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STUDY OF THE SOLID SOLUTION OF MoO_3 IN $Fe_2V_4O_{13}$

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Differential thermal and phase X-ray analyses have shown that MoO_3 and $Fe_2V_4O_{13}$ form a solid substitution solution, in which Mo^{6+} ions are incorporate into the crystal lattice of $Fe_2V_4O_{13}$ in place of V^{5+} ions. The solubility limit of MoO_3 in $Fe_2V_4O_{13}$ at ambient temperature is 18 mole % of MoO_3. The phase equilibria in the system $Fe_2V_4O_{13}$—$FeVMoO_7$ were also studied. Results are presented in the form of a phase diagram.

A comprehensive review of the literature concerned with the compound $Fe_2V_4O_{13}$ has disclosed that its properties are still insufficiently known.

The compound is reported to melt incongruently, depositing solid $FeVO_4$. In [1] the melting point of $Fe_2V_4O_{13}$ is given as 692°, and in [2] as 715°, while we have found a value of 665° [3].

In our experiments with the system Fe_2O_3—V_2O_5, we obtained $Fe_2V_4O_{13}$ by two methods:

(a) through a reaction in the solid phase between Fe_2O_3 and V_2O_5, or between $FeVO_4$ and V_2O_5

(b) by a precipitation method [3].

We have also found that a mixture of $Fe_2V_4O_{13}$ with MoO_3 forms a solid substitution solution, in which Mo^{6+} ions are incorporated into the $Fe_2V_4O_{13}$ crystal lattice, in place of V^{5+} ions [4].

Solid solutions involved in the process of incorporation of transition metal ions into the crystal networks of oxysalts are expected to manifest properties interesting from a catalytic aspect. This led us to investigate the kind of solution developed, the solubility limit for MoO_3 in $Fe_2V_4O_{13}$, and the site of pseudobinary intersection of the three-component system Fe_2O_3—V_2O_5—MoO_3.

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Experimental

The samples were prepared from α-Fe_2O_3, V_2O_5 (commercial product of p.a. grade) and MoO_3 obtained by thermal decomposition of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, in air at 150–550°. Weighed in appropriate proportions, the oxides were ground, pastilled and heated in air, in the following cycles: 400–500°—1 h; 500°—24 h; 550°—48 h; 600°—72 h. The preparations obtained were gradually cooled to ambient temperature and then ground.

The phase compositions of the samples were ascertained by phase X-ray analysis (DRON-3, CoK_α) and the data from ASTM cards [5] and the literature [2, 3].

Thermal analysis (DTA) was accomplished with the aid of a derivatograph (MOM, Budapest), in quartz crucibles, in air atmosphere, at a heating rate of 10 degree/min and in the temperature range 20–1000°. The mass of the samples examined was in each case 1000 g. The accuracy of temperature readings of effects in the DTA curves, assessed from repetitions, was $\pm 5°$.

Results and discussion

The aim of the preliminary experiments was to establish the kind of solid solution of MoO_3 in $Fe_2V_4O_{13}$. Accordingly, two mixtures were prepared: one composed of $Fe_2V_4O_{13}$ and MoO_3, and the other of Fe_2O_3, V_2O_5 and MoO_3; the $Fe_2V_4O_{13}$ and MoO_3 contents of the two mixes were the same, 85 and mole 15%, respectively. The samples were calcined under given conditions and the resultant preparations were determined by means of DTA and phase X-ray analyses.

The results of X-ray analysis revealed that the preparations, irrespective of the kind of substrates employed, were mixtures of two phases, $Fe_2V_4O_{13(S.S)}$ and V_2O_5, no MoO_3 or any other phases known to contain iron vanadium or molybdenum being observed. The DTA curves of the two preparations were identical (Fig. 1). In each curve, three endothermic effects were recorded. The first, with peak start temperature at 620°, was produced by melting of the $Fe_2V_4O_{13}$—V_2O_5 mixture [3, 4], the second by incongruent melting of $Fe_2V_4O_{13(S.S)}$, and the third was associated with the melting of $FeVO_4$, a phase deposited during the incongruent melting of $Fe_2V_4O_{13(S.S)}$ [1–3]. Both the phase compositions of the two preparations and the results of DTA measurements imply that a reaction in the solid phase takes place between $Fe_2V_4O_{13}$ and MoO_3:

$$Fe_2V_4O_{13(S)} + MoO_{3(S)} \rightarrow Fe_2V_4O_{13(S.S)} + V_2O_{5(S)} \qquad (1)$$

The result also demonstrated that Mo^{6+} ions are incorporated into the $Fe_2V_4O_{13}$ lattice, in place of V^{5+} ions.

