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Note

Phase diagram of the $FeVO_4$–Fe_2WO_6 system

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Abstract

A diagram for the phase equilibria established in the two-component $FeVO_4$–Fe_2WO_6 system has been constructed from measurements made by DTA and X-ray phase analysis. The diagram shows that the system investigated does not appear as a real two-component system, not even below the solidus line, and that its components form a eutectic mixture with a melting temperature of 810 ± 5°C (at a 15.00 mol% content of Fe_2WO_6).

INTRODUCTION

Multi-component systems of transition metal oxides are an interesting subject of study, due to the catalytic properties of the phases present. The knowledge of the phase equilibria established in such systems provides a solid foundation for studies on the catalytic reaction mechanism of the components of the system. In previous work, we have investigated equilibria of the three-component systems Fe_2O_3–V_2O_5–MoO_3 [1, 2] and Cr_2O_3–V_2O_5–MoO_3 [3]. Recently, we have undertaken studies on a three-component system, Fe_2O_3–V_2O_5–WO_3, that has not been investigated previously.

Fe_2O_3–V_2O_5–WO_3 can be considered as a system composed of three two-component systems: Fe_2O_3–V_2O_5, V_2O_5–WO_3, and Fe_2O_3–WO_3. The first has been studied thoroughly, with reference both to the establishment of phase equilibria [4] and to some of the properties of the phases formed in the system [5, 6]. It is known from the literature that merely heating the components of the V_2O_5–WO_3 system in air, under atmospheric pressure, leads to a solid solution of WO_3 in V_2O_5. The solubility limit of WO_3 in V_2O_5 is 7 mol% under these conditions [7, 8].

From the published diagrams of the Fe_2O_3–WO_3 system, it follows that only one compound, Fe_2WO_6, was formed [9, 10]. However the nature and the temperature of melting of the compound given in these publications are

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different. According to ref. 9, Fe_2WO_6 melts congruently at 1142 ± 5°C whereas ref. 10 states that it melts incongruently at 1156 ± 4°C. Our own studies, carried out to verify these findings, showed that in the Fe_2O_3–WO_3 system a single compound, Fe_2WO_6, was indeed formed. The compound melted incongruently at 1100 ± 10°C to deposit α-Fe_2O_3 [11].

From our investigations of the Fe_2O_3–V_2O_5–WO_3 system, we established that a new compound was formed in the solid state. The compound was formed from all three components of the system and has the formula $Fe_8V_{10}W_{16}O_{85}$ [12]. The compound melts incongruently at 830 ± 5°C to yield two solid compounds Fe_2WO_6 and WO_3 [11]. The studies were made with respect to the reactivity of iron(III) tungstate in the Fe_2O_3–V_2O_5–WO_3 system. It was found that a solid solution of V_2O_5 in Fe_2WO_6 was formed [13].

The present work refers to the phase behavior in one region of composition of the three-component Fe_2O_3–V_2O_5–WO_3 system, namely, the pseudo-two-component $FeVO_4$–Fe_2WO_6 system.

Iron(III) orthovanadate crystallizes in a triclinic system [14] and melts incongruently at 850 ± 5°C, depositing α-Fe_2O_3 [4]. $FeVO_4$ does not display polymorphism at atmospheric pressure, but there are known polymorphous varieties formed at high pressure [15–17].

To date, iron(III) tungstate has been known to occur in two polymorphic forms: a low- and a high-temperature form. The low-temperature form, with a columbite structure, was obtained by reaction at 800–850°C [18, 19]. The high-temperature form, however, was obtained by two methods. The first method was the monotropic transformation of the low-temperature form above 950°C [18, 19]. The second method was to heat the oxides at 900–1000°C [18–20]. Our studies on iron(III) tungstate confirmed that when synthesis is carried out from an equimolar mixture of oxides, reaction begins at as high a temperature as 650°C, but at quite a low rate. Between 650 and 850°C, α-Fe_2WO_6 with a columbite structure is formed [21] at first, followed by its monotropic transformation after prolonged heating in that temperature range to give a new form, β-Fe_2WO_6. The β-form crystallizes in a monoclinic system [21]. β-Fe_2WO_6 was not known before our studies. Furthermore, above 950°C, this form undergoes enantiotropic transformation to γ-Fe_2WO_6 which is characterized by an α-PbO_2 structure. Polymorphic transformation of the reconstruction type is attributable to both the transformations [21].

EXPERIMENTAL

The materials used were α-Fe_2O_3 p.a., VEB Laborchemie Apolda (Germany) production, calcinated at 1000°C in three 24 h cycles, V_2O_5 p.a., POCh (Poland) production, and WO_3 p.a., Fluka AG, Switzerland, calcinated at 700°C for 24 h.

