

PHASE EQUILIBRIA IN THE $\text{Fe}_8\text{V}_{10}\text{W}_{16}\text{O}_{85}$ - Fe_2O_3 AND $\text{Fe}_8\text{V}_{10}\text{W}_{16}\text{O}_{85}$ - Fe_2WO_6 SYSTEMS

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Abstract

Using DTA and X-ray phase diffraction methods, a diagram of phase equilibria established in two sections of a tricomponent oxide triangle Fe_2O_3 - V_2O_5 - WO_3 was constructed, that is, in the sections: $\text{Fe}_8\text{V}_{10}\text{W}_{16}\text{O}_{85}$ - Fe_2O_3 and $\text{Fe}_8\text{V}_{10}\text{W}_{16}\text{O}_{85}$ - Fe_2WO_6 .

Keywords: DTA, phase equilibria, system Fe_2O_3 - V_2O_5 - WO_3 , XRD

Introduction

Literature studies reveal that unlike the two-component systems of metal oxides which have been studied fairly well, three-component systems of such oxides call for further comprehensive studies. The two kinds of transition metal oxide systems stimulate scientists' interest in establishing phase equilibria, and the reactions taking place in these systems. The reactions have often led to formation of phases not known before. The systems below may serve as examples: Fe_2O_3 - V_2O_5 - MoO_3 [1, 2], Cr_2O_3 - V_2O_5 - MoO_3 [3, 4], Al_2O_3 - V_2O_5 - MoO_3 [5, 6], as well as a system of our present interest: Fe_2O_3 - V_2O_5 - WO_3 [7, 8]. The subject has been studied both in the cognitive and utilitarian aspects. The components of the system, their mixtures and some phases formed are used as catalysts in a number of chemical processes [9-14]. The phases discovered in the systems studied are a source of new materials with a large variety of applications.

The work on the Fe_2O_3 - V_2O_5 - WO_3 system has been started by studying the information available on the Fe_2O_3 - WO_3 system, which is one of the sides of the Gibbs triangle to be used as a graphical illustration of the system. The studies led to the conclusion that the sole compound existing in the system occurs not in two, but three polymorphic modifications [7]. Furthermore, it was found that all the components of the Fe_2O_3 - V_2O_5 - WO_3 system are involved in the solid-state for-

mation of a new compound, to which a molecular formula $\text{Fe}_8\text{V}_{10}\text{W}_{16}\text{O}_{85}$ has been assigned [8], and a solid solution of V_2O_5 in Fe_2WO_6 [15].

This work presents our studies on phase equilibria established in two sections of the system Fe_2O_3 – V_2O_5 – WO_3 , in which one of the components is the newly discovered phase $\text{Fe}_8\text{V}_{10}\text{W}_{16}\text{O}_{85}$, that is, in the systems: $\text{Fe}_8\text{V}_{10}\text{W}_{16}\text{O}_{85}$ – Fe_2O_3 and $\text{Fe}_8\text{V}_{10}\text{W}_{16}\text{O}_{85}$ – Fe_2WO_6 .

$\text{Fe}_8\text{V}_{10}\text{W}_{16}\text{O}_{85}$ melts incongruently at $830\pm 5^\circ\text{C}$, depositing two phases, viz. Fe_2WO_6 and WO_3 [16]. The compound crystallizes in an orthorhombic system; its X-ray characteristics are also known [17].

Iron(III) oxide, at temperatures above 427°C , occurs as α - Fe_2O_3 [18], crystallizing in rhombohedral system [19]. At temperatures over 1000°C , α - Fe_2O_3 is transformed into Fe_3O_4 [20].

As already mentioned, iron(III) tungstate occurs in three polymorphic modifications, the thermodynamically stable phase at temperatures between 740 and 900°C being β - Fe_2WO_6 , crystallizing in monoclinic system; the X-ray characteristics of all the three Fe_2WO_6 modifications are also known [7]. Iron(III) tungstate (Fe_2WO_6) melts incongruently at $1100\pm 10^\circ\text{C}$ to deposit Fe_2O_3 [16].

Experimental

The following chemicals were used in the experiments:

- α - Fe_2O_3 a commercial analytical reagent (VEB Laborchemie Apolda, Germany) additionally calcined at 1000°C in three 24 h cycles,
- V_2O_5 a commercial analytical reagent (POCh, Gliwice, Poland),
- WO_3 a commercial analytical reagent (Fluka AG, Switzerland), additionally calcined at 700°C for 24 h.

