

Phase equilibria in the Fe–Cr–V system at 900°C

V.N. KUZNETSOV¹, E.G. KABANOVA^{1*}, G.P. ZHMURKO¹

¹ Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory, 1, Build. 3, 119992 Moscow, Russian Federation

* Corresponding author. E-mail: kabanova@general.chem.msu.ru

Received May 30, 2008; accepted December 15, 2008; available on-line March 19, 2009

The phase equilibria in the Fe–Cr–V ternary system at 900°C (1173 K) were studied using XRD, metallography and EPMA. The main attention was focused on the character of propagation of the σ phase from the Fe–V edge into the ternary system. As shown by the present data, at 900°C the field of the σ phase is directed from the Fe–V side towards the composition of the σ phase of the Fe–Cr binary edge (which is virtual at that temperature). The solubility of Cr in the σ phase at 900°C reaches about 40 at.-%.

Transition metal alloys and compounds / Phase diagrams / Metallography / X-ray diffraction

Introduction

Chromium and vanadium belong to the most important alloying elements of ferritic steels which have wide industrial applications. Unfortunately both form σ phases with iron, which cause severe degradation of material properties. Consequently, to control the conditions of formation and the stability fields of the σ phases in multi-component systems is an actual practical problem, which can be solved on the basis of knowledge about appropriate phase diagrams. For multicomponent systems thermodynamic modeling seems to be the only way to get information about the phase equilibria. This needs, in turn, detailed experimental data for the boundary ternary systems.

The constitution of the Fe–Cr and Fe–V binaries is well known [1,2]. The σ phases in both systems are formed by congruent transformation from the bcc solid solution at nearly the same compositions (47 at.% Cr and 48 at.% V), but at different temperatures (830 and 1219°C, respectively). In the Cr–V system only liquid and bcc phases exist; neither compound formation, nor miscibility gap were reported [2,3].

The phase equilibria in the Fe–Cr–V ternary system were studied by Martens and Duwez [4], who plotted the isothermal section of the system at 700°C, using metallography and XRD. Kornilov and Matveeva [5] used thermal analysis, metallography, XRD and measurements of hardness and electric conductivity to investigate the temperatures of the σ →bcc transition and study the vertical sections FeCr–FeV, and Fe–Cr:V = 3:1, 1:1 and 1:3 (mass ratio). In addition the “room temperature” section of

the system was constructed using samples that had been furnace cooled after annealing at 700°C. The resulting section proved to be close to that of [4]. Wasman and Demidenko [6] measured the temperatures of the σ →bcc transformation, as well as some physical properties of the σ phase, for two alloys (Fe₅₀Cr₂₅V₂₅ and Fe₆₀Cr₂₀V₂₀). In our laboratory the isothermal section at 1150°C was plotted [7] using the diffusion couple method, supplemented by a study of two specially chosen bulk alloys.

The two known isothermal sections of the Fe–Cr–V system are presented in Fig. 1. At the lower temperature (left panel) a continuous solid solution exists between the σ phases of the Fe–Cr and Fe–V edges, but at the higher temperature (right panel) the homogeneity range of the σ phase is limited and directed toward the Cr corner instead of the composition of the σ phase of Fe–Cr binary. The aim of the present work was to establish the character of penetration of the field of the phase into the Fe–Cr–V ternary system at 900°C, which is midway between the temperatures of the previous studies.

Experimental

The equilibria between the bcc and σ phases were studied by metallography, XRD and EPMA analysis of 17 samples. The starting materials were Armco iron (99.95% purity) and electrolytic vanadium (99.17%) and chromium (99.47%). Samples of 5 g mass were prepared by arc melting with a non-consumable tungsten electrode in an atmosphere of purified argon. They were re-melted several times with turning to achieve homogeneity. The mass losses after the melting were typically about 0.5-0.7% and never

Table 1 Identification of phases and their lattice parameters.

