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PHASE EQUILIBRIA UP TO THE SOLIDUS LINE IN THE SYSTEM Fe_2O_3–$Fe_8V_{10}W_{16}O_{85}$

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Abstract

Phase equilibria up to the solidus line in the system Fe_2O_3–$Fe_8V_{10}W_{16}O_{85}$ were determined 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 studies revealed that this is not a real binary system, even in the solid state.

Keywords: phase equilibria, system Fe_2O_3 – $Fe_8V_{10}W_{16}O_{85}$

Introduction

Multicomponent systems of transition metal oxides are mainly of interest because of the catalytic properties both of their components and of the resultant phases. Studies on the phase equilibria in such systems are of importance in work on new catalysts with high activity and selectivity. The studies also lead to the discovery of new materials.

The present work covers studies on the phase equilibria up to the solidus line of the system Fe_2O_3–$Fe_8V_{10}W_{16}O_{85}$, one of the sections of the three-component system Fe_2O_3–V_2O_5 – WO_3.

Fe_2O_3 crystallizes in the rhombohedral system at temperatures higher than 427°C [1]. At temperatures higher than 1000°C, α-Fe_2O_3 undergoes thermal decomposition, loses part of its oxygen, and is converted into Fe_3O_4 [2, 3].

Our experiments with the system under discussion led to a new compound in the solid state, involving all three components of the system, to which the following molecular formula has been attributed: $Fe_8V_{10}W_{16}O_{85}$ [4]. The compound crystallizes in the orthorhombic system; its X-ray characteristics are known [5]. $Fe_8V_{10}W_{16}O_{85}$ melts incongruently at 830±5°C to yield two solid products: Fe_2WO_6 and WO_3 [6]. Further investigations demonstrated that a solid solution of V_2O_5 is formed in the three-component system, occurring in two of three possible polymorphic modifications of Fe_2WO_6 [7]. The form β-Fe_2WO_6 was described and characterized recently [8].

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Experimental

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

Mixtures of the oxides, weighed in appropriate proportions, were homogenized by grinding, shaped into pastilles and then heated in air at the given temperatures and in the given heating cycles. Both the temperature and the duration of heating were established in preliminary tests.

17 samples were prepared for the experiments, covering the whole component concentration range for the system under study. The compositions of the samples are given in Table 1. The samples were heated as follows:

$$650°C(24\ h\times2)+700°C(24\ h+48\ h)+710°C(120\ h\times2)$$

After each heating cycle, the samples were slowly cooled down to ambient temperature, ground and examined by X-ray phase powder diffraction and DTA. The powdered samples were again shaped into pastilles and heated in a new cycle. Preparations were considered to be at equilibrium if the phase composition did not undergo any change between two successive heating cycles.

The phase compositions of the samples were established from their powder diffraction patterns, obtained by using an X-ray diffractometer (DRON-3, Russia). The radiation source was a Co lamp equipped with a Fe filter. The resultant phases were identified with the aid of data listed in PDF cards [9] and in publications [5, 8].

DTA measurements were carried out at 20–1000°C in air with a Paulik-Paulik-Erdey derivatograph (MOM, Budapest). Samples of 1000 mg were placed in quartz crucibles, and the heating rate was 10 deg·min^{-1}. The accuracy of the temperature reading in repeated measurements found to be ±5 deg.

Results and discussion

Table 1 gives the compositions of the initial mixtures and the results of phase analysis of preparations at equilibrium. The data reveal that preparations formed from initial mixtures containing 98.00 or 95.00 mol% of Fe_2O_3 are three-phase mixtures, composed of α-Fe_2O_3, $FeVO_4$ and β-$Fe_2WO_{6(s.s.)}$. The diffraction patterns of preparations obtained from initial mixtures containing from 90.00 to 42.50 mol% of α-Fe_2O_3 displayed diffraction lines of three phases: $FeVO_4$, $Fe_8V_{10}W_{16}O_{85}$ and β-$Fe_2WO_{6(s.s.)}$. The diffraction patterns of other equilibrium preparations exhibited reflexions characteristic of $Fe_8V_{10}W_{16}O_{85}$ and $FeVO_4$. However, investigations on the system $FeVO_4$–WO_3 [6] give grounds for

Table 1 Composition of initial mixtures and results of X-ray phase analysis of preparations being at equilibrium in the Fe_2O_3–$Fe_8V_{10}W_{16}O_{85}$ system