The following samples were prepared from the oxides:

- 17 samples for the $\text{Fe}_8\text{V}_{10}\text{W}_{16}\text{O}_{85}$ – Fe_2O_3 system,
- 18 samples for the $\text{Fe}_8\text{V}_{10}\text{W}_{16}\text{O}_{85}$ – Fe_2WO_6 system,

covering the entire component concentration ranges of the two systems. The oxide mixtures weighed in suitable proportions were homogenized by triturating, shaped into pellets and heated in air at temperatures determined in preliminary tests allowing to achieve a state of equilibrium. Thus, samples of the system $\text{Fe}_8\text{V}_{10}\text{W}_{16}\text{O}_{85}$ – Fe_2O_3 were heated in the following way: 650°C (24 h \times 2)+ 700°C (24 h+48 h)+ 710°C (120 h \times 2). Samples of the system $\text{Fe}_8\text{V}_{10}\text{W}_{16}\text{O}_{85}$ – Fe_2WO_6 were heated in the cycles: 650°C (24 h \times 2)+ 700°C (48 h \times 2)+ 705°C (240 h+96 h). After each of the heating cycles the samples were slowly cooled to ambient temperature, triturated and subjected to examination by DTA and X-ray diffraction methods, followed by a repeated pelleting and heating of the samples. Afterwards, the samples were shaped into pellets and heated again. The temperatures

of successive heating stages were fixed on the basis of DTA results. The samples with phase contents remaining unchanged after two consecutive heating cycles were considered to be in equilibrium.

The DTA measurements were made using a Paulik–Paulik–Erdey derivatograph (MOM, Budapest Hungary). The given samples in weighed amounts of 1000 mg were placed in quartz crucibles and heated from 20 to 1000°C at a rate of 10°C min⁻¹. The accuracy of temperature reading for the thermal effects in the DTA curves was established by repetition tests, and the error was found to be ±5°C.

The phase compositions of the samples were established using X-ray powder diffraction patterns of the samples taken with a DRON-3 X-ray diffractometer (Bourestnik, St. Petersburg, Russia) equipped with a cobalt lamp (CoK_α) as a radiation source and an Fe filter, and using the data compiled in PDF charts [21] and in publications [8, 17].

In order to specify the type of phases being in equilibrium with the liquid, some equilibrium samples of both systems were additionally heated for 4–6 h at the given temperatures and then quenched to ambient temperature, triturated and examined to identify the phases formed. Thus, some selected samples of the Fe₈V₁₀W₁₆O₈₅–Fe₂O₃ system were additionally heated at the following temperatures: 750, 800, 815, 820, 840, 880, 890, 940 and 960°C. On the other hand, some equilibrium samples of the Fe₈V₁₀W₁₆O₈₅–Fe₂WO₆ system were additionally heated at 800, 850, 890, 900, 925 and 940°C.

Results and discussion

The Fe₈V₁₀W₁₆O₈₅–Fe₂O₃ system

The phase compositions of equilibrium samples of this system were as follows:

- samples containing up to 90.00 mol% of Fe₂O₃ (in terms of the phase components) in their initial mixtures resulted in a mixture that consisted of three phases: Fe₈V₁₀W₁₆O₈₅, FeVO₄ and β-Fe₂WO_{6(s,s)},
- the other samples were three-phase substances and contained FeVO₄, β-Fe₂WO_{6(s,s)} and α-Fe₂O₃.

The DTA curves of samples containing up to 90.000 mol% of Fe₂O₃ (in terms of the system components) show that the first endothermic effect has a peak onset temperature of 760±5°C. This effect is considered to be caused by the melting of a three-component mixture, Fe₈V₁₀W₁₆O₈₅–FeVO₄–β-Fe₂WO_{6(s,s)} [16]. The first effect noted at 815±5°C in the DTA curves of the other samples can be attributed to the melting of the FeVO₄–β-Fe₂WO_{6(s,s)}–α-Fe₂O₃ mixture [22]. The endothermic effect with a 830±5°C peak onset temperature recorded in the DTA curves of

samples composed of up to 85.00 mol% of Fe_2O_3 has been associated with the melting of the $\text{Fe}_8\text{V}_{10}\text{W}_{16}\text{O}_{85}$ phase [16], whereas the effect recorded at $910 \pm 5^\circ\text{C}$ in the DTA curves of samples composed of up to 65.00 mol% of Fe_2O_3 (in terms of the phase components) may be caused by the melting of a mixture when it contains $\beta\text{-Fe}_2\text{WO}_6$ and WO_3 that remain in equilibrium with the liquid phase.