TABLE 1

Compositions of initial mixtures in mol% and results of X-ray phase analysis of preparations at equilibrium in the $FeVO_4$–Fe_2WO_6 system

No.	Compositions of initial mixtures				Phase composition of equilibrium samples [a]
	Fe_2O_3	V_2O_5	WO_3	Fe_2WO_6 in terms of compon. system	
1	50.00	45.24	4.76	5.00	$FeVO_4$, β-Fe_2WO_6(ss), α-Fe_2O_3
2	50.00	40.91	9.09	10.00	$FeVO_4$, β-Fe_2WO_6(ss), α-Fe_2O_3
3	50.00	36.95	13.05	15.00	$FeVO_4$, β-Fe_2WO_6(ss), α-Fe_2O_3
4	50.00	33.33	16.67	20.00	$FeVO_4$, β-Fe_2WO_6(ss), α-Fe_2O_3
5	50.00	30.00	20.00	25.00	$FeVO_4$, β-Fe_2WO_6(ss), α-Fe_2O_3
6	50.00	26.92	23.08	30.00	$FeVO_4$, β-Fe_2WO_6(ss), α-Fe_2O_3
7	50.00	24.07	25.93	35.00	β-Fe_2WO_6(ss), $FeVO_4$, α-Fe_2O_3
8	50.00	21.43	28.57	40.00	β-Fe_2WO_6(ss), $FeVO_4$, α-Fe_2O_3
9	50.00	18.97	31.03	45.00	β-Fe_2WO_6(ss), $FeVO_4$, α-Fe_2O_3
10	50.00	16.67	33.33	50.00	β-Fe_2WO_6(ss), $FeVO_4$, α-Fe_2O_3
11	50.00	14.52	35.48	55.00	β-Fe_2WO_6(ss), $FeVO_4$, α-Fe_2O_3
12	50.00	12.51	37.49	60.00	β-Fe_2WO_6(ss), $FeVO_4$, α-Fe_2O_3
13	50.00	10.61	39.39	65.00	β-Fe_2WO_6(ss), $FeVO_4$, α-Fe_2O_3
14	50.00	10.00	40.00	66.67	β-Fe_2WO_6(ss), $FeVO_4$, α-Fe_2O_3
15	50.00	8.83	41.17	70.00	β-Fe_2WO_6(ss), $FeVO_4$, α-Fe_2O_3
16	50.00	7.14	42.86	75.00	β-Fe_2WO_6(ss), $FeVO_4$, α-Fe_2O_3
17	50.00	5.55	44.45	80.00	β-Fe_2WO_6(ss), $FeVO_4$, α-Fe_2O_3
18	50.00	4.06	45.94	85.00	β-Fe_2WO_6(ss), α-Fe_2O_3
19	50.00	2.63	47.37	90.00	β-Fe_2WO_6(ss), α-Fe_2O_3
20	50.00	1.28	48.72	95.00	β-Fe_2WO_6(ss), α-Fe_2O_3

[a] In order of decreasing phase content.

Preparation of samples

All the samples were prepared from the oxide components of the Fe_2O_3–V_2O_5–WO_3 system. The oxides, weighed in the given proportions, were mixed, homogenized by grinding and finally shaped into pastilles. Then, the samples were placed in porcelain crucibles and heated in air. For heating of the samples, syllite furnaces equipped with temperature controllers were used. Both the temperature and the heating cycles were established in preliminary experiments. Twenty samples with compositions shown in Table 1 were prepared for the experiments. The samples were heated in the following cycle: 550°C (24 h) + 600°C (48 h) + 650°C (48 h) + 700°C (24 h + 48 h + 120 h × 2 + 144 h) + 720°C (120 h × 2).

After each heating cycle, the samples were cooled slowly and ground, and then DTA and X-ray powder diffraction measurements were made, followed by pastilling and further heating of the samples. Attainment of equilibrium was presumed for those preparations whose phase composition remained unchanged after successive heating cycles.

In order to establish the kind of phases remaining at equilibrium with the liquid, selected preparations were additionally heated for an additional 5 h at 780, 800, 820, 840, 870, 880, 900, 930, 950, 980 and 1000°C, respectively. After heating, the samples were cooled rapidly to ambient temperature, ground, and analyzed by X-ray powder diffraction.

Methods

The phase composition of the samples was established from their X-ray powder diffraction diagrams, obtained using a DRON-3 (Russian Federation) diffractometer with Co $K\alpha$ radiation and an Fe filter. Identification of the phases was accomplished with the aid of data in the Powder Diffraction File (PDF) cards [22] and in the literature [19–21].

The DTA was run at 20–1000°C using a Paulik–Paulik–Erdey derivatograph (MOM, Budapest). Measurements were carried out in air from 20 to 1000°C with a heating rate of $10\ \mathrm{K\ min^{-1}}$. The samples, 1×10^{-3} kg each, were placed in quartz crucibles. The solidus line in the phase diagram was constructed on the basis of the first endothermic onset effect recorded on the DTA curves of preparations remaining at equilibrium. The precision of the temperature measurement was established by repeated determinations and was found to be ± 5°C.