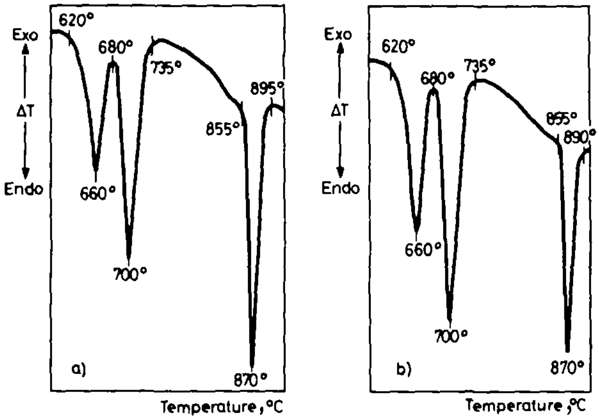

Fig. 1 DTA curves of preparations related to 85% mol of $Fe_2V_4O_{13}$ and 15% mol of MoO_3; a) substrates: $Fe_2V_4O_{13}+MoO_3$; b) substrates: $Fe_2O_3+V_2O_5+MoO_3$

The substitution of V^{5+} by Mo^{6+} ions in the $Fe_2V_4O_{13}$ network furnishes an excess positive charge, the compensation of which would be possible by: (a) the cationic vacancies arising in the Fe^{3+} sublattice, with the concurrent removal of an equivalent amount of Fe^{3+} ions from the $Fe_2V_4O_{13}$ crystal lattice, the process being described in terms of the formula:

$$Fe_{2-x}\Phi_xV_{4-3x}Mo_{3x}O_{13} \tag{I}$$

(b) the cationic vacancies arising in the V^{5+} sublattice, the resultant solid solution being described by the formula:

$$Fe_2V_{4-6x}\Phi_xMo_{5x}O_{13} \tag{II}$$

(c) the reduction of either Fe^{3+} to Fe^{2+} ions, or of V^{5+} to V^{4+} ions:

$$Fe^{3+}_{2-x}Fe^{2+}_xV_{4-x}Mo_xO_{13} \tag{IIIA}$$

$$Fe_2V^{5+}_{4-2x}V^{4+}_xMo_xO_{13} \tag{IIIB}$$

The situation of the alternative models of the solid solution in the area of the three-component system Fe_2O_3—V_2O_5—MoO_3 is shown in Fig. 2. It follows from the pattern that it is the reduction model of the solid solution (III) that determines the pseudobinary intersection of the three-component system between two phases. The boundary phases of this intersection are $Fe_2V_4O_{13}$ and $FeVMoO_7$, a compound existing in the Fe_2O_3—V_2O_5—MoO_3 system and melting incongruently at 680 ± 5° [6] with deposition of solid $Fe_4V_2Mo_3O_{20}$, another compound, also incongruent, occurring in the Fe_2O_3—V_2O_5—MoO_3 system [7, 8].

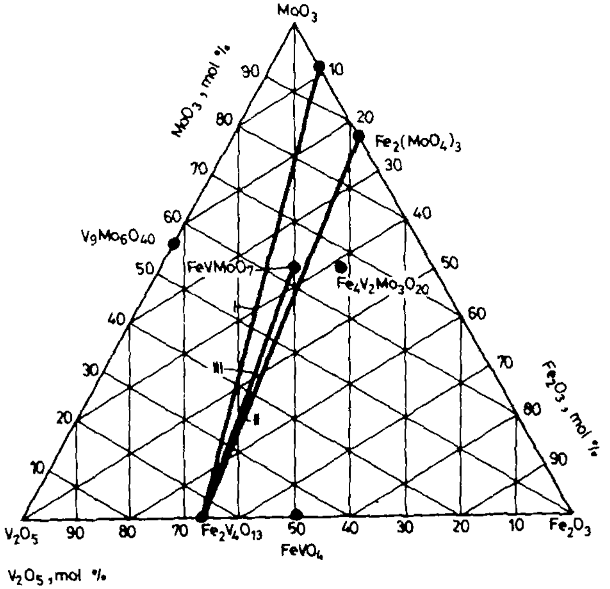

Fig. 2 Site of solid solution models I, II, III in the triangle area of concentrations of the components: Fe_2O_3—V_2O_5—MoO_3.
I: $Fe_{2-x}\Phi_xV_{4-3x}Mo_{3x}O_{13}$; II: $Fe_2V_{4-6x}\Phi_xMo_{5x}O_{13}$;
IIIA: $Fe^{3+}_{2-x}Fe^{2+}_xV_{4-x}Mo_xO_{13}$; IIIB: $Fe_2V^{5+}_{4-2x}V^{4+}_xMo_xO_{13}$

In order to ascertain which of the theoretical solid solution models develop, preparations were synthesized with compositions corresponding to those of the models, with the values of x matched so that each of the models would be represented by samples containing the same amount of MoO_3 in the starting mixtures of oxides, say, 5, 10 and 15 mole % of MoO_3, respectively.