Sample No.	Gross composition	Phases	Lattice parameters, pm	
			<i>a</i>	<i>c</i>
1	Cr ₅₅ Fe ₄₀ V ₅	bcc	288.1(2)	
2	Cr ₄₅ Fe ₅₀ V ₅	bcc	288(1)	
3	Cr ₃₅ Fe ₆₀ V ₅	bcc σ (traces)	287.7(2)	
4	Cr ₂₅ Fe ₇₀ V ₅	bcc	287.5(2)	
5	Cr ₄₅ Fe ₄₅ V ₁₀	bcc	288.2	
6	Cr ₃₅ Fe ₅₅ V ₁₀	σ	880.5(8)	446.34(2)
7	Cr ₂₅ Fe ₆₅ V ₁₀	bcc σ	288.48 881.6(1)	461.7(1)
8	Cr ₅₀ Fe ₃₅ V ₁₅	bcc	288.8(2)	
9	Cr ₄₀ Fe ₄₅ V ₁₅	bcc σ	288.1(1) 881.4(2)	457.0(2)
10	Cr ₂₅ Fe ₆₀ V ₁₅	σ	880.8(3)	457.0(2)
11	Cr ₁₅ Fe ₇₀ V ₁₅	bcc σ (traces)	288.7(2)	
12	Cr ₃₀ Fe ₄₅ V ₂₅	bcc σ	289.6(2) 886.97(3)	459.3(3)
13	Cr ₃₀ Fe ₃₅ V ₃₅	bcc	290.1(1)	
14	Cr ₃₀ Fe ₂₅ V ₄₅	bcc	290.4(2)	
15	Cr ₂₀ Fe ₄₀ V ₄₀	bcc σ	289.7(2) 889.9(2)	459.9(2)
16	Cr ₂₀ Fe ₃₅ V ₄₅	bcc	290.1(2)	
17	Cr ₂₀ Fe ₃₀ V ₅₀	bcc	290.2(1)	

exceeded 1.5%. The actual composition of a number of samples was controlled by EPMA.

The samples were annealed in evacuated silica ampoules and annealed at 900°C for 650 h with subsequent quenching in cold water.

Phase analysis was performed by scanning electron microscopy using a CARL ZEISS apparatus, and powder XRD using a DRON-4 diffractometer (monochromatized CuK_α radiation). Powders were obtained by either grinding the samples in an agate mortar, or using a diamond file, and were annealed at 600°C for 6 h to eliminate the stress. STOE programs were used for phase identification and for the calculation of the lattice parameters.

The chemical composition of the phases was determined by EPMA using energy dispersive add-on EVO-50 XVP. K_α Fe, K_β Cr, and K_β V were used as analytical lines.

Results and discussion

The results of the XRD analysis (phases detected in the samples and their lattice parameters) are summarized in **Table 1**. As may be expected, only bcc and σ phases were found to exist at the temperature of our study. In the samples Nos. 3 and 11 the amount of precipitated σ phase was small, and its lattice parameters could not be determined. The bcc phase clearly prevailed also in the samples 7 and (to a lesser extent) 9.

Table 2 Compositions of phases as obtained by EPMA.

Sample No.	Phase	Composition, at.%		
		Fe	Cr	V
5	bcc	45.8	44.4	9.8
6	σ	54.3	36.2	9.5
7	bcc	64.6	25.8	9.6
8	bcc	35.8	49.6	14.6
9	bcc	45.2	40.8	14
	σ	49.5	35.8	14.7
10	σ	59.7	25.5	14.8
	bcc	36.9	38.6	24.5
12	σ	47.2	29.6	23.3

The identification of the phase compositions of the samples was confirmed by scanning electron microscopy.

EPMA of single-phase samples was performed for an extra check of their compositions, and for two-phase samples the compositions of the co-existing phases were measured, *i.e.* conodes of the two-phase equilibrium were established. The results of EPMA are presented in **Table 2**. The labeling of the samples in this table corresponds to **Table 1**.

