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STUDY OF PHASE EQUILIBRIA ESTABLISHED UP TO THE SOLIDUS LINE IN THE SYSTEM $Fe_2V_4O_{13}$–WO_3

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Abstract

The phase equilibria established up to the solidus line in the system $Fe_2V_4O_{13}$–WO_3, one of the intersections of the three-component system Fe_2O_3–V_2O_5–WO_3, have been studied. The system appears not to be a real two-component system.

Keywords: $Fe_2V_4O_{13}$–WO_3 system, phase equilibria

Introduction

Study of the phase equilibria established in multicomponent systems of transition metal oxides provides information contributing to the explanation of the mechanism of catalytic processes taking place on the surface of catalysts that are mixtures or compounds of metal oxides. Such studies often lead to the discovery of new chemical compounds. Thus, the new phases $FeVMoO_7$ [1], $Fe_4V_2Mo_3O_{20}$ [2] and $CrVMoO_7$ [3] have been found to occur in the systems Fe_2O_3–V_2O_5–MoO_3 and Cr_2O_3–V_2O_5–MoO_3. The subject of our current studies is the hitherto unknown three-component system Fe_2O_3–V_2O_5–WO_3, mainly due to the fact that both mixtures and compounds of its components exhibit noteworthy catalytic properties [4–8].

The system Fe_2O_3–V_2O_5–WO_3 may be regarded as a three-component system built up from three two-component systems: Fe_2O_3–V_2O_5, V_2O_5–WO_3 and Fe_2O_3–WO_3. The phase equilibria established in the first of these two-component systems have been reported in some detail [9]. The formation conditions and properties of iron(III) vanadates have likewise been described [9]. Information on the system V_2O_5–WO_3 appears scanty. It is only known that, in air, at ambient pressure, the system involves a solid solution of WO_3 in V_2O_5 with a solubility limit of 7 mol% [6, 10]. Phase equilibria established in the third of the systems, i.e. Fe_2O_3–WO_3, were published earlier [11, 12], but the authors

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did not agree concerning the temperature and mode of melting of Fe_2WO_6, the sole compound in the system. This made it necessary to carry out verifying investigations [13].

Cognitive studies on the system Fe_2O_3–V_2O_5–WO_3 revealed that a new compound is formed in the solid state, and the molecular formula $Fe_8V_{10}W_{16}O_{85}$ was ascribed to it [13, 14]. The compound melts incongruently at 830±5°C to yield two solid phases: Fe_2WO_6 and WO_3 [13].

The work reported in the present paper was performed to determine the phase equilibria established in the solid state in the system $Fe_2V_4O_{13}$–WO_3, one of the intersections of the three-component system Fe_2O_3–V_2O_5–WO_3.

$Fe_2V_4O_{13}$ is one of the two compounds formed in the two-component system Fe_2O_3–V_2O_5 [9]. The compound crystallizes in a monoclinic system [15] and melts incongruently at 665±5°C to deposit solid $FeVO_4$ [9]. At ambient temperature, after grinding, WO_3 assumes triclinic symmetry [16] and melts congruently at 1473°C [17].

Experimental

α-Fe_2O_3 p.a. (VEB, Germany), calcined at 1000°C in three 24 h cycles, V_2O_5 p.a. (POCh, Poland) and WO_3 p.a. (Fluka AG, Switzerland) were used in the experiments in this work. 19 samples were subjected to study, covering the whole concentration range of the components of the system. Mixtures of the oxides, weighed in suitable proportions, were homogenized by grinding, then shaped into pastilles and subjected to calcination in air, in a syllite furnace, at temperatures fixed in screening tests. All the samples were heated under the following conditions:

$$550°C\ (24\ h)+600°C(2\times72\ h)+610°C\ (3\times72\ h+3\times48\ h).$$

After each heating cycle, the samples were cooled to ambient temperature, ground down and examined by DTA and X-ray phase analysis, and subsequently ones more moulded, heated and analysed. As confirmation of equilibrium the phase compositions of the preparations after two successive heating cycles remained unchanged.

Powder diffraction patterns subjected to X-ray phase analysis were produced with a DRON-3 diffractometer (Russia) and filtered CoK_α radiation. Phases were identified with the aid of index data on PDF cards [18] and in publications [9, 19].

