Phase equilibria in the systems Fe_2O_3–WO_3 and $FeVO_4$–WO_3

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Abstract

Diagrams of phase equilibria of the systems Fe_2O_3–WO_3 and $FeVO_4$–WO_3 have been constructed based on the results of DTA and X-ray phase powder diffraction. It was found that Fe_2WO_6 melts incongruently at $1100 \pm 10°C$ yielding solid α-Fe_2O_3, and that the $FeVO_4$–WO_3 system is not a two-component system, even below the solidus line.

INTRODUCTION

Multi-component systems of transition metal oxides are an interesting topic of investigation, mainly because of the catalytic properties of their components which are can be used to oxidise a number of organic substances. Studies on the phase equilibria established in such systems can lead to the identification of new phases that are also of interest. The study of the structure and thermal properties of the new phases can elucidate the mechanism of their catalytic activity. In the investigation of the three-component systems Fe_2O_3–V_2O_5–MoO_3 and Cr_2O_3–V_2O_5–MoO_3, the previously unknown compounds $FeVMoO_7$ [1], $Fe_4V_2Mo_3O_{20}$ [2] and $CrVMoO_7$ [3], were found to form in the solid state. At present, we are studying the phase equilibria established in the hitherto unknown three-component system Fe_2O_3–V_2O_5–WO_3. The system comprises three two-component systems: Fe_2O_3–V_2O_5, V_2O_5–WO_3 and Fe_2O_3–WO_3. The investigations of these systems have advanced to different degrees: only the phase equilibria in the Fe_2O_3–V_2O_5 system are known, the phase diagram having been published in ref. 4. For the V_2O_5–WO_3 system, we have determined only that its components in the oxygen atmosphere under

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atmospheric pressure are inert to each other and form a solid solution of WO_3 in V_2O_5 with a solubility limit of 7 mol.% WO_3 [5–7]. The literature reports two diagrams for the phase equilibria in the third system, Fe_2O_3–WO_3 [8, 9]. Both publications indicate that only one compound, Fe_2WO_6, is formed in the system, although reports of its melting behaviour are contradictory: according to Trumm [8], Fe_2WO_6 melts incongruently at $1156 \pm 4°C$, whereas Gardiner and Chang [9] found that Fe_2WO_6 melts congruently at $1142 \pm 5°C$.

Until quite recently, Fe_2WO_6 was thought to occur in two polymorphic varieties of which the low-temperature form with a columbite structure, which is formed at 800°C, undergoes a monotropic transformation at 950°C to a high-temperature variety with an α-PbO_2 structure [10, 11]. Our studies have shown that the low-temperature variety of Fe_2WO_6 with a columbite structure, formed at 650–800°C and designated α-Fe_2WO_6, is an unstable unit; it transforms monotropically at 750–900°C into β-Fe_2WO_6, a variety stable under these conditions which crystallizes in a monoclinic system [12]. At 950°C upwards, β-Fe_2WO_6 undergoes an enantiotropic polymorphic transformation to γ-Fe_2WO_6 with an α-PbO_2 structure, described in the literature as a high-temperature form of that compound [11].

Primary investigations of the three-component Fe_2O_3–V_2O_5–WO_3 system have shown that a new, hitherto unknown phase is formed in the system, to which the molecular formula $FeVW_2O_{10}$ has been assigned [13]. However, further work on the phase has revealed that its composition varies somewhat from that given previously, its molecular formula being $Fe_8V_{10}W_{16}O_{85}$ [14].

The present study considers the experimental results of investigations of the phase equilibria established in the Fe_2O_3–WO_3 system and in a system that forms a section of the Fe_2O_3–V_2O_5–WO_3 system, the pseudo-two-component system, $FeVO_4$–WO_3. The investigation of the first system was necessary because of the contradictory literature information.

The components of the $FeVO_4$–WO_3 system, as well as the oxides, Fe_2O_3 and V_2O_5, are well known. Iron(III) orthovanadate crystallizes in a triclinic system [15] and melts incongruently forming solid α-Fe_2O_3 at 840–890°C [16]. Powdered tungsten(VI) oxide, however, has a triclinic symmetry at ambient temperature [17] and melts congruently at 1473°C [18].