The actual compositions of the single-phase specimens proved to be nearly identical to the nominal ones. Two phases were clearly distinguished in the two-phase samples 9 and 12, and their compositions were measured. The composition of the σ phase in the

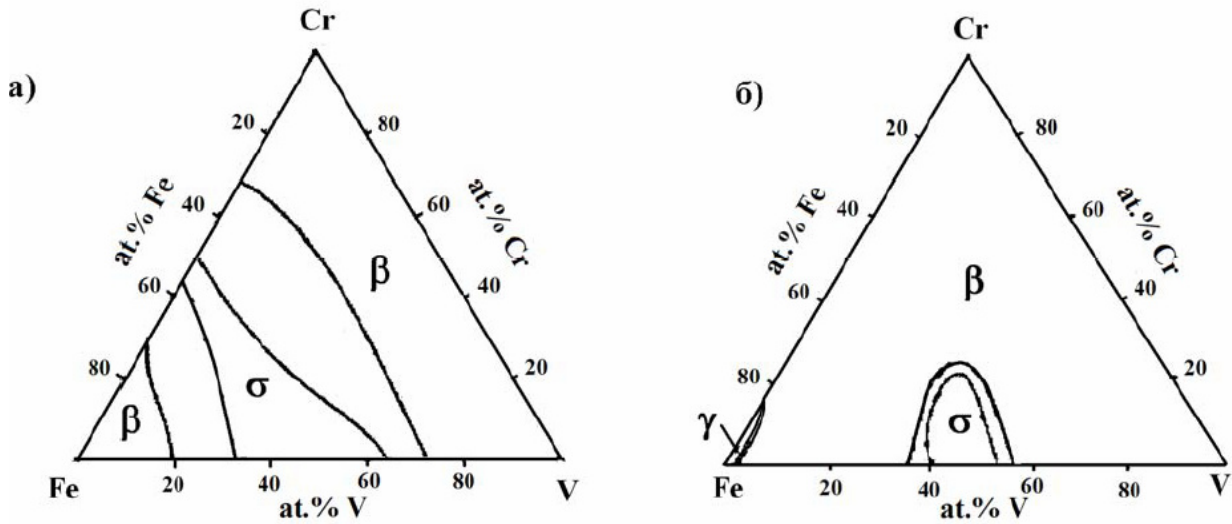


Fig. 1 Isothermal sections of the Fe–Cr–V system at (a) 700°C [4] and (b) 1150°C [7].

