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Diagram of phase equilibria in the $Fe_2V_4O_{13}$–WO_3 system

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Abstract

A diagram for the phase equilibria established in the two-component $Fe_2V_4O_{13}$–WO_3 system (one of the intersections of the Fe_2O_3–V_2O_5–WO_3 three-component system) has been constructed based on the measurements made by DTA and X-ray phase analysis. The diagram shows that the system investigated does not appear to be a true two-component system, even below the solidus line.

Keywords: Binary system; DTA; Iron tungstate (Fe_2WO_6); Iron vanadate ($FeVO_4$); Phase diagram

1. Introduction

Our studies on multicomponent systems of transition metal oxides have been carried out mainly in respect of the formation of new phases and establishment of their equilibria in the systems. The information is necessary to gain knowledge about the mechanisms of reactions taking place in the systems, e.g. during catalytic reaction of the metal oxide mixtures.

The new compounds: $FeVMoO_7$ [1], $CrVMoO_7$ [2], $AlVMoO_7$ [3] and $Fe_4V_2Mo_3O_{20}$ [4] were found to form in the previously investigated three-component systems: Fe_2O_3–V_2O_5–MoO_3, Cr_2O_3–V_2O_5–MoO_3 and Al_2O_3–V_2O_5–MoO_3. Solid solutions of MoO_3 were also found in the iron(III) and chromium(III) vanadates synthesized [5, 6]. The latest subject of our work is the hitherto unknown Fe_2O_3–V_2O_5–WO_3 system.

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The start of our studies on the Fe_2O_3–V_2O_5–WO_3 system involved verification of the literature data concerning the two-component systems making up the three-component system of interest. A new polymorphic modification of iron(III) tungstate(VI), viz. β-Fe_2WO_6, was found to exist in this system [7]. β-Fe_2WO_6 arises through the monotropic transformation of α-Fe_2WO_6, which takes place at 700–840°C, or the enantiotropic transformation of γ-Fe_2WO_6 at temperatures below 950°C [7]. β-Fe_2WO_6 crystallizes in a monoclinic system; its X-ray characteristics are known [7]. Further work on the Fe_2O_3–V_2O_5–WO_3 system led to the discovery that the new compound $Fe_8V_{10}W_{16}O_{85}$ was formed by contributions from all the three components [8]. The compound melts incongruently at 830 ± 5°C to deposit two products: Fe_2WO_6 and WO_3 [8]. The X-ray characteristics of $Fe_8V_{10}W_{16}O_{85}$ have been published [9].

The present work gives the experimental results for the phase equilibria established in one of the intersections of the Fe_2O_3–V_2O_5–WO_3 system, that is, the up-to 1000°C equilibria in the $Fe_2V_4O_{13}$–WO_3 system. $Fe_2V_4O_{13}$ is one of the two compounds formed in the Fe_2O_3–V_2O_5 system [10]. The compound melts incongruently at 665 ± 5°C to yield solid $FeVO_4$ [10].

WO_3 is the most stable of all tungsten oxides. It is known to occur in a number of polymorphic varieties; in the form of a powder at ambient temperature it exists as a triclinic modification [11]. WO_3 melts congruently at 1473°C [12].

2. Experimental

2.1. Materials

The following reagents were used for the experiments. The α-Fe_2O_3 was the p.a. product from VEB Laborchemie Apolda (Germany), roasted at 1000°C in three 24-h cycles. V_2O_5 p.a. was from POCh Gliwice (Poland). The WO_3 was the p.a. product from Fluka AG (Switzerland), roasted at 700°C for 24 h.

2.2. Preparation of samples

To cover the whole component concentration range, 19 samples were prepared from the oxides. Mixtures of the oxides weighed in the given proportions were homogenized by grinding and then formed into pastilles. The samples were placed in porcelain crucibles and heated in air. The conditions for bringing the preparations to the equilibrium state were determined by preliminary experiments. All the samples were heated in the following cycles: 550°C (24 h), 600°C (72 h × 2), and 610°C (72 h × 3 + 48 h × 3).