The results of the phase X-ray analysis of the preparations obtained, as well as the compositions of their starting mixtures, are given in Table 1. The DTA curves of the samples referred to as model II or III indicated only the melting effects of $Fe_2V_4O_{13(S.S)}$ and $FeVO_4$, respectively, i.e. a phase evolved during the incongruent melting of $Fe_2V_4O_{13(S.S)}$ [1-3]. In contrast, the DTA curves of samples whose compositions related to model I exhibited an additional effect induced by melting of the mixture of $Fe_2V_4O_{13(S.S)}$ with V_2O_5 [3, 4]. Consequently, the results of the measurements rule out model I, i.e. a solution whose Fe^{3+} sublattice would suffer vacancies due to the charge compensation. Nonetheless, the actual existence of either of the other two models can not be conclusively proved, due to an inappreciable difference in composition between the starting mixtures relating to models II and III, the efficiency of the measuring techniques applied in our experiments appearing inadequate for this purpose (Fig. 2).

Table 1 Compositions of starting mixtures and results from phase X-ray analysis of the preparations obtained

Pattern of a solution	x	Composition of a starting mixture, mol %			Phases discovered in the preparations
		Fe_2O_3	V_2O_5	MoO_3	
1	2	3	4	5	6
	0.0508	31.95	63.05	5.00	
I: $Fe_{2-x}\Phi_xV_{4-3x}Mo_{3x}O_{13}$	0.0103	30.57	59.43	10.00	$Fe_2V_4O_{13(S.S)}$;
	0.1580	29.16	55.84	15.00	V_2O_5
	0.0310	32.66	62.34	5.00	$Fe_2V_4O_{13(S.S)}$
II: $Fe_2V_{4-6x}\Phi_xMo_{5x}O_{13}$	0.0630	32.00	58.00	10.00	$FeVO_4$ –
	0.0960	31.33	53.67	15.00	possible trace amounts
IIIA: $Fe^{3+}_{2-x}Fe^{2+}_xV_{4-x}Mo_xO_{13}$	0.1540	32.50	62.50	5.00	
	0.3160	31.67	58.33	10.00	$Fe_2V_4O_{13(S.S)}$
IIIB: $Fe_2V^{5+}_{4-2x}V^{4+}_xMo_xO_{13}$	0.4860	30.84	54.16	15.00	

Further investigations to pinpoint the model and to determine its solubility range were carried out by assuming $Fe_2V_4O_{13}$ and $FeVMoO_7$ as substrates, mixed in various molar proportions. Accordingly, eight mixtures of $Fe_2V_4O_{13}$ with $FeVMoO_7$ were prepared containing 90–25 mole % of $Fe_2V_4O_{13}$ and 10–75 mole % $FeVMoO_7$.

The mixtures were calcined under given conditions, and the resultant preparations were examined by DTA, their phase compositions being established afterwards.

Figure 3 shows the DTA curves of two optional preparations. The DTA curve of a preparation produced by the reaction of 70 mole % of $Fe_2V_4O_{13}$ with 30 mole % of $FeVMoO_7$ indicated two effects: one from the melting of $Fe_2V_4O_{13(S.S)}$ and the other from the melting of $FeVO_4$, a phase separating during the incongruent melting of $Fe_2V_4O_{13(S.S)}$. On the other hand, the DTA curve of a preparation whose starting mixture consisted of 25 mole % of $Fe_2V_4O_{13}$ and 75 mole % of $FeVMoO_7$ additionally demonstrated effects brought about by the melting of $FeVMoO_7$ and that of a phase deposited during the incongruent melting of $FeVMoO_7$, i.e. $Fe_4V_2Mo_3O_{20}$.