EXPERIMENTAL

The starting materials of the experiments were α-Fe_2O_3, p.a. (VEB, Germany), recalcinated at 1000°C in three 24 h cycles; V_2O_5, p.a. (POCh, Poland); WO_3, p.a., (Fluka AG, Switzerland), recalcinated at 700°C for 24 h, and $FeVO_4$ obtained by the method published in ref. 4.

The oxide mixtures, weighed in calculated amounts, were homogenized

TABLE 1

Compositions of the initial mixtures in mol.% and results of Roentgen analyses of equilibrium samples of the Fe_2O_3–WO_3 system

No.	Fe_2O_3	WO_3	Phase composition of equilibrium sample
1	80	20	γ-Fe_2WO_6, α-Fe_2O_3
2	70	30	γ-Fe_2WO_6, α-Fe_2O_3
3	65	35	γ-Fe_2WO_6, α-Fe_2O_3
4	60	40	γ-Fe_2WO_6, α-Fe_2O_3
5	55	45	γ-Fe_2WO_6, α-Fe_2O_3
6	50	50	γ-Fe_2WO_6
7	45	55	γ-Fe_2WO_6, WO_3
8	40	60	γ-Fe_2WO_6, WO_3

by powdering, then pastilled and heated at given temperatures during given time cycles. Eight oxide mixtures, with the compositions shown in Table 1, were prepared for experiments in order to check the phase equilibria established in the Fe_2O_3–WO_3 system. They were heated as follows: 900°C (24 h), then 950°C (24 h).

Twenty samples, with the compositions shown in Table 2, were prepared to study the phase equilibria established in the $FeVO_4$–WO_3 system. The samples were heated in the following cycles: 550°C (24 h), 600°C (48 h), 700°C (48 h × 2), 720°C (24 h × 2). After each of the cycles, the preparations were cooled slowly to ambient temperature, and powdered. Then DTA and X-ray phase powder diffraction patterns were made, followed by repastilling the samples and subjecting them to further heating. In order to establish the type of phases remaining at equilibrium with liquid, a few selected equilibrium samples were heated for an additional 4 h at 800, 820, 840, 860, 880, 900, 920, 940, 960 and 980°C, respectively, then cooled rapidly to ambient temperature powdered, and analysed by X-ray phase powder diffraction.

The phase compositions of the preparations were determined from their powder diffraction patterns obtained by a Roentgen DRON-3 diffracto-meter, using Co Kα radiation and an Fe filter. The phases were identified from data in the PDF charts [19] and from published data [12, 20].

The DTA measurement of samples of the Fe_2O_3–WO_3 system was made in the range 20–1200°C using a MOM Q-500 (Budapest) derivatograph. DTA of samples of the $FeVO_4$–WO_3 system was carried out on a Paulik–Paulik–Erdey derivatograph at 20–1000°C. The samples (1000 mg) were placed in quartz crucibles, in air, and were heated at 10°C min^{-1}. To construct the phase equilibrium diagrams, the solidus line was taken to be the temperature of the first endothermic effect as recorded on the DTA curves. The accuracy of the temperature reading during experiments up to

TABLE 2

Compositions of the initial mixtures in mol.% and results of Roentgen analyses of equilibrium samples of the $FeVO_4$–WO_3 system