After each heating cycle, the samples were slowly cooled to ambient temperature, ground and then examined by DTA and X-ray phase powder diffraction. The powdered samples were shaped anew into pastilles for further heating. Preparations whose composition remained unchanged after two successive heating cycles were considered to be in the equilibrium state.

In order to determine the types of phase remaining at equilibrium with a liquid, selected preparations were additionally heated for 5 h at temperatures of 620, 630, 650, 660, 670, 680, 700, 750, 770, 780, 790, 800, 810, 820, 830, 840, 850, 860, 870, 880, 900, 910, 920, 930 and 960°C, respectively. After the samples had been heated they were rapidly quenched to ambient temperature, ground and analysed by X-ray powder diffraction.

2.3. Methods

The phase compositions of the preparations obtained were determined from their powder diffraction patterns. The instrument used for measurements was a DRON-3 diffractometer (Russia). A cobalt lamp with a Fe filter served as a radiation source. Identification of the phases was achieved using PDF cards [13] and other publications [7,9,10].

DTA was carried out using a derivatograph of Paulik–Paulik–Erdey type (MOM Budapest). The measurements were performed in quartz crucibles with samples each weighing 1 g. The measurements were conducted in air over the range 20–1000°C with a heating rate of 10 K min^{-1}.

The solidus line on the diagram of phase equilibria was established on the basis of the onset temperature of the first endothermic effect recorded on the DTA curves of preparations at equilibrium. The accuracy of temperature reading was ±5°C, as established by repeated measurements.

3. Results and discussion

Table 1 shows the components of the initial mixtures and the X-ray phase analyses of the preparations at equilibrium. The data indicate that the components of the $Fe_2V_4O_{13}$–WO_3 system do not remain at permanent equilibrium. The table also shows that preparations initially containing up to 75.00 mol% of WO_3 (in terms of components of the system) are mixtures of three phases: $Fe_8V_{10}W_{16}O_{85}$, $Fe_2V_4O_{13}$ and V_2O_5. A preparation which contained 80.00 mol% of WO_3 in the initial mixture (in terms of components of the system) consisted of only two phases: $Fe_8V_{10}W_{16}O_{85}$ and V_2O_5. The other preparations were three-phase substances, comprising mixtures of the phases $Fe_8V_{10}W_{16}O_{85}$, WO_3 and V_2O_5.

Several endothermic effects were recorded in the DTA curves of samples comprising up to 75.00 mol% of WO_3 in their initial mixtures. The first effect, with an onset peak temperature of 615±5°C, is indicative of the melting temperature of a triple eutectic mixture of $Fe_8V_{10}W_{16}O_{85}$, $Fe_2V_4O_{13}$ and V_2O_5. Increases in temperature lead to three endothermic effects being recorded in the DTA curves of preparations comprising up to 15.00 mol% of WO_3 . The first of the effects with a peak onset temperature of 635±5°C is probably associated with melting of the mixture of $Fe_8V_{10}W_{16}O_{85}$ and $Fe_2V_4O_{13}$. The second effect, with a peak starting at 660±5°C, implies incongruent melting of $Fe_2V_4O_{13}$, and the third at 850±5°C is indicative of incongruent melting of $FeVO_4$ [10]. The DTA curves of preparations which contained 20–70 mol% of WO_3 showed other effects apart from the endothermic effects at 615±5°C and 635±5°C.

Table 1
Compositions of initial mixtures and results of X-ray phase analyses of preparations at equilibrium in the $Fe_2V_4O_{13}$–WO_3 system