For starting mixtures with the $FeVMoO_7$ content confined within the range 10–40 mole % and for those with the $FeVMoO_7$ content in the range 90–60 mole %, no presence of $FeVMoO_7$ in the reaction products was found, the resultant preparations containing purely a solid solution. However, starting

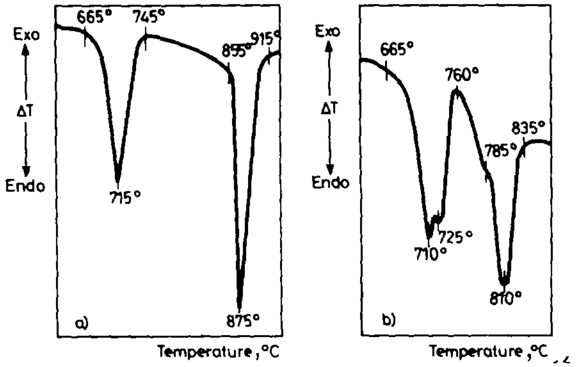

Fig. 3 DTA curves of the reaction products: a) 70% mol of $Fe_2V_4O_{13}$ + 30% mol of $FeVMoO_7$; b) 25% mol of $Fe_2V_4O_{13}$ + 75% mol of $FeVMoO_7$

mixtures with upwards of 50 mole % content of $FeVMoO_7$ are thought to give rise to reaction products comprising a solid solution accompanied by unreacted $FeVMoO_7$.

The results of investigation of this series have proved that the resultant solid solution does not occur in the whole range of concentrations of the component of the $Fe_2V_4O_{13}$—$FeVMoO_7$ system, but only in a limited range of the component concentrations. They also suggest that the $FeVMoO_7$ phase of hitherto unknown structure [6] is not a product following the solubility limit of MoO_3 in $Fe_2V_4O_{13}$, in accordance with model III, that is, when at $x = 2$ all the vanadium ions undergo reduction to V^{4+}, or all the Fe^{3+} ions are converted into Fe^{2+}, which can be described by the formula $Fe_2V_2Mo_2O_{13}$.

In order to establish the maximum solubility of MoO_3 in $Fe_2V_4O_{13}$ and to establish the phase equlibria in the whole range of concentrations of the components of the system $Fe_2V_4O_{13}$—$FeVMoO_7$, 25 mixtures were prepared from Fe_2O_3, V_2O_5 and MoO_3 in 2 mole % steps of MoO_3. The mixtures were calcined under the given conditions, the resultant preparations being examined by DTA and phase X-ray methods.

Figure 4 shows a phase diagram of the system $Fe_2V_4O_{13}$—$FeVMoO_7$. The solidus lines were determined on the basis of the DTA effect start temperatures, and the liquidus lines from the effect peak temperatures. The close positions of the melting effects of $Fe_2V_4O_{13(S.S)}$ and $FeVMoO_7$ prevented accurate reading of the melting start of $FeVMoO_7$. The diagram has therefore been plotted for the melting peak temperature in line of the melting start temperature, while the line indicating the incongruent melting of $FeVMoO_7$ has been drawn at 680°, i.e. at the melting point of the compound [6]. In the subsolidus area there are two phases: a solid solution of MoO_3 in $Fe_2V_4O_{13}$ and $FeVMoO_7$. The range of occurrence of the

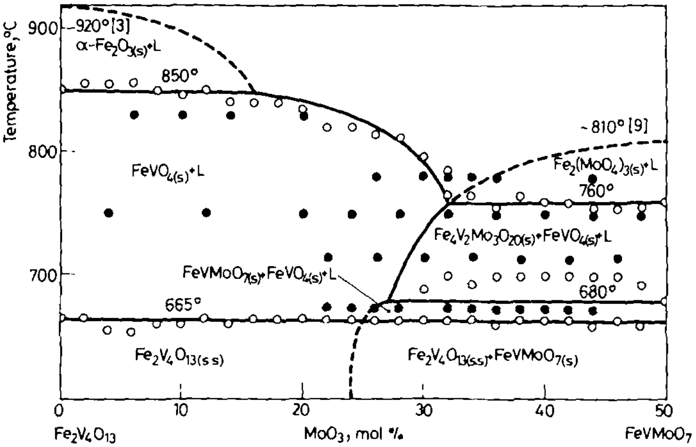

Fig. 4 Phase diagram of the system: $Fe_2V_4O_{13}-FeVMoO_7$. ○ points indicate DTA; ● X-ray investigation after air quenching

solid solution amounts to 18 mole % of MoO_3 at ambient temperature, which in terms of the components of the system is equal to 54.20 mole % of $Fe_2V_4O_{13}$ and 45.80 mole % of $FeVMoO_7$, respectively. Above that content of MoO_3, $Fe_2V_4O_{13(S.S)}$ and $FeVMoO_7$ coexist in the solid phase.