No.	Composition of initial mixtures /mol%				Phase composition of equilibrium samples[a]
	Fe_2O_3	V_2O_5	WO_3	Fe_2O_3 in terms of component system	
1	2	3	4	5	6
1	71.62	6.76	21.62	98.00	α-Fe_2O_3, $FeVO_4$, β-$Fe_2WO_{6(s.s.)}$
2	52.27	11.36	36.36	95.00	$FeVO_4$, α-Fe_2O_3, β- $Fe_2WO_{6(s.s.)}$
3	38.23	14.71	47.06	90.00	$FeVO_4$, $Fe_8V_{10}W_{16}O_{85}$, β-$Fe_2WO_{6(s.s.)}$
4	31.52	16.30	52.18	85.00	$FeVO_4$, $Fe_8V_{10}W_{16}O_{85}$, β-$Fe_2WO_{6(s.s.)}$
5	27.59	17.24	55.17	80.00	$FeVO_4$, $Fe_8V_{10}W_{16}O_{85}$, β-$Fe_2WO_{6(s.s.)}$
6	25.00	17.86	57.14	75.00	$Fe_8V_{10}W_{16}O_{85}$, $FeVO_4$, β-$Fe_2WO_{6(s.s.)}$
7	23.17	18.29	58.54	70.00	$Fe_8V_{10}W_{16}O_{85}$, $FeVO_4$, β-$Fe_2WO_{6(s.s.)}$
8	21.81	18.62	59.57	65.00	$Fe_8V_{10}W_{16}O_{85}$, $FeVO_4$, β-$Fe_2WO_{6(s.s.)}$
9	20.75	18.87	60.38	60.00	$Fe_8V_{10}W_{16}O_{85}$, $FeVO_4$, β-$Fe_2WO_{6(s.s.)}$
10	19.91	19.07	61.02	55.00	$Fe_8V_{10}W_{16}O_{85}$, $FeVO_4$, β-$Fe_2WO_{6(s.s.)}$
11	19.23	19.23	61.54	50.00	$Fe_8V_{10}W_{16}O_{85}$, $FeVO_4$, β-$Fe_2WO_{6(s.s.)}$
12	18.41	19.43	62.16	42.50	$Fe_8V_{10}W_{16}O_{85}$, $FeVO_4$, β-$Fe_2WO_{6(s.s.)}$
13	17.77	19.58	62.65	35.00	$Fe_8V_{10}W_{16}O_{85}$, $FeVO_4$
14	17.26	19.70	63.04	27.50	$Fe_8V_{10}W_{16}O_{85}$, $FeVO_4$
15	16.83	19.80	63.37	20.00	$Fe_8V_{10}W_{16}O_{85}$, $FeVO_4$
16	16.48	19.88	63.64	12.50	$Fe_8V_{10}W_{16}O_{85}$, $FeVO_4$
17	16.18	19.96	63.86	5.00	$Fe_8V_{10}W_{16}O_{85}$, $FeVO_4$

[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_2O_3–$Fe_8V_{10}W_{16}O_{85}$ system

Sample	Composition of initial mixtures / mol%				Calculated phase composition of equilibrium samples / mol%		
No	Fe_2O_3	V_2O_5	WO_3	Fe_2O_3 in terms of component system	β-Fe_2WO_6	$FeVO_4$	$Fe_8V_{10}W_{16}O_{85}$
1	2	3	4	5	6	7	8
13	17.77	19.58	62.65	35.00	0.92	20.15	78.93
14	17.26	19.70	63.04	27.50	0.69	15.02	84.29
15	16.83	19.80	63.37	20.00	0.48	10.22	89.30
16	16.48	19.88	63.64	12.50	0.29	5.92	93.79
17	16.18	19.96	63.86	5.00	0.11	2.55	97.34

assuming that these preparations too should be three-phase ones and contain not only $Fe_8V_{10}W_{16}O_{85}$ and $FeVO_4$, but also β-$Fe_2WO_{6(s.s.)}$, though in very low amounts. Individual detectability tests relating to β-Fe_2WO_6 in the presence of a large amount of $Fe_8V_{10}W_{16}O_{85}$ demonstrated that β-Fe_2WO_6 cannot be detected by X-ray phase powder diffraction unless its content is at least 1.5 mol%. This suggests that the content of β-$Fe_2WO_{6(s.s.)}$ in these preparations is below the detectability level. In order to support this viewpoint, calculations were made and the findings are tabulated in Table 2 (columns 6–8). They confirm that the β-$Fe_2WO_{6(s.s.)}$ content in the preparations remains below the detectability limit of X-ray phase powder diffraction.

The experimental results indicate that the system Fe_2O_3–$Fe_8V_{10}W_{16}O_{85}$ is not a real two-component system, even in the solid state.

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Zusammenfassung — Mittels Röntgenpulverdiffraktion und Differentialthermoanalyse wurde das Phasengleichgewicht bis zur Solidus-Linie im System Fe_2O_3-$Fe_8V_{10}W_{16}O_{85}$ bestimmt. Dieses System ist eine der Schnittlinien des Dreikomponentensystemes Fe_2O_3-V_2O_5-WO_3. Die Untersuchungen ergaben, daß es sich hier im festen Zustand um kein echtes binäres System handelt.