Compositions of initial mixtures in mol%					Phase composition of equilibrium samples[a]
No.	Fe_2O_3	V_2O_5	WO_3	WO_3 in terms of comp. system	
1	2	3	4	5	6
1	32.76	65.52	1.72	5.00	V_2O_5, $Fe_2V_4O_{13}$, $Fe_8V_{10}W_{16}O_{85}$
2	32.14	64.29	3.57	10.00	V_2O_5, $Fe_2V_4O_{13}$, $Fe_8V_{10}W_{16}O_{85}$
3	31.48	62.96	5.56	15.00	V_2O_5, $Fe_2V_4O_{13}$, $Fe_8V_{10}W_{16}O_{85}$
4	30.77	61.54	7.69	20.00	$Fe_2V_4O_{13}$, $Fe_8V_{10}W_{16}O_{85}$, V_2O_5
5	30.00	60.00	10.00	25.00	$Fe_2V_4O_{13}$, $Fe_8V_{10}W_{16}O_{85}$, V_2O_5
6	29.17	58.33	12.50	30.00	$Fe_2V_4O_{13}$, $Fe_8V_{10}W_{16}O_{85}$, V_2O_5
7	28.26	56.52	15.22	35.00	$Fe_2V_4O_{13}$, $Fe_8V_{10}W_{16}O_{85}$, V_2O_5
8	27.27	54.55	18.18	40.00	$Fe_2V_4O_{13}$, $Fe_8V_{10}W_{16}O_{85}$, V_2O_5
9	26.19	52.38	21.43	45.00	$Fe_2V_4O_{13}$, $Fe_8V_{10}W_{16}O_{85}$, V_2O_5
10	25.00	50.00	25.00	50.00	$Fe_2V_4O_{13}$, $Fe_8V_{10}W_{16}O_{85}$, V_2O_5
11	23.68	47.37	28.95	55.00	$Fe_2V_4O_{13}$, $Fe_8V_{10}W_{16}O_{85}$, V_2O_5
12	22.22	44.44	33.33	60.00	$Fe_2V_4O_{13}$, $Fe_8V_{10}W_{16}O_{85}$, V_2O_5
13	20.59	41.18	38.23	65.00	$Fe_2V_4O_{13}$, $Fe_8V_{10}W_{16}O_{85}$, V_2O_5
14	18.75	37.50	43.75	70.00	$Fe_2V_4O_{13}$, $Fe_8V_{10}W_{16}O_{85}$, V_2O_5
15	16.67	33.33	50.00	75.00	$Fe_2V_4O_{13}$, $Fe_8V_{10}W_{16}O_{85}$, V_2O_5
16	14.29	28.57	57.14	80.00	$Fe_8V_{10}W_{16}O_{85}$, V_2O_5
17	11.54	23.08	65.38	85.00	$Fe_8V_{10}W_{16}O_{85}$, WO_3, V_2O_5
18	8.33	16.67	75.00	90.00	$Fe_8V_{10}W_{16}O_{85}$, WO_3, V_2O_5
19	4.55	9.09	86.36	95.00	$Fe_8V_{10}W_{16}O_{85}$, WO_3, V_2O_5

[a] In order of decreasing phase content.

Accordingly, the first effect with a peak starting at 760 ± 5°C corresponds with melting of the triple eutectic mixture of $Fe_8V_{10}W_{16}O_{85}$, Fe_2WO_6 and $FeVO_4$ [14]; the second at a temperature of 820 ± 5°C is linked to the melting of the double eutectic mixture of $FeVO_4$ and Fe_2WO_6 [15] and the third at 830 ± 5°C is indicative of melting of the $Fe_8V_{10}W_{16}O_{85}$ phase [14].

Three endothermic effects were recorded in the DTA curves of preparations at equilibrium which had contained 80.00 mol% or more of WO_3 (in terms of components of the system) in their initial mixture. The first of the effects, with a peak onset temperature of 620 ± 5°C, is probably related with melting of the triple eutectic mixture of $Fe_8V_{10}W_{16}O_{85}$, WO_3 and V_2O_5. The second effect with peak onset at 830 ± 5°C corresponds to incongruent melting of the $Fe_8V_{10}W_{16}O_{85}$ phase [14]. The third endothermic effect recorded in the DTA curves of these preparations with a peak starting at 920 ± 5°C is typical of melting of a mixture of Fe_2WO_6 and WO_3. That effect was also evident in the DTA curves of the $FeVO_4$–WO_3 system [14].

