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PHASE EQUILIBRIA UP TO THE SOLIDUS LINE IN THE SYSTEM Fe_2WO_6–$Fe_8V_{10}W_{16}O_{85}$

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Abstract

Phase equlibria in the solid state in the system Fe_2WO_6–$Fe_8V_{10}W_{16}O_{85}$ were studied by means of X-ray phase powder diffraction and differential thermal analysis, This system is one of the intersections of the three-component system Fe_2O_3–V_2O_5–WO_3. The investigation demonstrated that the system is not a real two-component system even below the solidus line.

Keywords: phase equilibria, system Fe_2WO_6–$Fe_8V_{10}W_{16}O_{85}$

Introduction

Pure transition metal oxides and their derivative compounds have interesting catalytic properties, and are mainly finding use as catalysts for the oxidation of organic substances [1–3]. We are therefore interested in multicomponent systems of such oxides, and especially in new phases occurring in the system and the phase equilibria in them. The three-component system Fe_2O_3–V_2O_5–MoO_3 [4] and Cr_2O_3–V_2O_5–MoO_3 [5, 6] were investigated previously. The present investigations relate to the three-component system Fe_2O_3–V_2O_5–WO_3, and in particular to the phase equilibria in the solid state in one of the intersections of this system.

Fe_2WO_6 was known before we started our work [7, 8]. It was recently found to occur in three polymorphic modifications [9], and not in two as had been thought earlier [7, 8]. The characteristics of the three modifications are known [9] as is the crystallographic structure of the high-temperature variety, γ-Fe_2WO_6 [10]. Fe_2WO_6 is reported to melt incongruently, at 1156°C [11] or at 1136°C [10]. We found that Fe_2WO_6 melts at 1100±10°C [12] to deposit solid α-Fe_2O_3 [12]. We also earlier found that a solid solution of V_2O_5 in α- and β-Fe_2WO_6 modifications is formed in the system Fe_2O_3–V_2O_5–WO_3 [13].

The other component of the investigated system, $Fe_8V_{10}W_{16}O_{85}$, is a new compound, obtained by us and found to arise in the solid state when all three components of the system Fe_2O_3–V_2O_5–WO_3 are used [14]. The compound

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crystallizes in the othorhombic system; its X-ray characteristics have been established [15]. $Fe_8V_{10}W_{16}O_{85}$ melts incongruently at 830±5°C, depositing two solid products: WO_3 and Fe_2WO_6 [12].

Experimental

The compounds used for the experiments were α-Fe_2O_3, p.a., a product of VEB Laborchemie, Apolda (Germany), additionally heated at 1000°C in 3×24 h cycles; V_2O_5, p.a., a product of POCh, Gliwice (Poland); and WO_3, p.a., a product of Fluka AG (Switzerland), calcined at 700°C for 24 h.

18 samples were prepared for the experiments, so as to cover the whole component concentration range for the system under study. Mixtures of the oxides, weighed in the given proportions, were homogenized by grinding and then shaped into pastilles. The pastilles were placed in porcelain crucibles and heated in air in a sylite furnace equipped with a temperature regulator. The conditions for establishment of the equilibrium state were determined in preliminary tests. All samples were heated in the following cycles:

$$650°C(24\ h\times2)+700°C(48\ h\times2)+705°C(240\ h+96\ h).$$

After each heating cycle, the samples were slowly cooled to ambient temperature, ground down and examined by DTA and X-ray phase powder diffraction. The ground samples were again shaped into pastilles and subjected to further heating. Preparations were considered to be at equilibrium if the phase composition was found to be unchanged between two successive heating cycles.

The phase compositions of the preparations were established from their X-ray powder diffraction patterns. An X-ray diffractometer (DRON-3, Russia) was used for the measurements. A Co lamp with an Fe filter served as radiation source. The phases were identified on the basis of data listed in PDF cards [16] and in publications [9, 15].

DTA investigations were carried out with a Paulik-Paulik-Erdey derivatograph (MOM, Budapest). Measurements were made on samples of 1000 mg in quartz crucibles, in air, over the range 20–1000°C, at a heating rate of 10 deg·min^{-1}. The accuracy of the temperature reading was found after repeated readings to be ±5 deg.

Results and discussion

Table 1 lists the compositions of the initial mixtures and the X-ray phase powder diffraction data on the equilibrium preparations. It follows from the data in Table 1 that the first preparation formed at a Fe_2WO_6 content of 99.00 mol%

Table 1 Composition of initial mixtures and results of X-ray phase analysis of preparations being at equilibrium in the Fe_2WO_6–$Fe_8V_{10}W_{16}O_{85}$ system

