 - 2700	Orthorhombic
V_3B_4	2400 - 2700	Orthorhombic
V_2B_3	2500 - 2900	Orthorhombic
VB_2	2400 - 3700	Hexagonal
T-ternary phase	2900 - 3100	Unknown
BCC	200 - 700	Cubic
FCC	150	Cubic

its solubility in these phases according to [4, 6, 7] is negligible. Phases as sigma, liquid and rhombohedral B have not been investigated in regard to alloys composition and temperatures.

Besides the binary phases, a ternary boride T was found in 45Fe-34B-21V alloy at 1353 K and in 61Fe--22B-17V alloy at both temperatures. No ternary phase was found in the ternary system by Kuzma and Starodub [2]. However, phase T was found in 67Fe--18B-15V alloy in our earlier work [3] (Fig. 1c). New experimental results confirm the existence of the ternary phase in the system. The phase coexists with BCC and VB phase in 61Fe-22B-17V alloy at 903 K, and with BCC and Fe₂B phase in 61Fe-22B-17V and 45Fe--34B-21V alloys at 1353 K (Fig. 1a). Its boron content is approx. 40 at.%, it also contains approx. 28 at.% of Fe.

4.2. Comparison with calculations

The experimental results were used for verification of the phase diagram. Two isothermal sections



Fig. 4. Calculated isothermal sections of the phase diagram of Fe-B-V system: a) at 1353 K, b) at 903 K, with marked experimental alloys.

at 1353 K and 903 K were calculated (Fig. 4). Results of phase analyses for all alloys at 1353 K besides 2Fe-61B-37V alloy are in a very good agreement with calculations (Fig. 4a). The alloy 2Fe-61B-37V does not completely correspond to the calculated equilibrium, nevertheless, it exhibits the phase composition corresponding to the neighbouring phase field. With respect to small uncertainties in establishing of the precise overall composition of alloys, this agreement is very good.

The comparison of our experimental results and calculations for 903 K showed that results for alloys 98Fe-0.7B-1.3V, 16Fe-60B-24V and 73Fe-25B-2V are in good agreement with calculations (Fig. 4b). The experimentally found phase composition of alloys 50Fe-45B-5V and 61Fe-22B-17V corresponds to the neighbouring phase field. The difference between experimental results and calculations at this temperature can be explained similarly as at higher temperature.

4.3. Micro-hardness

Micro-hardness of BCC phase was found to increase with increasing vanadium amount in the phase from 200 to 700. For iron with very small amount of vanadium (about 0.86 at.%), the micro-hardness of 150 HV was found. Comparative value of micro-hardness for pure iron about 130 HV was found by Ozdemir [8].

Generally, vanadium borides can be said to have higher values of HV than iron borides, which was the expected result. Order of vanadium borides with increasing micro-hardness is following: V_3B_2 , VB, V_3B_4 , V_2B_3 , and VB₂ (Table 2). Regarding vanadium borides, only a pair of information has been found in literature.

The only values of vanadium boride micro-hardness found in literature are those by Goncarov [9]. He studied thin layer of VB₂ boride on steels and determined values of its micro-hardness in the range 12–20 GPa (1224–2039 HV). The values given in Table 2 for this phase are considerably higher (2400–3700 HV). However, Goncarov himself admitted the possible effect of supporting material. This could explain lower values in [9] than those in Table 2, because the alloys with VB₂ phase are harder than arbitrary steels. In our case, the borides were present in a whole volume of alloys.

The range of micro-hardness values of Fe_2B phase obtained in this work is 1600–1900 HV (Table 2). Ozdemir et al. [8] mentioned micro-hardness of Fe_2B phase > 1700 HV, Kulka et al. [10, 11] published values 1300–1600 HV, and according to Sen [12], the values ranged from 1160 to 1920 HV. Micro-hardness of the iron boride given in literature was measured in a thin layer on steels or pure iron, what was comparable with our conditions when the borides were embedded in the iron-BCC phase. It also explains better agreement of micro-hardness of Fe_2B phase with literature values than that for VB_2 .

5. Conclusions

In the present work, the phases and phase compositions of Fe-B-V alloys were studied by experimental method. Experimental results were compared with calculations. Conclusions can be summarized as follows:

- The existence of ternary phase T in the system was confirmed by more alloys.

– Experimental results are in good agreement with thermodynamic calculations.

- Micro-hardness of phases found in the studied system at 1353 K was determined.

Acknowledgements

The presented work was supported by the Slovak Grant Agency (VEGA) under grant No. 2/0153/12 and the Czech Science Foundation under grant No. P108/10/1908.

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