

## PHASE EQUILIBRIA IN THE SYSTEM $\text{FeVO}_4\text{-WO}_3$ IN THE SOLID STATE

*J. Walczak and I. Rychlowska-Himmel*

INSTITUTE OF FUNDAMENTAL CHEMISTRY, TECHNICAL UNIVERSITY OF SZCZECIN,  
AL. PIASTÓW 42, 71-065 SZCZECIN, POLAND

The DTA and X-ray powder diffraction imply the following equilibria in the system  $\text{FeVO}_4\text{-WO}_3$  up to the solidus line: from 550 to 650-670°C, the system components remain inert towards each other in the whole concentration range; above 670°C, at up to 66.67 mol% of  $\text{WO}_3$ ,  $\text{FeVO}_4$  and  $\text{FeVW}_2\text{O}_{10}$  are in equilibrium, whereas from 66.67 mol% of  $\text{WO}_3$  upwards  $\text{FeVW}_2\text{O}_{10}$  and  $\text{WO}_3$  are in equilibrium.

Studies on the three-component system  $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5\text{-WO}_3$ , which is interesting from a catalytic point of view, indicate that the system components react to yield at least one hitherto unknown compound, to which the molecular formula  $\text{FeVW}_2\text{O}_{10}$  has been ascribed [1]. This compound can be written as  $\text{FeVO}_4.2\text{WO}_3$ . In order to continue studies on the system  $\text{Fe}_2\text{O}_3\text{-V}_2\text{O}_5\text{-WO}_3$ , it seemed advisable to establish first the phases with which  $\text{FeVW}_2\text{O}_{10}$  is in permanent equilibrium in the system  $\text{FeVO}_4\text{-WO}_3$  in the entire component concentration range.

The components of the system  $\text{FeVO}_4\text{-WO}_3$ , as well as  $\text{Fe}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$ , are well known. Iron(III) orthovanadate crystallizes in a triclinic system [2] and melts incongruently, depositing solid  $\text{Fe}_2\text{O}_3$  at 540-890° [3]. At ambient temperature,  $\text{WO}_3$  has triclinic symmetry after being ground down [4], and melts congruently at 1473° [5].

### Experimental

Analar  $\alpha\text{-Fe}_2\text{O}_3$  (VEB, GDR), analar  $\text{V}_2\text{O}_5$  (POCh, Poland), analar  $\text{WO}_3$  (Fluka AG, Switzerland), and  $\text{FeVO}_4$  obtained by calcining an equimolar mixture of  $\text{Fe}_2\text{O}_3$  and  $\text{V}_2\text{O}_5$  at 600° for 24 h, at 650° for 24 h, and at 700° for 24 h were used. Two series of samples were prepared: a basic compound

series of 17 mixtures of the appropriate oxides, and a reference series whose samples were mixtures of the system components, i.e.  $\text{FeVO}_4$  and  $\text{WO}_3$ . The compositions of the basic series samples are shown in Table 1. In both series, the mixtures were homogenized by grinding, then pastilled and calcined in air. The samples of the basic series were heated in a cycle: at  $550^\circ$  for 24 h; at  $600^\circ$  for 48 h x 2; at  $650^\circ$  for 48 h; at  $670^\circ$  for 48 h; and at  $700^\circ$  for 48 h x 3 + 24 h. After each of the calcination stages, the preparations were cooled down slowly to ambient temperature, ground down and analyzed by DTA and X-ray powder diffraction.

**Table 1** Compositions of initial mixtures, preparation conditions, and X-ray powder diffraction results on preparations obtained from the oxides