RESULTS AND DISCUSSION

Table 1 shows the compositions of the initial mixtures and the results from the XRD measurements of the preparations after the final heating cycle. It follows from the data shown that the components of the system of interest do not remain at permanent equilibrium with each other. The fact is evidenced by the presence in all preparations of a phase which is not an original component of the system under study, i.e. α-Fe_2O_3. At the same time, no evidence of $FeVO_4$ was found in the preparations when their initial mixtures contained ≥ 85.00 mol% Fe_2WO_6 (in terms of the system components). Such a phase composition supports our earlier observations [13] that a solid solution of V_2O_5 in iron(III) tungstate is formed. Formation of such a solution can be described by

$$Fe_2WO_6(s) + FeVO_4(s) \rightarrow Fe_2WO_6(ss) + \alpha\text{-}Fe_2O_3(s)$$

On the DTA curves of preparations obtained at 720°C and containing up to 80.00 mol% of Fe_2WO_6 in their initial mixtures, the peak onset of the first endothermic effect was found to be in the range 810–815°C, which indicates the occurrence, at this temperature, of a triple eutectic mixture. The eutectic mixture was also found to occur in $FeVO_4$–WO_3 system [11]. The second

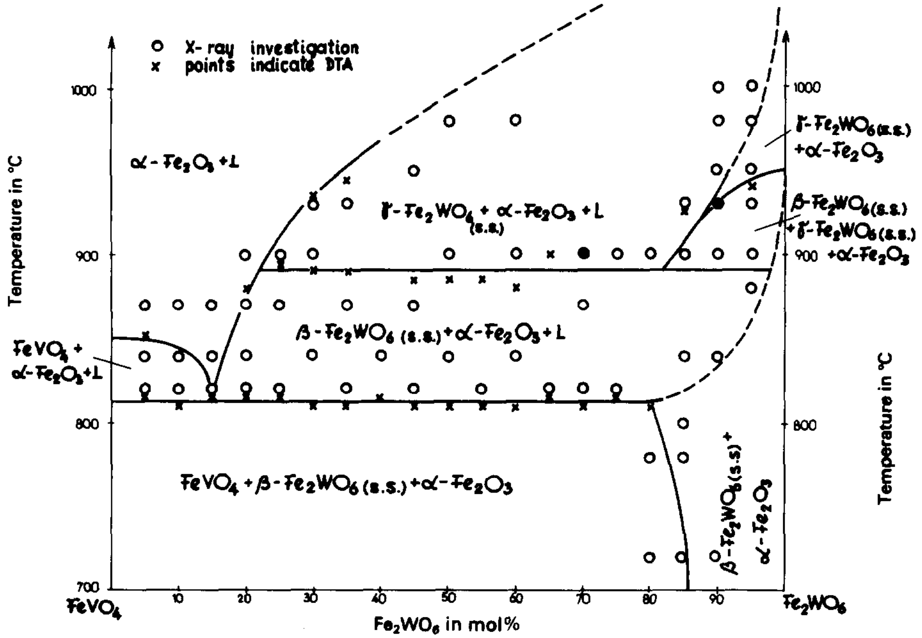

Fig. 1. Diagram of the phase equilibria in the $FeVO_4$–Fe_2WO_6 system.

endothermic effect, with a peak onset at 855 ± 5°C, could be seen on DTA curves of preparations with a 15.00 mol% Fe_2WO_6 content in their initial mixtures. This effect can be associated with incongruent melting of $FeVO_4$ [4]. A second effect, although quite a small one, with an 880–900°C peak onset, was recorded on the DTA curves of most of the preparations containing 25.00–70.00 mol% Fe_2WO_6 in their initial mixtures. This effect seems attributable to the polymorphic transformation

$$\beta\text{-}Fe_2WO_6(ss) \rightarrow \gamma\text{-}Fe_2WO_6(ss)$$

CONCLUSIONS

Finally, a phase diagram has been constructed (see Fig. 1) for the $FeVO_4$–Fe_2WO_6 system, over the whole component concentration range, up to 1000°C. Construction of the diagram was based on information obtained from the DTA curves of the preparations investigated and from the X-ray powder diffraction results. Roentgen analysis was made for the samples obtained at 720°C and for those additionally heated to higher temperatures and then rapidly cooled. The diagram constructed has shown that the intersection of the Fe_2O_3–V_2O_5–WO_3 system is not a real two-component system, not even below the solidus line. It also follows from the diagram that in the three-component Fe_2O_3–V_2O_5–WO_3 system, a solid solution of

V_2O_5 in Fe_2WO_6 is formed with both the β- and γ-iron(III) tungstate forms.

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