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THE $V_9Mo_6O_{40}$–$FeVMoO_7$ SYSTEM

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DTA and X-ray powder diffraction methods were used to study the phase equilibria established in the $V_9Mo_6O_{40}$–$FeVMoO_7$ system up to 1000° throughout the whole component concentration range. The experimental results are presented in the form of a phase diagram.

$V_9Mo_6O_{40}$, one of the phases existing in the V_2O_4–MoO_3–O system, has been the subject of various investigations for many years, primarily with regard to its interesting catalytic properties [1].

The other component of the system, $FeVMoO_7$, was discovered quite recently [2], and has not hitherto been studied from the aspects of catalytic activity and selectivity. However, it is known that $V_9Mo_6O_{40}$ reacts with Fe_2O_3 [3]:

$$V_9Mo_6O_{40(s)} + 3\,Fe_2O_{3(s)} + 0.25\,O_{2(g)} = 6\,FeVMoO_{7(s)} + 1.5\,V_2O_{5(s)} \qquad (1)$$

It seemed advisable to study the phase equilibria in the $V_9Mo_6O_{40}$–$FeVMoO_7$ system throughout the whole component concentration range up to 1000°.

The properties of the components of this system are well known. $V_9Mo_6O_{40}$ crystallized in a monoclinic system; structurally, it belongs to a homologous series M_nO_{3n-1} [4, 5]. In this phase, 1/9 of the vanadium atoms are in the form of V^{4+} [6]. $V_9Mo_6O_{40}$ has been reported to melt congruently at 635° [6] at 677° [5]. We have found that the melting point of $V_9Mo_6O_{40}$ is $640 \pm 10°$.

The structure of $FeVMoO_7$ has not so far been refined. The properties are not known in every respect. It is only clear that $FeVMoO_7$ melts incongruently at $680 \pm 5°$, depositing $Fe_4V_2Mo_3O_{20}$ [2]. The X-ray powder diffractogram of this phase in the angle range $2\theta = 10$–$70°$ Co–K_α is also known [2].

Experimental

V_2O_5 p.a. (Reachim), MoO_3 p.a. (POCH Gliwice) and α-Fe_2O_3 obtained by precipitation of $Fe(OH)_3$, followed by drying and thermal decomposition at 450° in

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air during several days, were used in the experiments. Separately obtained $V_9Mo_6O_{40}$ and $FeVMoO_7$ were also used in the experiments. $V_9Mo_6O_{40}$ was obtained by precipitation [5, 7], and $FeVMoO_7$ by annealing a mixture of Fe_2O_3, V_2O_5 and MoO_3 in a molar ratio of 1:1:2 under the following conditions: 400 →500° (1 h); 500° (24 h); 550° (72 h) and 600° (24 h) [2].

The DTA studies were made in quartz crucibles in a Paulik–Paulik–Erdey derivatograph in air at 20–1000° at a heating rate of 10 deg min^{-1}. The weight of the specimens under investigation was 1000 mg. In the construction of a phase diagram, the solidus was determined from the initial temperature of DTA effect, whereas the liquidus curves were assigned to the peak temperature of the effect. The temperature reading accuracy, determined on repetitions, was ± 5 deg in each case.

The phase compositions of preparations were established by X-ray powder diffraction (DRON–3, Co-K_α) and from the data included in the ASTM cards [8] and in the literature [2, 5, 7, 9].

A fundamental series of preparations comprising 23 samples was made from the oxides. The oxides, weighed in appropriate proportions, were ground, pastilled and heated in air under conditions allowing the establishment of equilibrium i.e. 400 →500° (1 h); 500° (24 h); 550° (72 h); and 570° (24 h). The preparations obtained were cooled slowly to ambient temperature, ground and then studied by DTA, and the phase composition was established.

In order to verify the equilibrium state of the samples of the fundamental series, seven mixtures were prepared from the phases present in the considered system, viz. from $V_9Mo_6O_{40}$ and $FeVMoO_7$. The mixtures containing $V_9Mo_6O_{40}$ and $FeVMoO_7$ in appropriate proportions were heated at 570° for 7 h, and afterwards X–RPD was performed. In this way, the phase composition of the subsolidus area was confirmed. Next, all verification samples and the preparations selected from the fundamental series were heated during 2 h at 620, 640, 675, 680, 700, 740 and 780°, respectively. After each cycle of heating, the samples were rapidly cooled to ambient temperature and their phase compositions were studied. On the basis of the results, it was established which of the solid phases coexist in equilibrium with liquid above the solidus temperature.

