Journal of Thermal Analysis, Vol. 34 (1988) 679–584

PHASE EQUILIBRIA IN THE V_2O_5–$FeVMoO_7$ SYSTEM

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(Received June 22, 1987)

The behaviour of V_2O_5 against $FeVMoO_7$ up to 1000 °C in the whole range of component concentrations was investigated using DTA and X-ray powder diffraction methods. The experimental results are presented in the form of a phase diagram.

Vanadium pentoxide and phases existing in systems in which the former is one of the components have been for years objects of many-sided studies, first of all, owing to their catalytic properties [1–6].

The other component, $FeVMoO_7$, of the system is formed in the reaction [7]:

$$Fe_2O_{3(s)} + V_2O_{5(s)} + 2\,MoO_{3(s)} = 2\,FeVMoO_{7(s)} \qquad (1)$$

or

$$FeVO_{4(s)} + MoO_{3(s)} = FeVMoO_{7(s)} \qquad (2)$$

Though the behaviour of $FeVMoO_7$ against excessive F_2O_3 and MoO_3 is known [7, 8], the reaction of $FeVMoO_7$ with the third component, from which the phase may originate, has not so far been investigated.

The properties and the structure of V_2O_5 are well known [9, 10]. Vanadium pentoxide reacts with Fe_2O_3 to form two compounds $Fe_2V_4O_{13}$ and $FeVO_4$ [5, 6]. V_2O_5 reacts, too, with MoO_3 to give a substitution solid solution of MoO_3 in V_2O_5 as well as a compound, $V_9Mo_6O_{40}$ [1–4].

Besides, V_2O_5 reacts also with $Fe_2(MoO_4)_3$ a compound existing in the Fe_2O_3–MoO_3 system [11], yielding $FeVMoO_7$ and $V_9Mo_6O_{40}$, respectively [12]; whereas iron(III) molibdate reacts with $FeVO_4$ to yield $Fe_4V_2Mo_3O_{20}$ [13, 14].

$FeVMoO_7$ is a compound known since a short time. Thus, zhe properties of the phase have not yet been investigated in every respect. It is only known that $FeVMoO_7$ melts at 680 ± 5° depositing $Fe_4V_2Mo_3O_{20}$, the second compound

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beside $FeVMoO_7$ originating in the three component Fe_2O_3–V_2O_5–MoO_3 system [7]. The density of $FeVMoO_7$ is 3.74 ± 0.05 g/cm^3 [7].

The X-ray characteristics of this compound in the angle range of 2θ: 12–70° (CoK_α) is also known [7].

Experimental

V_2O_5, MoO_3 (commercial products of p.a. grade) were used experimentally as well as α-Fe_2O_3 obtained by depositing, drying and thermal decomposition of $Fe(OH)_3$ at 450° in air for many hours. The oxides in weighed proportions were ground, pastilled and heated in air under conditions established in separate screening tests, i.e., $400 \div 500° - 1$ h, $500° - 24$ h, $550° - 72$ h and $570° - 24$ h.

The obtained preparations were slowly cooled to ambient temperature, ground and studied by the DTA method, their phase composition being established. Next, on repeated pastilling, the oxides were additionally heated at the final preparation temperature, i.e., at 570° for 72 h, cooled rapidly to ambient temperature, ground and the X-ray powder diffraction of the sample taken. In this way, the kinds of arising phases and the ranges of their coexistence in the subsolidus areas were established. On the other hand, the kinds of solid phases being at equilibrium with liquid at temperatures higher than the solidus line temperature were established by investigating the phase composition of preparations heated additionally for 2 h at temperatures, 620–800°, and cooled rapidly to ambient temperature.

The phase composition of preparations was established based on the X-ray powder diffraction results (diffractometer with a goniometer HZG–4 A2), on the data included in the ASTM cards and on the publications [6, 7, 13–15].

Investigations by the DTA method were made using a derivatograph Paulik–Paulik–Erdey, in quartz crucibles, in air, at temperatures 20–1000° and at a heating rate of 10 deg/min. Considering the phase diagram, the solidus lines were assigned on the grounds of the DTA initial effect temperatures, whereas the liquidus curves were determined on the apex effect temperatures. The accuracy of temperature readings, ± 5° was established by the repeated readings.

