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SOLID-STATE PHASE EQUILIBRIA IN THE V_2O_5–$Fe_8V_{10}W_{16}O_{85}$ SYSTEM

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Abstract

Phase equilibria being established in the solid state in the system V_2O_5–$Fe_8V_{10}W_{16}O_{85}$ were examined by X-ray phase powder diffraction and DTA. It has been found that the system of interest is a real two-component system with an eutectic temperature 620±5°C.

Keywords: phase equilibria, V_2O_5–$Fe_8V_{10}W_{16}O_{85}$ system

Introduction

Multicomponent systems of transition metal oxides are interesting objects of investigations, mainly on account of the catalytic properties of components and phases occurring in these systems. Studies on phase equilibria being established in such systems contributes remarkably to works on new highly active and selective catalysts. They often give rise to discovery of new compounds.

It has been found through cognitive studies on the hitherto unknown three-component Fe_2O_3–V_2O_5–WO_3 system that components of the system react with each other to form a new compound to which has finally been attributed a molecular formula, $Fe_8V_{10}W_{16}O_{85}$ [1]. Phase equilibria being established in one of the intersections of the $FeVO_4$–WO_3 system have been studied while the works on the Fe_2O_3–V_2O_5–WO_3 were continued [2]. The work presented deals with phase equilibria being established in the solid-state system whose one of the components is a new phase, $Fe_8V_{10}W_{16}O_{85}$.

Oxides: α-Fe_2O_3 and WO_3 are known well. Vanadium(V) oxide crystallizes in an orthorhombic system [3], its melting temperature given by different authors is: 658°C [4], 670°C [5] or 675°C [6].

The new compound, $Fe_8V_{10}W_{16}O_{85}$, which is formed in the Fe_2O_3–V_2O_5–WO_3 system by engaging all the components of the system, melts incongruently at 830±5°C depositing two solid phases: Fe_2WO_6 and WO_3 [2].

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Experimental

For the experiments were used α-Fe_2O_3, p.a. of VEB (Germany) production, additionally calcinated at 1000°C within three 24 h cycles; V_2O_5, p.a. (POCh, Poland) and WO_3, p.a. (Fluka AG Switzerland), additionally calcinated at 700°C during 24 h.

Mixtures of the oxides, weighed in appropriate proportions, were homogenized by grinding, shaped in pastilles and heated in air at the given temperatures and heating cycles.

Table 1 Compositions of initial mixtures and X-ray analysis of preparations at equilibrium

No.	Composition of initial mixtures / %mol				Phase composition of preparations at equilibrium
	Fe_2O_3	V_2O_5	WO_3	V_2O_5 in term of system of component	
1	2	3	4	5	6
1	9.09	54.55	36.36	95.00	V_2O_5, $Fe_8V_{10}W_{16}O_{85}$
2	11.76	41.18	47.06	90.00	V_2O_5, $Fe_8V_{10}W_{16}O_{85}$
3	13.04	34.78	52.17	85.00	V_2O_5, $Fe_8V_{10}W_{16}O_{85}$
4	13.79	31.03	55.17	80.00	V_2O_5, $Fe_8V_{10}W_{16}O_{85}$
5	14.29	28.57	57.14	75.00	$Fe_8V_{10}W_{16}O_{85}$, V_2O_5
6	14.63	26.83	58.54	70.00	$Fe_8V_{10}W_{16}O_{85}$, V_2O_5
7	14.89	25.53	59.57	65.00	$Fe_8V_{10}W_{16}O_{85}$, V_2O_5
8	15.09	24.53	60.38	60.00	$Fe_8V_{10}W_{16}O_{85}$, V_2O_5
9	15.25	23.73	61.02	55.00	$Fe_8V_{10}W_{16}O_{85}$, V_2O_5
10	15.38	23.08	61.54	50.00	$Fe_8V_{10}W_{16}O_{85}$, V_2O_5
11	15.49	22.54	61.97	45.00	$Fe_8V_{10}W_{16}O_{85}$, V_2O_5
12	15.58	22.08	62.34	40.00	$Fe_8V_{10}W_{16}O_{85}$, V_2O_5
13	15.66	21.69	62.65	35.00	$Fe_8V_{10}W_{16}O_{85}$, V_2O_5
14	15.73	21.35	62.92	30.00	$Fe_8V_{10}W_{16}O_{85}$, V_2O_5
15	15.79	21.05	63.13	25.00	$Fe_8V_{10}W_{16}O_{85}$, V_2O_5
16	15.84	20.79	63.37	20.00	$Fe_8V_{10}W_{16}O_{85}$, V_2O_5
17	15.89	20.56	63.55	15.00	$Fe_8V_{10}W_{16}O_{85}$, V_2O_5
18	15.93	20.35	63.72	10.00	$Fe_8V_{10}W_{16}O_{85}$, V_2O_5
19	15.96	20.17	63.87	5.00	$Fe_8V_{10}W_{16}O_{85}$, V_2O_5