No.	Fe_2O_3	V_2O_5	WO_3	$FeVO_4$ in terms of comp. of the system	Phase composition of equilibrium sample [a]
1	47.50	47.50	5.00	95.00	$FeVO_4$, N, β-Fe_2WO_6
2	45.00	45.00	10.00	90.00	$FeVO_4$, N, β-Fe_2WO_6
3	42.50	42.50	15.00	85.00	$FeVO_4$, N, β-Fe_2WO_6
4	40.00	40.00	20.00	80.00	$FeVO_4$, N, β-Fe_2WO_6
5	37.50	37.50	25.00	75.00	$FeVO_4$, N, β-Fe_2WO_6
6	35.00	35.00	30.00	70.00	N, $FeVO_4$, β-Fe_2WO_6
7	33.33	33.33	33.33	66.67	N, $FeVO_4$, β-Fe_2WO_6
8	32.50	32.50	35.00	65.00	N, $FeVO_4$, β-Fe_2WO_6
9	30.00	30.00	40.00	60.00	N, $FeVO_4$, β-Fe_2WO_6
10	27.50	27.50	45.00	55.00	N, $FeVO_4$, β-Fe_2WO_6
11	25.00	25.00	50.00	50.00	N, $FeVO_4$, β-Fe_2WO_6
12	22.50	22.50	55.00	45.00	N, $FeVO_4$, β-Fe_2WO_6
13	20.00	20.00	60.00	40.00	N, $FeVO_4$, β-Fe_2WO_6
14	17.50	17.50	65.00	35.00	N, β-Fe_2WO_6
15	16.67	16.67	66.67	33.33	N, β-Fe_2WO_6, WO_3
16	12.50	12.50	75.00	25.00	N, WO_3, β-Fe_2WO_6
17	10.00	10.00	80.00	20.00	N, WO_3, β-Fe_2WO_6
18	7.50	7.50	85.00	15.00	N, WO_3, β-Fe_2WO_6
19	5.00	5.00	90.00	10.00	WO_3, N, β-Fe_2WO_6
20	2.50	2.50	95.00	5.00	WO_3, N

[a] Recorded in decreasing phase content of the samples.

1000°C was established as ±5°C, a value that was consistent in several repetitions of the experiments; the accuracy was ±10°C when the experiments were carried out above 1000°C.

RESULTS AND DISCUSSION

Table 1 shows the compositions of the initial mixtures and the X-ray phase powder diffraction results for the equilibrium preparations of the Fe_2O_3–WO_3 system under verification. On the DTA curves of preparations containing 20.00–50.00 mol.% WO_3, only one endothermic effect was recorded, with an onset peak temperature of 1095–1105°C. On the DTA curves of the other samples, two endothermic effects were recorded, with onset peak temperatures of 1005–1010°C and 1100–1110°C. Figure 1 shows the phase equilibria of the Fe_2O_3–WO_3 system constructed from the data obtained. The diagram indicates that our experimental results are in good accord with the results achieved by Trumm [8] who maintains that Fe_2WO_6 melts incongruently to give solid α-Fe_2O_3. We have determined the melting
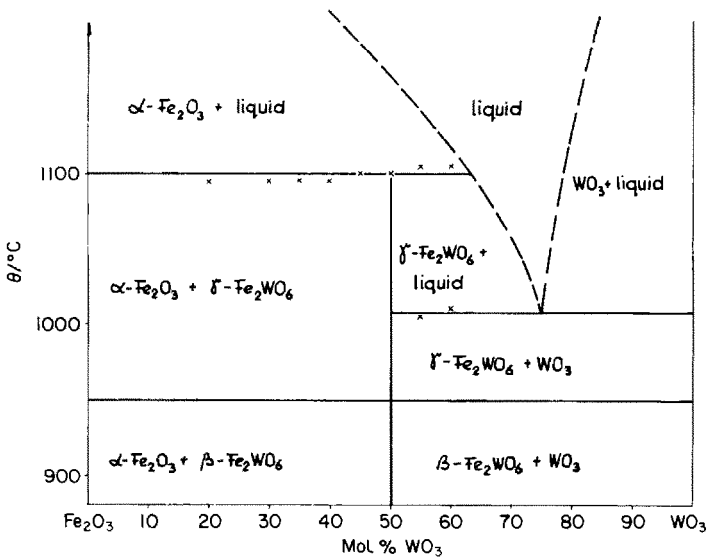
Fig. 1. Diagram of phase equilibria of the Fe_2O_3–WO_3 system.

temperature of Fe_2WO_6 to be $1100 \pm 10°C$, compared with that given by Trumm ($1156 \pm 4°C$) [8].

Table 2 shows the phase compositions of preparations of the $FeVO_4$–WO_3 system and the Roentgen phase analysis results of the samples in the equilibrium state. The data presented imply that the components of the system do not remain at permanent equilibrium but react with each other to give a new phase (N) with molecular formula, $Fe_8V_{10}W_{16}O_{85}$, and iron(III) tungstate. Hence, preparations containing up to 60.00 mol.% WO_3 in their initial mixtures, are, up to the solidus line, a mixture of the three phases N, $FeVO_4$ and β-Fe_2WO_6; whereas preparations with a content of 66.67 mol.% WO_3 or more in their initial mixtures are a mixture of the phases N, WO_3 and β-Fe_2WO_6.