Results and discussion

Table 1 shows the compositions of the initial mixtures and X-ray powder diffraction results of preparations obtained on the last heating cycle at 570° for 72 h and on rapid cooling to ambient temperature. The data of Table 1 show that V_2O_5 does not remain at permanent equilibrium with $FeVMoO_7$. X-ray powder

Table 1 The composition of starting mixtures and the X-ray powder diffraction results of the preparations at equilibrium

The composition of samples in terms of the system component (% mol V_2O_5)	Phases found
5.0; 10.0; 20.0; 30.0; 40.0; 50.0; 60.0; 62.5;	$FeVMoO_7$, $Fe_2V_4O_{13(s.s)}$ $V_2O_{5(s.s)}$
65.0; 67.5; 70.0; 75.0; 80.0; 85.0; 90.0;	$Fe_2V_4O_{13(s.s)}$, $V_2O_{5(s.s)}$
92.5; 95.0; 97.5;	$V_2O_{5(s.s)}$

diffraction of preparations which in their initial mixture comprised of 5.0 to 62.5% mol of V_2O_5 has shown that they are a mixture of three phases: $FeVMoO_7$, $Fe_2V_4O_{13(s.s)}$ and $V_2O_{5(s.s)}$. It suggests that V_2O_5 in contents up to 62.5% mol reacts to completion with $FeVMoO_7$ yielding two solid solutions, that is, the solid solution of MoO_3, $Fe_2V_4O_{13}$ and also the solid solution of MoO_3 but with a structure of V_2O_5. It implies, that only in that component concentration range $FeVMoO_7$ is a stable phase coexisting with $Fe_2V_4O_{13(s.s)}$ and $V_2O_{5(s.s)}$. It also suggests that in the solid state a reaction takes place at this component concentration range:

$$FeVMoO_{7(s)} + V_2O_{5(s)} \rightarrow Fe_2V_4O_{13(s.s)} + V_2O_{5(s.s)} \qquad (3)$$

The phase composition of the preparation corresponding to the contents of 65.0% mol of V_2O_5 and 35.0% mol of $FeVMoO_7$ proves that at the molar ratio of $FeVMoO_7 : V_2O_5$ equal to 7 : 13 the reaction is quantitative i.e., the components of the system react to completion giving two solid solutions:

$Fe_2V_4O_{13(s.s)}$ and $V_2O_{5(s.s)}$, respectively.

In these solutions, both the solubility limit of MoO_3 in $Fe_2V_4O_{13}$ and that of MoO_3 in V_2O_5 shows maximum under given conditions, i.e., it is ~20% mol of MoO_3 ($X \cong 0.6$) in the case of $Fe_2V_4O_{13}$ [16, 17] and ~30.0% mol of MoO_3 in the case of V_2O_5 [2]. The mechanism of reaction 3 is not known and requires a special investigation. But the results of our other works [8, 18] permit to suppose that in the V_2O_5–$FeVMoO_7$ system the following reaction takes place in the solid state:

$$2\,FeVMoO_{7(s)} + V_2O_{5(s)} \rightarrow Fe_2V_4O_{13(s)} + 2\,MoO_{3(s)} \qquad (4)$$

MoO_3 liberated in that reaction under the experimental conditions is immediately incorporated into the crystal lattice of either $Fe_2V_4O_{13}$ or V_2O_5 to form appropriate solid solutions.

$$Fe_2V_4O_{13(s)}+MoO_{3(s)} \rightarrow Fe_2V_4O_{13(s.s)}+V_2O_{5(s)} \quad (5)$$

$$V_2O_{5(s)}+MoO_{3(s)} \rightarrow V_2O_{5(s.s)} \quad (6)$$

Thus reaction 3 may be treated as a total of reactions 4, 5 and 6.

At 65.0–90.0% mol of V_2O_5 in the initial mixtures only two solid solutions remain at equilibrium: $Fe_2V_4O_{13(s.s)}$ and $V_2O_{5(s.s)}$, respectively. In the other component concentration range a solid solution with a structure of V_2O_5 was identified exclusively.

However, it cannot be excluded that Fe_2O_3, too, is in a quite small range incorporated in the V_2O_5 lattice to form a solid solution [6].

Figure 1 shows a phase diagram of the $FeVMoO_7$–V_2O_5 system constructed from the DTA curves and the X-ray powder diffraction results of 19 peeparations remaining at equilibrium. On the other hand, the kinds of solid phases remaining at equilibrium with liquid were established on the results of X-ray powder diffraction of samples from selected diagram areas which were additionally heated for 2 h at 620, 640, 670, 700, 740, 750, 780 and 800°, respectively and then cooled rapidly to ambient temperature. The composition of samples subject to the studies are shown in Fig. 1.

It follows from the diagram shown in Fig. 1 that the $FeVMoO_7$–V_2O_5 system is not a real two-component system in the whole range of the component concentrations, not even in the subsolidus area. Above the solidus line of the system, meritectic reactions take place due to result from incongruent melting.