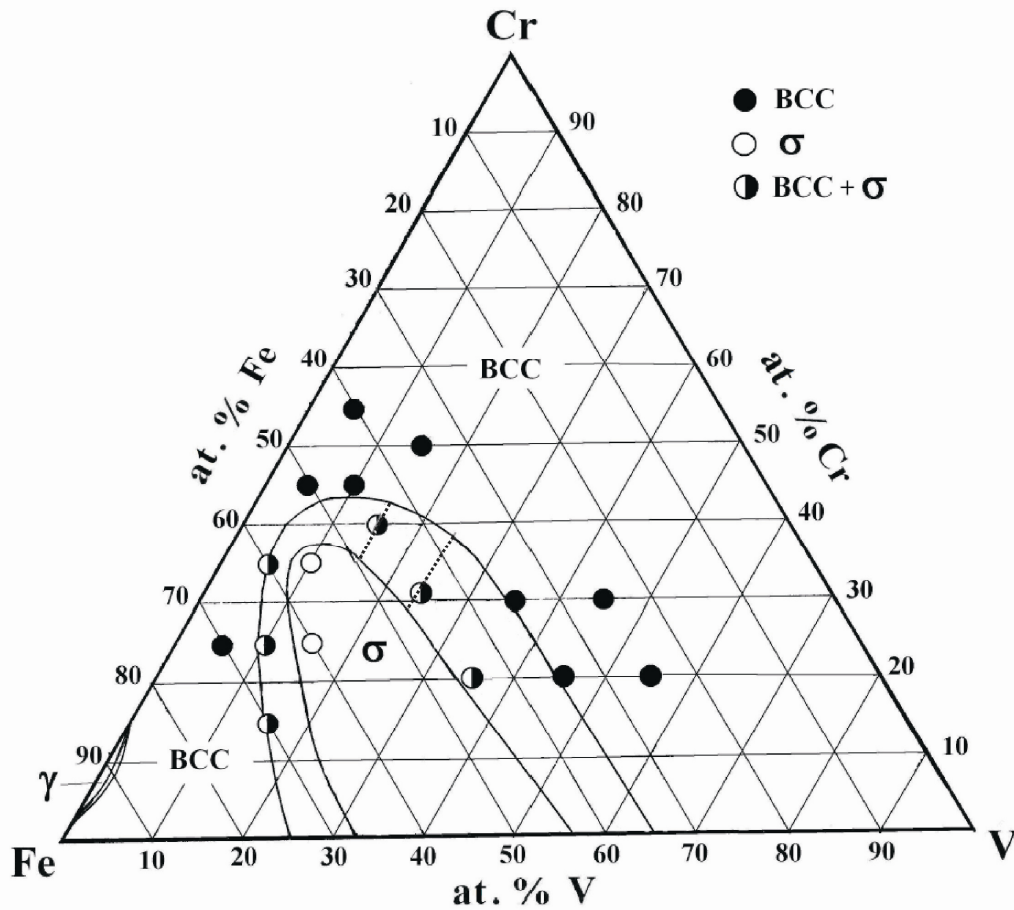


Fig. 2 Isothermal section of the Fe–Cr–V system at 900°C. Dotted lines are conodes, determined by EPMA.

sample No. 7 could not be determined due to the small amount and high dispersion of the precipitates.

The results enabled us to plot the isothermal section of the Fe–Cr–V system at 900°C, which is presented in Fig. 2. The points in this figure

correspond to samples with ascertained phase composition, and the dotted lines are conodes, determined by EPMA.

Comparing Fig. 2 with Fig. 1, it may be seen that the character of the equilibria between the bcc and σ

phases at 900°C is closer to that at 700°C. The field of the σ phase is directed to the composition range of the phase in the Fe–Cr binary. The solubility of Cr in the phase σ -FeV is about 40 at.%, and the phase closely approaches the Fe–Cr side. It may be related to the fact that the temperature of the present investigation is not much higher than the upper limit of stability of the σ phase in the Fe–Cr binary system, which is 830°C. The change of direction of penetration of σ -FeV into the ternary system takes place at higher temperatures.

Acknowledgements

This work was performed under partial support of the Russian Foundation of Basic Research, project No. 06-03-33152.

References

- [1] O. Kubaschewski, *Iron Binary Phase Diagrams*, Springer-Verlag, Berlin, 1982 (Russ. transl.: Metallurgiya, Moscow, 1985).
- [2] T.B. Massalski (Ed.), *Binary Alloy Phase Diagrams*, 2nd Ed., ASM International, Materials Park, OH, 1990.
- [3] B.-J. Lee, *Z. Metallkd.* 83 (1992) 292-299.
- [4] H. Martens, P. Duwez, *Trans. ASM* 44 (1952) 484-494.
- [5] I.I. Kornilov, N.M. Matveeva, *Zh. Neorg. Khim.* 2 (1957) 355-366.
- [6] G.I. Wasman, W.S. Demidenko, *Coll. Abstr. X All-Union Conf. Cryst. Chem. Intermet. Compds.*, Lviv, 1989, p. 180.
- [7] Zh.N. Toybayev, Ph.D. Thesis Abstr., Lomonosov Moscow State University, 1998.