DTA was performed with a Paulik-Paulik-Erdey derivatograph (MOM, Hungary). Samples of 1000 mg each were placed in quartz crucibles. Measurements were conducted in air, at 20–1000°C and a heating rate of 10 deg/min.

The temperature of the solidus line was fixed on the basis of the temperatures of onset of the first endothermic effects recorded in the DTA curves of preparations at equilibrium. The accuracy of temperature reading was shown by repetition of measurements to be ±5 deg.

Results and discussion

The Table presents the compositions of three initial mixtures and the phase compositions of preparations at equilibrium. It follows from the tabulated data that at equilibrium the preparations containing 75.00% mol WO_3 are mixtures of three phases: V_2O_5, $Fe_2V_4O_{13}$ and $Fe_8V_{10}W_{16}O_{85}$, the latter a compound formed in the three-component system Fe_2O_3–V_2O_5–WO_3 [14]. The preparation containing 80.00% mol WO_3 in the initial mixture gives, in the equilibrium

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

No.	Compositions of initial mixtures /mol%				Phase composition of equilibrium samples*
	Fe_2O_3	V_2O_5	WO_3	WO_3 *in terms* of comp. system	
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	$Fe_8V_{10}W_{16}O_{85}$, $Fe_2V_4O_{13}$, V_2O_5
7	28.26	56.52	15.22	35.00	$Fe_8V_{10}W_{16}O_{85}$, $Fe_2V_4O_{13}$, V_2O_5
8	27.27	54.55	18.18	40.00	$Fe_8V_{10}W_{16}O_{85}$, $Fe_2V_4O_{13}$, V_2O_5
9	26.19	52.38	21.43	45.00	$Fe_8V_{10}W_{16}O_{85}$, $Fe_2V_4O_{13}$, V_2O_5
10	25.00	50.00	25.00	50.00	$Fe_8V_{10}W_{16}O_{85}$, $Fe_2V_4O_{13}$, V_2O_5
11	23.68	47.37	28.95	55.00	$Fe_8V_{10}W_{16}O_{85}$, $Fe_2V_4O_{13}$, V_2O_5
12	22.22	44.44	33.33	60.00	$Fe_8V_{10}W_{16}O_{85}$, $Fe_2V_4O_{13}$, V_2O_5
13	20.59	41.18	38.23	65.00	$Fe_8V_{10}W_{16}O_{85}$, $Fe_2V_4O_{13}$, V_2O_5
14	18.75	37.50	43.75	70.00	$Fe_8V_{10}W_{16}O_{85}$, $Fe_2V_4O_{13}$, V_2O_5
15	16.67	33.33	50.00	75.00	$Fe_8V_{10}W_{16}O_{85}$, $Fe_2V_4O_{13}$, 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

*Succession in records has resulted from the decreasing phase contents.

state, a mixture of two phases: $Fe_8V_{10}W_{16}O_{85}$ and V_2O_5. The preparations whose initial mixtures contain 85.00% mol WO_3 or more also consist of three phases at equilibrium, but in this component concentration range the equilibrium phase is no longer $Fe_2V_4O_{13}$; besides $Fe_8V_{10}W_{16}O_{85}$ and V_2O_5, the third phase is WO_3.

The first effect in the DTA curves of equilibrium mixtures of preparations initially containing up to 75.00% mol WO_3 is the endothermic effect with a temperature onset of 615±5°C. The peak start temperature of the first endothermic effect in the DTA curves of the other preparations at equilibrium differs slightly, at 620±5°C. It may be suggested that the temperatures of the solidus lines for the system $Fe_2V_4O_{13}$–WO_3, obtained by means of DTA measurements, are most probably the temperatures of two triple eutectics occurring in the three-component system Fe_2O_3–V_2O_5–WO_3.

The experimental data obtained allow of statement that the system $Fe_2V_4O_{13}$–WO_3 is not a real two-component system, not even below the solidus line.

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Zusammenfassung — Es wurde eine Untersuchung des Phasengleichgewichtes durchgeführt, welches bezüglich der Solidus-Linie im System $Fe_2V_4O_{13}$–WO_3, einer der Zwischenbereiche im Dreikomponentensystem Fe_2O_3–V_2O_5–WO_3, nachgewiesen wurde. Dieses System scheint kein echtes Zweikomponentensystem zu sein.