No.	Composition of initial mixtures / mol%				Phase composition of equilibrium samples[a]
	Fe_2O_3	V_2O_5	WO_3	Fe_2WO_6 in terms of component system	
1	2	3	4	5	6
1	46.19	2.24	51.57	99.00	β-$Fe_2WO_{6(S.S.)}$, WO_3
2	41.75	4.85	53.40	97.50	WO_3, β-$Fe_2WO_{6(S.S.)}$, $Fe_8V_{10}W_{16}O_{85}$
3	36.51	7.94	55.55	95.00	WO_3, $Fe_8V_{10}W_{16}O_{85}$, β-$Fe_2WO_{6(S.S.)}$
4	30.23	11.63	58.14	90.00	WO_3, $F_{e8}V_{10}W_{16}O_{85}$, β-$Fe_2WO_{6(S.S.)}$
5	26.61	13.76	59.63	85.00	WO_3, $Fe_8V_{10}W_{16}O_{85}$, β-$Fe_2WO_{6(S.S.)}$
6	24.24	15.15	60.61	80.00	$Fe_8V_{10}W_{16}O_{85}$, WO_3, β-$Fe_2WO_{6(S.S.)}$
7	22.58	16.13	61.29	75.00	$Fe_8V_{10}W_{16}O_{85}$, WO_3, β-$Fe_2WO_{6(S.S.)}$
8	21.35	16.85	61.80	70.00	$Fe_8V_{10}W_{16}O_{85}$, WO_3, β-$Fe_2WO_{6(S.S.)}$
9	20.40	17.41	62.19	65.00	$Fe_8V_{10}W_{16}O_{85}$, WO_3, β-$Fe_2WO_{6(S.S.)}$
10	19.64	17.86	62.50	60.00	$Fe_8V_{10}W_{16}O_{85}$, WO_3, β-$Fe_2WO_{6(S.S.)}$
11	19.03	18.22	62.75	55.00	$Fe_8V_{10}W_{16}O_{85}$, WO_3, β-$Fe_2WO_{6(S.S.)}$
12	18.52	18.52	62.96	50.00	$Fe_8V_{10}W_{16}O_{85}$, WO_3, β-$Fe_2WO_{6(S.S.)}$
13	17.90	18.88	63.22	42.50	$Fe_8V_{10}W_{16}O_{85}$, WO_3,
14	17.40	19.18	63.42	35.00	$Fe_8V_{10}W_{16}O_{85}$, WO_3,
15	17.00	19.41	63.59	27.50	$Fe_8V_{10}W_{16}O_{85}$
16	16.67	19.61	63.72	20.00	$Fe_8V_{10}W_{16}O_{85}$
17	16.38	19.78	63.84	12.50	$Fe_8V_{10}W_{16}O_{85}$
18	16.14	19.92	63.94	5.00	$Fe_8V_{10}W_{16}O_{85}$

[a] In order of decreasing phase content

Table 2 Composition of initial mixtures and calculated phase composition of preparations being at equilibrium in the Fe_2WO_6–$Fe_8V_{10}W_{16}O_{85}$ system

	Composition of initial mixtures / mol%				Calculated phase composition of equilibrium samples / mol%		
Sample No.	Fe_2O_3	V_2O_5	WO_3	Fe_2WO_6 in terms of component systems	β-Fe_2WO_6	$Fe_8V_{10}W_{16}O_{85}$	WO_3
1	2	3	4	5	6	7	8
13	17.90	18.88	63.22	42.50	1.39	83.72	14.89
14	17.40	19.18	63.42	35.00	1.05	87.77	11.18
15	17.00	19.41	63.59	27.50	0.77	90.97	8.26
16	16.67	19.61	63.72	20.00	0.52	94.27	5.21
17	16.38	19.78	63.84	12.50	0.30	96.45	3.25
18	16.14	19.92	63.94	5.00	0.11	98.90	0.99

is a mixture of two phases: β-$Fe_2WO_{6(s.s.)}$ and WO_3. Preparations formed from 97.50–50.00 mol% of Fe_2WO_6 (in terms of the system components) are three-phase mixtures of $Fe_8V_{10}W_{16}O_{85}$, WO_3 and β-$Fe_2WO_{6(s.s.)}$. The diffraction patterns of preparations obtained from initial mixtures containing 42.50 and 35.00 mol% of Fe_2WO_6 exhibited lines typical of the phases $Fe_8V_{10}W_{16}O_{85}$ and WO_3, whereas the diffraction patterns of preparations obtained from mixtures containing 27.50 mol% or less of Fe_2WO_6 displayed lines characteristic only of the phase $Fe_8V_{10}W_{16}O_{85}$. However, the results of earlier studies [12] imply that all preparations with compositions lying on that section should be three-phase mixtures and contain β-$Fe_2WO_{6(s.s.)}$ besides WO_3 and $Fe_8V_{10}W_{16}O_{85}$. Detectability tests on phases containing $Fe_8V_{10}W_{16}O_{85}$ in large excess demonstrated that X-ray phase powder diffraction is suitable for the detection of at least 1.50 mol% of β-Fe_2WO_6 and at least 10 mol% of WO_3. It can be assumed that the contents of β-Fe_2WO_6 and WO_3 in preparations in which the presence of these phases was not ascertained are below the detection limits. In order to support this, calculations were made and the findings are presented in columns 6–8 of Table 2. The results confirmed that it was impossible to detect either β-Fe_2WO_6 (column 6) or WO_3 (column 8, No. 15 and the following) by X-ray phase powder diffraction.

It can inferred from the experiments that the system Fe_2WO_6–$Fe_8V_{10}W_{16}O_{85}$ is not a real two-component system, even below the solidus line.

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Zusammenfassung — Mittels Röntgenpulverdiffraktion und Differentialthermoanalyse wurde das Phasengleichgewicht im festen Zustand des Systemes Fe_2WO_6-$Fe_8V_{10}W_{16}O_{85}$ untersucht. Dieses System ist eine der Schnittlinien des Dreikomponentensystemes Fe_2O_3-V_2O_5-WO_3. Die Untersuchungen zeigen, daß das System unterhalb der Solidus-Linie kein echtes Zweikomponentensystem ist.