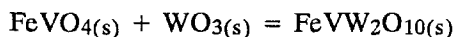
Compositions of samples in terms of system components, mol % $\text{WO}_3$	Preparation condition	X-ray powder diffraction
5.00; 10.00; 15.00;	$550^\circ\text{C}(24 \text{ h}) + 600^\circ\text{C}(48 \text{ h})$	$\text{FeVO}_4$ , $\text{WO}_3$
20.00; 25.00; 30.00;	$600^\circ\text{C}(48 \text{ h}) + 650^\circ\text{C}(48 \text{ h})$	$\text{FeVO}_4$ , $\text{WO}_3$
33.33; 35.00; 40.00;	$670^\circ\text{C}(48 \text{ h}) + 700^\circ\text{C}(24 \text{ hx}3)$	$\text{FeVO}_4$ , $\text{FeVW}_2\text{O}_{10}$
45.00; 50.00; 55.00;		
60.00; 65.00		
	$550^\circ\text{C}(24 \text{ h}) + 600^\circ\text{C}(48 \text{ h})$	$\text{FeVO}_4$ , $\text{WO}_3$
66.67	$600^\circ\text{C}(48 \text{ h}) + 650^\circ\text{C}(48 \text{ h})$	$\text{FeVO}_4$ , $\text{WO}_3$
	$670^\circ\text{C}(48 \text{ h}) + 700^\circ\text{C}(24 \text{ hx}3)$	$\text{FeVW}_2\text{O}_{10}$
	$550^\circ\text{C}(24 \text{ h}) + 600^\circ\text{C}(48 \text{ h})$	$\text{FeVO}_4$ , $\text{WO}_3$
75.00; 85.00; 95.00	$600^\circ\text{C}(48 \text{ h}) + 650^\circ\text{C}(48 \text{ h})$	$\text{FeVO}_4$ , $\text{WO}_3$
	$670^\circ\text{C}(48 \text{ h}) + 700^\circ\text{C}(24 \text{ hx}3)$	$\text{WO}_3$ , $\text{FeVW}_2\text{O}_{10}$

DTA was performed in air, in quartz crucibles, using a derivatograph of Paulik-Paulik-Erdey type (MOM, Budapest). All measurements were made under the same conditions, i.e.  $20$ - $1000^\circ$ , a heating rate of  $10 \text{ deg/min}$ , and a sample weight of  $1000 \text{ mg}$ . X-ray powder diffraction was performed with a diffractometer of GDR make, type  $A_2$ , with an HZG-4 goniometer and  $\text{CoK}\alpha$  radiation. The phase compositions of the samples were established through the use of ASTM cards [6].

## Results and discussion

Table 1 gives not only the compositions, but also the conditions of preparation and the X-ray powder diffraction results on the preparations obtained from the oxides after the successive stages of calcination. The

phase compositions of the preparations show, that by 600° Fe<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> react to completion, yielding FeVO<sub>4</sub>. The iron(III) orthovanadate formed remains in permanent equilibrium with WO<sub>3</sub> up to 650°. It is only when the preparations are heated at 670° that their diffraction patterns show a set of reflexions attributed to the phase FeVW<sub>2</sub>O<sub>10</sub> [1]. This implies that in this system a reaction takes place in the solid state:



The preparation which contains 66.67 mol% of WO<sub>3</sub> in its initial mixture provides evidence of this reaction (Table 1).

The DTA and X-ray powder diffraction data imply the following equilibria in the system FeVO<sub>4</sub>-WO<sub>3</sub> up to the solidus line:

- from 550 to 650-670°, the system components remain inert towards each other in the entire concentration range,
- above 670°, at up to 66.67 mol% of WO<sub>3</sub>, FeVO<sub>4</sub> and FeVW<sub>2</sub>O<sub>10</sub> are in equilibrium, whereas from 66.67 mol% of WO<sub>3</sub> upwards FeVW<sub>2</sub>O<sub>10</sub> and WO<sub>3</sub> are in equilibrium.

## References

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- 2 B. Robertson and K. Kostiner, *J. Solid State Chem.*, 4 (1972) 29.
- 3 O. Kubaschewski, F. L. Evans and C. B. Alcock, *Metallurgical Thermochemistry*, London, 1967.
- 4 E. Salje and K. Viswanathan, *Acta Cryst.*, A 31 (1975) 356.
- 5 *Physico-chemical Handbook*, WNT, Warsaw 1974.
- 6 Joint Committee of Powder Diffraction File: 13-534, 9-387, 32-1395, 25-418.

**Zusammenfassung** — DTA Untersuchungen und Debye-Scherrer-Aufnahmen lassen darauf schließen, daß im System FeVO<sub>4</sub>-WO<sub>3</sub> bis zur Soliduslinie folgende Gleichgewichte festgestellt wurden: von 550 bis 650-670°C bleiben die Systemkomponenten im ganzen Konzentrationsbereich voneinander unberührt, oberhalb 670°C sind bis zu 66.67 Molprozent WO<sub>3</sub> die Verbindungen FeVO<sub>4</sub> und FeVW<sub>2</sub>O<sub>10</sub> im Gleichgewicht vorhanden, oberhalb 66.67 Molprozent WO<sub>3</sub> hingegen die Verbindungen FeVW<sub>2</sub>O<sub>10</sub> und WO<sub>3</sub>.