At temperatures higher than 665°, say, above the temperature at which a liquid would appear, the system ceased to be a two-component arrangement on account of the incongruent melting of both $Fe_2V_4O_{13(S.S)}$ and $FeVMoO_7$:

$$Fe_2V_4O_{13(S.S)} \rightarrow FeVO_{4(S)} + \text{liquid} \tag{2}$$

$$FeVMoO_{7(S)} \rightarrow Fe_4V_2Mo_3O_{20(S)} + \text{liquid} \tag{3}$$

Both $FeVO_4$ and $Fe_4V_2Mo_3O_{20}$ melt incongruently:

$$FeVO_{4(S)} \rightarrow \alpha\text{-}Fe_2O_{3(S)} + \text{liquid} \tag{4}$$

$$Fe_4V_2Mo_3O_{20(S)} \rightarrow Fe_2(MoO_4)_{3(S)} + \alpha\text{-}Fe_2O_{3(S)} + \text{liquid} \tag{5}$$

The result of the meritectic reactions is that phases coexisting with a liquid appear in the system. The kinds of phases and the scope of their existence have been ascertained from the results of phase X-ray analysis of preparations additionally heated for 2 hours at 675, 715, 750, 785 and 830°, and afterwards cooled to ambient temperature. The compositions of the samples subjected to such examinations have been denoted on the phase diagram.

Conclusions

1. Molybdenum (VI) oxide forms a solid substitution solution in $Fe_2V_4O_{13}$. The solubility limit of MoO_3 in $Fe_2V_4O_{13}$ at ambient temperature is 18 mole % of MoO_3. The solution arises due to the incorporation of Mo^{6+} ions into the crystal lattice of $Fe_2V_4O_{13}$, in place of V^{5+} ions. The charge compensation seems to proceed through the reduction of V^{5+} to V^{4+} or Fe^{3+} to Fe^{2+}, in accordance with model III. Conclusive proof of the charge compensation route requires a continuation of the invstigation.

2. A phase diagram of the system $Fe_2V_4O_{13}$—$FeVMoO_7$ has been constructed. It is a real two-component system merely up to the solidus line temperature, i.e. up to 665°. Above this temperature, the system ceases to be a two-component structure because of the incongruent melting of the components, as well as due to the incongruent melting of some phases resulting from melting of the components.

References

1 A. A. Fotiev, S. M. Cheshnitskii and L. L. Surat, Zh. Neorg. Khim., 28 (1983) 988.

2 Y. Otsubo and K. Utsumi, J. Chem. Soc. Japan, Pure Chem. Sec., 92 (1971) 737.

3 J. Walczak, J. Ziółkowski, M. Kurzawa, J. Osten-Sacken and M. Łysio, Polish J. Chem., in press.

4 J. Walczak, M. Kurzawa and L. Trześniowska, 8th Internat. Conf. Therm. Anal., Bratislava, Czechoslovakia, August 19–23, 1985.

5 Joint Committee of Powder Diffraction Rile 5–508, 9–387, 13–543, 19–813, 20–526, 20–1377, 24–541, 25–418.

6 J. Walczak, M. Kurzawa and E. Filipek, J. Thermal Anal., in press.

7 J. Walczak, J. Ziółkowski, M. Kurzawa and L. Trześniowska, J. Thermal Anal., 29 (1984) 983.

8 J. Walczak, J. Ziółkowski, M. Kurzawa and L. Trześniowska, Polish J. Chem., in press.

9 J. Walczak, M. Kurzawa and K. Wasążnik, 8th Internat. Conf. Therm. Anal., Bratislava, Czechoslovakia, August 19–23, 1985.

Zusammenfassung — Durch DTA und Röntgenphasenanalyse wurde gezeigt, daß MoO_3 und $Fe_2V_4O_{13}$ Substitutionsmischkristalle bilden, in denen Mo^{6+}-Ionen anstelle von V^{5+}-Ionen in das Kristallgitter von $Fe_2V_4O_{13}$ eingebaut sind. Die Löslichkeitsgrenze von MoO_3 in $Fe_2V_4O_{13}$ beträgt bei Umgebungstemperatur 18 Mol-% MoO_3. Ebenfalls wurden die Phasengleichgewichte im System $Fe_2V_4O_{13}$—$FeVMoO_7$ untersucht. Die Ergebnisse sind in Form eines Phasendiagramms dargestellt.

Резюме — Дифференциальный термический и рентгено-фазовый анализы показали, что MoO_3 и $Fe_2V_4O_{13}$ образуют твердый раствор замещения, в котором ионы Mo^{6+} замещают ионы V^{5+} в кристаллической решетке $Fe_2V_4O_{13}$. Предел растворимости MoO_3 в $Fe_2V_4O_{13}$ при обычной температуре составляет 18 мольных %. Изучено также фазовое равновесие системы $Fe_2V_4O_{13}$—$FeVMoO_7$ и результаты представлены в форме фазовой диаграммы.