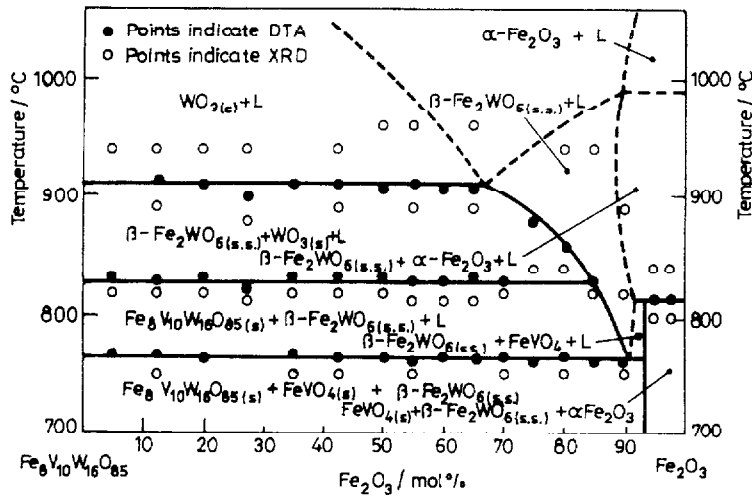


Fig. 1 Diagram of phase equilibria of the $\text{Fe}_8\text{V}_{10}\text{W}_{16}\text{O}_{85}\text{-Fe}_2\text{O}_3$ system

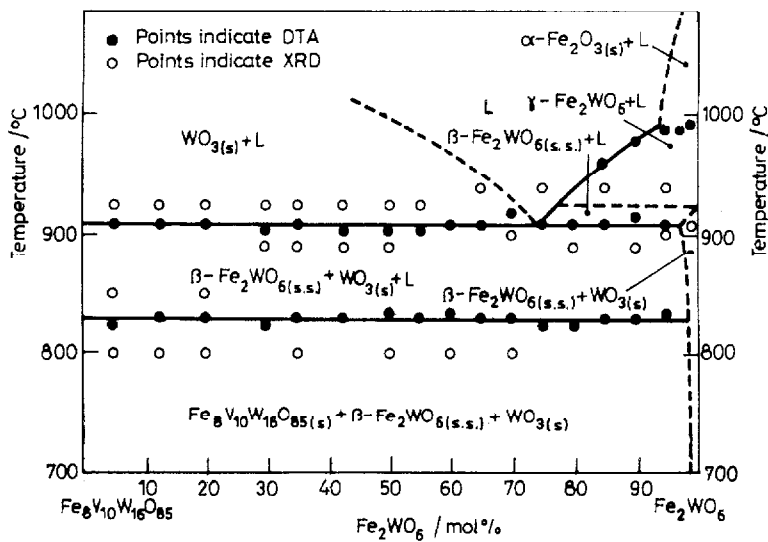


Fig. 2 Diagram of phase equilibria of the $\text{Fe}_8\text{V}_{10}\text{W}_{16}\text{O}_{85}\text{-Fe}_2\text{WO}_6$ system

The $Fe_8V_{10}W_{16}O_{85}-Fe_2WO_6$ system

The phase composition of equilibrium samples is as follows:

- the samples containing about 99.00 mol% of Fe_2WO_6 (in terms of the phase components) in their initial mixtures are three-phase materials and make a $Fe_8V_{10}W_{16}O_{85}-\beta-Fe_2WO_{6(s,s)}-WO_3$ mixture,
- the sample with its initial mixture containing 99.00 mol% of Fe_2WO_6 consists of two phases: $\beta-Fe_2WO_{6(s,s)}$ and WO_3 .

In the DTA curves of equilibrium samples that contain up to 95.00 mol% of Fe_2WO_6 , the first endothermic effect has a peak onset temperature of $830\pm 5^\circ C$, while the second endothermic effect has its peak onset temperature at $910\pm 5^\circ C$. The former effect can be accounted for by the melting of the $Fe_8V_{10}W_{16}O_{85}$ phase [16], while the latter may be caused by the melting of a mixture that contains $\beta-Fe_2WO_{6(s,s)}$ and WO_3 remaining in equilibrium with the liquid phase. An endothermic effect with a $990\pm 5^\circ C$ peak onset temperature can be observed in the DTA curves of samples containing 95.00, 97.50 and 99.00 mol% of Fe_2WO_6 , respectively. This effect is indicative of the melting of a mixture in which $\beta-Fe_2WO_{6(s,s)}$ and the liquid are in equilibrium.

Diagrams of phase equilibria of the systems under study, based on the temperatures of the endothermic effects in the DTA curves of equilibrium samples and in the XRD patterns of equilibrium samples and of samples additionally heated at the given temperatures and then 'frozen', have been constructed. The diagrams show that both sections of the three-component system $Fe_2O_3-V_2O_5-WO_3$ fail to produce real two-component systems, even below the solidus line.

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