Results and discussion

The Figure shows a phase diagram of the $V_9Mo_6O_{40}$–$FeVMoO_7$ system, constructed from the DTA curves and X–RPD results on 23 preparations of the fundamental series and 7 samples of the verification series. The ranges of coexistence of solid phases with liquid were established from the DTA results on preparations at equilibrium, whereas the natures of the phases were assigned from

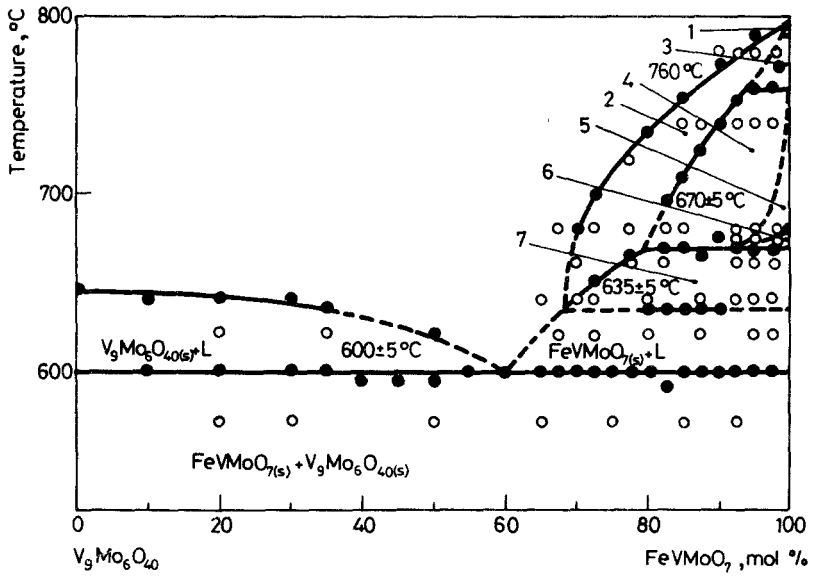

Fig. 1 Phase diagram of the $V_9Mo_6O_{40}$–$FeVMoO_7$ system. 1 – α-$Fe_2O_{3(s)}$ + liquid, 2 – $Fe_2(MoO_{43(s)}$ + liquid, 3 – $Fe_2(MoO_4)_{3(s)}$ + α-$Fe_2O_{3(s)}$ + liquid, 4 –$Fe_2(MoO_4)_{3(s)}$ + $Fe_4V_2Mo_3O_{20(s)}$ + liquid, 5 –$Fe_4V_2Mo_3O_{20(s)}$ + liquid, 6 – $Fe_4V_2Mo_3O_{20(s)}$ + $FeVMoO_{7(s)}$ + liquid, 7 – $Fe_2(MoO_4)_{3(s)}$ + $FeVMoO_{7(s)}$ + liquid. ● points indicate DTA, ○ X-ray investigation after air quenching

the X–RPD results on samples from selected diagram areas which were additionally heated during 2 h at 570–780°, and then rapidly cooled to ambient temperature.

It follows from the diagram that the components of the system remain at permanent equilibrium up to the solidus temperature. There is a eutectic point at contents of ~40.0% mol of $V_9Mo_6O_{40}$ and ~60.0% mol of $FeVMoO_7$, at 600 ± 5°. Above 635°, in the appropriate phase diagram areas, the solid phases also remain in equilibrium with liquid, the presence of which was not found in the subsolidus area. These phases occur in the system due to the incongruent melting of $FeVMoO_7$ [2]:

$$FeVMoO_{7(s)} \rightarrow Fe_4V_2Mo_3O_{20(s)} + \text{liquid} \quad (2)$$

and due to the incongruent melting of the solid product of a peritectic reaction: [2]:

$$Fe_4V_2Mo_3O_{20(s)} \rightarrow Fe_2(MoO_4)_{3(s)} + \alpha\text{-}Fe_2O_{3(s)} + \text{liquid} \quad (3)$$

From the results presented, it was impossible to establish strictly the existence ranges for all areas in which the solid phases remain in equilibrium with liquid. Therefore, some curves bordering the areas are drawn with dotted lines in the phase

diagram. Hence, the existence ranges for the areas $Fe_4V_2Mo_3O_{20(s)}$ + $FeVMoO_{7(s)}$ + liquid, $Fe_4V_2Mo_3O_{20(s)}$ + liquid and $Fe_2(MoO_4)_{3(s)}$ + α-$Fe_2O_{3(s)}$ + liquid were determined exclusively from the X–RPD results on preparations heated additionally at temperatures higher than the solidus temperature and cooled rapidly to ambient temperature. On the other hand, the existence range for the area α-$Fe_2O_{3(s)}$ + liquid was not confirmed experimentally on account of a quite small parameter range, i.e. temperature and component concentration. The existence of this area in the present diagram is confirmed by the positions of the neighbouring areas, viz. $Fe_2(MoO_4)_{3(s)}$ + α-$Fe_2O_{3(s)}$ + liquid, whose presence in the phase diagram of the $V_9Mo_6O_{40}$–$FeVMoO_7$ system is indisputable.

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Zusammenfassung — Mittels DTA und Röntgenbeugung wurden die Phasengleichgewichte im System $V_9Mo_6O_{40}$–$FeVMoO_7$ im gesamten Konzentrationsbereich bis 1000 °C untersucht. Aus den Ergebnissen wird das Phasendiagramm konstruiert.

Резюме — Методом ДТА и порошкового рентгенофазового анализа были использованы для изучения фазового равновесия в системе $V_9Mo_6O_{40}$–$FeVMoO_7$ во всей области концентраций исходных компомент и в области температур до 1000°. Экспериментальные результаты представлены в форме фазовой диаграммы.