4. Conclusions

A diagram for the phase equilibria in the $Fe_2V_4O_{13}$–WO_3 system (Fig. 1) has been constructed basing on the information furnished by the DTA curves of preparations at equilibrium in a given system and by X-ray analysis of both the equilibrium preparations and the samples heated additionally. The diagram covers the whole component concentration range up to 1000°C for the system under study. The course of the solid lines was fixed on the basis of the DTA and X-ray phase diffraction data. The dotted lines were drawn based only on the X-ray analysis data. The diagram shows that the $Fe_2V_4O_{13}$–WO_3 portion of the three-component Fe_2O_3–V_2O_5–WO_3 system is not a real two-component system, even below the solidus line.

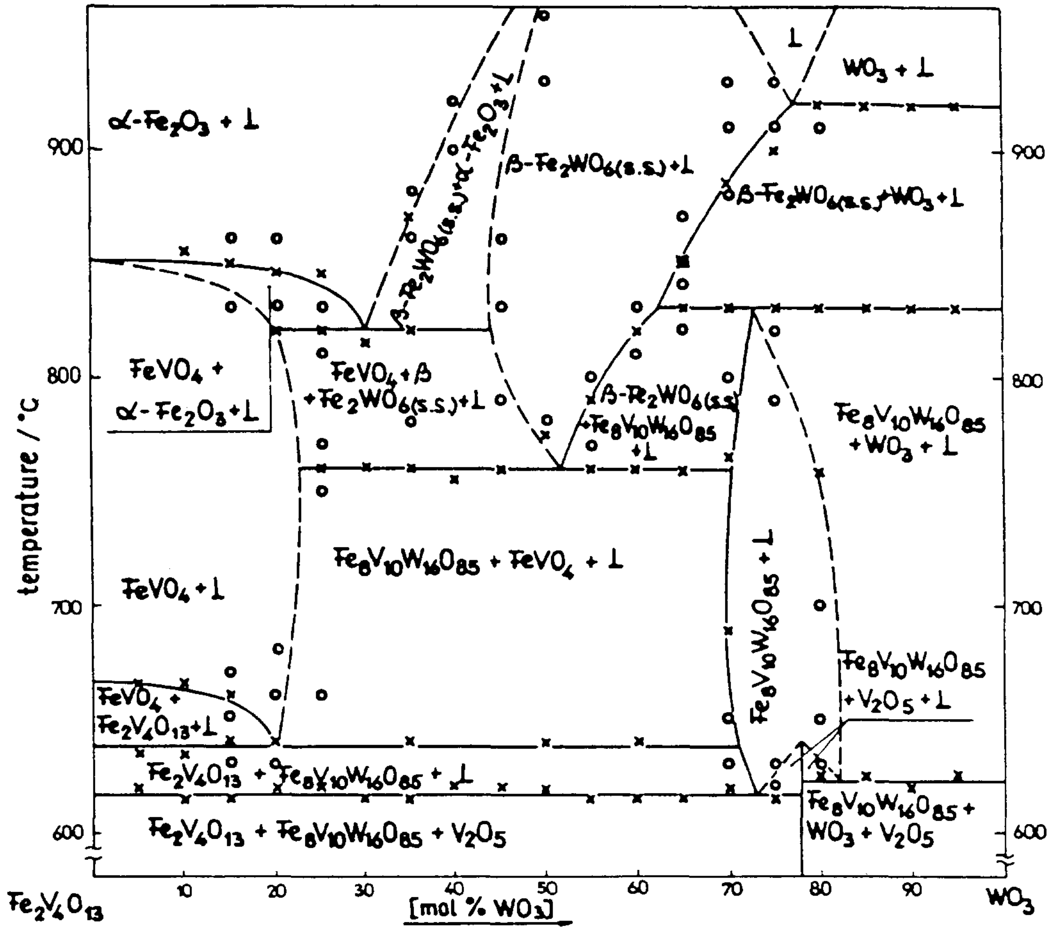

Fig. 1. Phase diagram of the $Fe_2V_4O_{13}$–WO_3 system; × —points indicate DTA; ○—X-ray investigation after quenching in air.

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