A few endothermic effects were recorded on the DTA curves of preparations containing up to 60.00 mol.% WO_3 in their initial mixtures. The first of the effects, with an onset peak temperature of 760–770°C, indicates the existence of a triple eutectic at that temperature. In the $FeVO_4$–WO_3 system, the eutectic occurs when the WO_3 content of the initial mixture falls within the range 33.33–35.00 mol.% of the oxide. Above 770°C, either one or two endothermic effects were recorded on the DTA curves. On the DTA curves of samples containing up to 15.00 mol.% WO_3 in their initial mixtures, there was an endothermic effect with an onset peak temperature of $850 \pm 5°C$, associated with the incongruent melting of $FeVO_4$. However, on the DTA curves of preparations containing 15.00–35.00 mol.% WO_3 in the initial mixtures, only one effect was recorded, the temperature of the effect onset being variable, ranging from 880°C

for a sample containing 20.00 mol.% WO_3 to 990°C for a sample with 35.00 mol.% WO_3. On the DTA curves of preparations containing 40.00–60.00 mol.% WO_3, three endothermic effects were recorded: the first had an onset peak temperature of 765–770°C, as discussed above; the second had an onset temperature of 830 ± 5°C, associated with the incongruent melting of the phase N [14]; and the third had an onset peak temperature of 855–920°C, depending on the initial WO_3 content of the mixture. Two endothermic effects were recorded on the DTA curves of preparations containing more than 65.00 mol.% WO_3 in the initial mixtures: the first had an onset peak temperature of 830 ± 5°C, and the second had an onset peak temperature of 920–925°C.

From the information obtained from the DTA curves of the preparations investigated, and from X-ray phase powder diffraction of the equilibrium samples and of samples subjected to additional heating followed by rapid cooling, a diagram of the phase equilibria of the $FeVO_4$–WO_3 system has been constructed over the whole component concentration range, up to 1000°C. The diagram is shown in Fig. 2. The solid lines were drawn from the DTA and Roentgen analysis results; the broken lines result from the proximity of the individual areas, the contents of which were determined on the basis of X-ray phase analysis.

The experimental results have shown that this section of the Fe_2O_3–V_2O_5–WO_3 system is not a real two-component system, even below the solidus line, where three phases remain at equilibrium. Above the
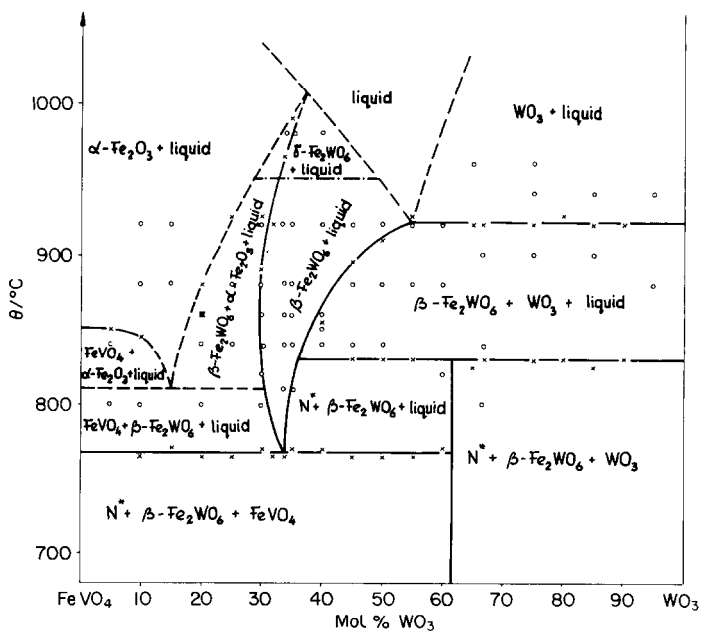

Fig. 2. Diagram of phase equilibria of the $FeVO_4$–WO_3 system: ×, DTA; ○, XRD.

solidus line, the system is complex because both the N phase and $FeVO_4$, as well as iron(III) tungstate, melt incongruently.

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