There was prepared a series of 19 samples with compositions given in Table 1. The samples were heated, as follows:

$$550°C\ (24\ h) + 600°C\ (24\ h + 96\ h) + 610°C\ (48\ h \times 6)$$

After each heating cycle, the samples were cooled slowly to ambient temperature, ground down and examined by X-ray phase powder diffraction and DTA. The preparations whose composition had not suffered alteration after two successive heating cycles were considered to be preparations at equilibrium.

The phase compositions of the samples were determined with the aid of powder diffraction patterns obtained by using a diffractometer DRON-3 with CoK_α radiation and Fe filter. The identification of the phases was performed basing on the data listed in the PDF index cards [7]. Table 2 shows the diffraction pattern of the phase $Fe_8V_{10}W_{16}O_{85}$.

Table 2 X-ray powder diffraction pattern of $Fe_8V_{10}W_{16}O_{85}$

No.	d_{obs} / Å	I_{obs} / %	No.	d_{obs} / Å	I_{obs} / %
1	2	3	1	2	3
1	6.987	5	15	2.248	13
2	4.658	38	16	2.202	2
3	3.654	33	17	2.043	6
4	3.490	100	18	1.995	26
5	3.425	9	19	1.860	12
6	3.289	7	20	1.834	8
7	3.115	2	21	1.746	13
8	3.079	2	22	1.732	7
9	2.792	13	23	1.728	6
10	2.708	37	24	1.662	14
11	2.611	6	25	1.641	6
12	2.469	18	26	1.561	7
13	2.373	7	27	1.537	8
14	2.328	6	28	1.485	2

DTA was made at 20–1000 °C, in air, using a derivatograph of MOM (Budapest) make. The object of analysis were samples of 1000 mg each placed in quartz crucibles; the heating rate was 10 deg·min^{-1}.

Results and discussion

Table 1 shows compositions of initial mixtures and X-ray analysis of the equilibrium preparations obtained. The data of Table 1 indicate that the components of the V_2O_5–$Fe_8V_{10}W_{16}O_{85}$ system in the solid state remain in stable mutual equilibrium. It seems that the first endothermic effect recorded on the DTA curves of equilibrium preparations, with a temperature of peak start being 620±5°C, can be ascribed to melting at that temperature of a eutectic mixture formed by the components of the system. The maximum height of the endothermic effect was observed on the DTA curves of preparations comprising 54.55 and 41.18% mol of V_2O_5 in initial mixtures of the oxides. It implies that the composition of the eutectic mixture is confined within the range of 95.00–90.00% mol of V_2O_5 in terms of components of the system under study. Stating the composition of the eutectic mixture precisely requires further studies.

Table 2 shows values for interplanar distances and relative intensities of corresponding reflexions characterizing the phase $Fe_8V_{10}W_{16}O_{85}$.

The investigations have shown that the V_2O_5–$Fe_8V_{10}W_{16}O_{85}$ system is a real two-component system with a eutectic temperature 620±5°C.

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Zusammenfassung — Mittels Röntgen-Phasen-Pulverdiffraktion und DTA wurde das im Festzustand des Systemes V_2O_5–$Fe_8V_{10}W_{16}O_{85}$ festgestellte Phasengleichgewicht untersucht. Man fand, daß das untersuchte System ein echtes Zweikomponentensystem mit einem Eutektikum bei 620±5°C ist.