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STUDIES ON THE $Fe_2(MoO_4)_3$–V_2O_5 SYSTEM

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The phase equilibria established in solid state in the whole range of component concentrations in the $Fe_2(MoO_4)_3$–V_2O_5 system were studied by DTA and X-ray powder diffraction. This system is not a real two-component system.

The catalytic properties of the components of the system presented prompted an investigation of the interaction of the components and their existence at equilibrium in the system.

Ferric molybdate exists in two polymorphic modifications: a low-temperature one (α) with monoclinic crystals, and a high-temperature variety (β) crystallizing in an orthorhombic system. The temperature of the phase transition has been variously reported as 499° [1], 513° [2] and 518° [3]. The structures of both modifications are known. $Fe_2(MoO_4)_3$ has been reported to melt congruently at 956° [4] or at 975° [5].

The structure and the properties of V_2O_5 are also well known. Vanadium pentoxide crystallizes in an orthorhombic system. V_2O_5 too has been reported to melt congruently, at 675° [6] or at 690° [7].

Experimental

V_2O_5, MoO_3 and α-Fe_2O_3 were used in the experiments. The oxides, in weighed proportions, were ground, pastilled and heated in air at 400° → 500° for 72 h and at 570° for 24 h. The preparations obtained were cooled slowly to ambient temperature and then ground. Some of the preparations were additionally heated for 72 h at 570°, and the cooled rapidly to ambient temperature.

The phase compositions of the preparations were established by X-ray powder diffraction (DRON–3, CoK_α).

The DTA measurements were made using a derivatograph, in quartz crucibles, in air at 20–1000°, at a heating rate of 10 deg/min. Each sample weighed 1000 mg.

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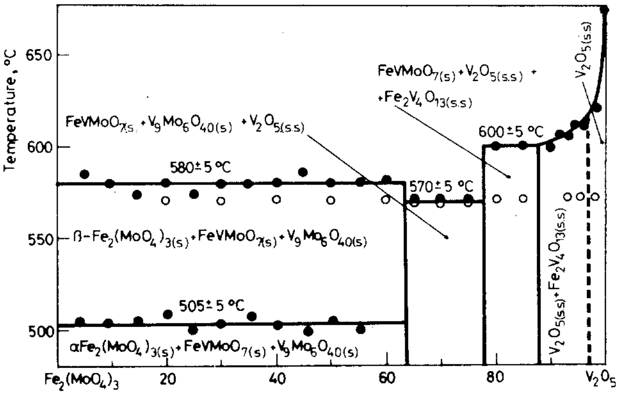

Fig. 1 Phase equilibria in subsolidus area of $Fe_2(MoO_4)_3$–V_2O_5 system, ○ points indicate DTA, ● X-ray investigation after air quenching

For investigation of the phase equilibria established in the solid-state system, 25 samples were prepared from the oxides, with compositions corresponding to the whole component concentration range. The samples were heated under the conditions mentioned above, and the preparations obtained were studied by means of DTA and X-RPD.

Results and discussion

The experimental results proved that V_2O_5 does not remain at constant equilibrium with $Fe_2(MoO_4)_3$. The phase compositions of the preparations containing 5.0 to 30.0 mol% of V_2O_5 in their starting mixtures indicated that V_2O_5 enters into a complete reaction with $Fe_2(MoO_4)_3$ to yield $FeVMoO_7$; a detectable amount of MoO_3 is present in the reaction product:

$$Fe_2(MoO_4)_3 + V_2O_5 = 2\,FeVMoO_7 + MoO_3 \tag{1}$$

There is another possible reaction:

$$6\,Fe_2(MoO_4)_3 + 10.5\,V_2O_5 = 12\,FeVMoO_7 + V_9Mo_6O_{40} + \frac{1}{4}O_2 \tag{2}$$

Hence, in samples containing up to 30 mol% of V_2O_5 and brought to equilibrium, a third phase should be detectable, i.e. either MoO_3 or $V_9Mo_6O_{40}$.

It has been found through screening analysis that under these conditions 2.5 mol% of MoO_3 can be detected, but as concerns $V_9Mo_6O_{40}$ only ~5.0 mol% of this compound can be detected. Provided that the original mixture contains

30 mol% of V_2O_5 and reaction (1) takes place in the system, the reaction products are assumed to comprise a mixture containing ~25.0 mol% of MoO_3, i.e. an amount readily detectable. Should the system contain $V_9Mo_6O_{40}$, then at 30.0 mol% of V_2O_5 in the starting mixture system the compound would barely be formed in 3.18 mol%. Thus $V_9Mo_6O_{40}$ is the third phase occurring in these samples.

It has been established that V_2O_5 in an amount of up to 60.0 mol% enters into a complete reaction with $Fe_2(MoO_4)_3$, giving $FeVMoO_7$ and $V_9Mo_6O_{40}$. This means that in the system with 36.36 mol% of $Fe_2(MoO_4)_3$ reaction (2) occurs.

When the amount of V_2O_5 in the system is increased, it becomes a stable phase, $V_9Mo_6O_{40}$ is decomposed, and a solid solution of MoO_3 in $Fe_2V_4O_{13}$ [8] appears, accompanied by $V_2O_{5(s.s)}$; this means that in this component concentration range $FeVMoO_7$ starts to decompose.

The phase equilibria established in the whole component concentration range in the solid-state system of $Fe_2(MoO_4)_3$–V_2O_5 are depicted in the Figure. This shows that the system is not a real two-component system, not even in the subsolidus area. This fact is supported by the presence of areas in which three solid phases remain at equilibrium.

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Zusammenfassung — Im gesamten Konzentrationsbereich der Komponenten des Systems $Fe_2(MoO_4)_3$-V_2O_5 wurde das im festen Aggregatzustand festgestellte Phasengleichgewicht mittels DTA und Pulverröntgendiffraktionsverfahren untersucht. Dieses System ist kein wirkliches Zweikomponentensystem.

Резюме — Методом ДТА и рентгеноструктурного анализа изучено фазовое равновесие твердотельной системы $Fe_2(MoO_4)_3$–V_2O_5 во всей области концентраций компонентов. Установлено, что в действительности данная система не является двухкомпонентной.