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

$$Fe_2V_4O_{13(s.s)} \rightarrow FeVO_{4(s)}+\text{liquid} \quad (8)$$

$$Fe_4V_2Mo_3O_{20(s)} \rightarrow \alpha\text{-}Fe_2O_{3(s)}+Fe_2(MoO_4)_{3(s)}+\text{liquid} \quad (9)$$

$$FeVO_{4(s)} \rightarrow \alpha\text{-}Fe_2O_{3(s)}+\text{liquid} \quad (10)$$

These reactions account for the formation of solid phases at 660° upwards which did not exist in the V_2O_5–$FeVMoO_7$ system in the subsolidus area.

The existence ranges of all areas in which the solid phases remain in equilibrium with the liquid could not be precisely established on the grounds of presented results.

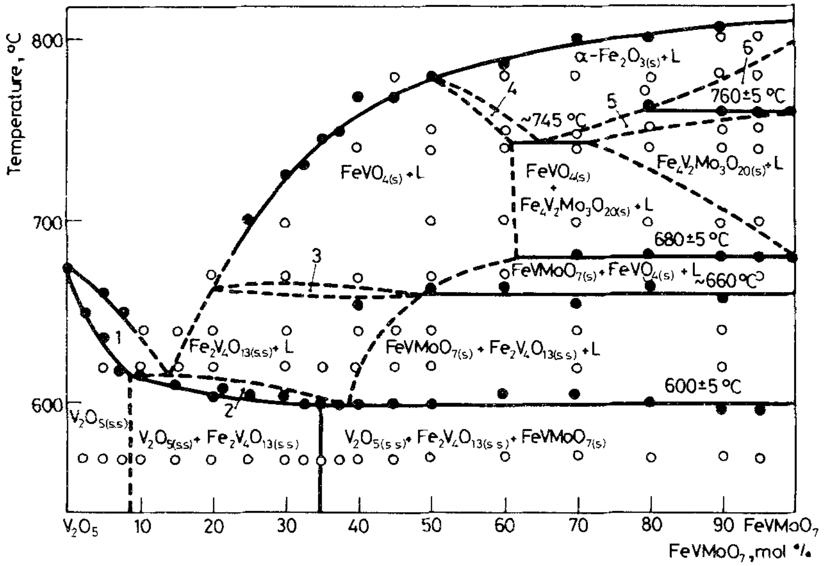

Fig. 1 The phase diagram of the V_2O_5–$FeVMoO_7$ system. 1 – $V_2O_{5(s.s)}$ + liquid; 2 – $Fe_2V_4O_{13(s.s)}$ + $V_2O_{5(s.s)}$ + liquid; 3 – $FeVO_{4(s)}$ + $Fe_2V_4O_{13(s.s)}$ + liquid; 4 – $FeVO_{4(s)}$ + α-$Fe_2O_{3(s)}$ + liquid; 5 – $Fe_4V_2Mo_3O_{20(s)}$ + α-$Fe_2O_{3(s)}$ + liquid; 6 – $Fe_2(MoO_4)_{3(s)}$ + α-$Fe_2O_{3(s)}$ + liquid; ● points indicate DTA; ○ X-ray investigation after quenching in air

The existence ranges of areas:

$$Fe_2(MoO_4)_{3(s)} + \alpha\text{-}Fe_2O_{3(s)} + \text{liquid},$$

$$Fe_4V_2Mo_3O_{20(s)} + \alpha\text{-}Fe_2O_{3(s)} + \text{liquid},$$

$$FeVO_{4(s)} + Fe_4V_2Mo_3O_{20(s)} + \text{liquid},$$

$$Fe_4V_2Mo_3O_{20(s)} + \text{liquid}$$

were partially determined based on the X-ray powder diffraction results of preparations additionally heated at temperatures higher than the solidus line temperature and cooled rapidly to ambient temperature. On the other hand, the existence ranges of areas:

$$Fe_2V_4O_{13(s.s)} + V_2O_{5(s.s)} + \text{liquid},$$

$$FeVO_{4(s)} + Fe_2V_4O_{13(s.s)} + \text{liquid},$$

$$FeVO_{4(s)} + \alpha\text{-}Fe_2O_{3(s)} + \text{liquid}$$

failed to be experimentally confirmed due to a quite narrow range of parameters, i.e., temperature and the component concentration at which they exist. However, their existence is well-founded by the position of neighbouring areas whose presence in the $FeVMoO_7$–V_2O_5 system is indisputable. Therefore some curves bordering the areas are marked on the phase diagram with dotted lines.

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Zusammenfassung — Mittels DTA- und Röntgenpulverdiffraktionsmethoden wurde das Verhalten von V_2O_5 gegenüber $FeVMoO_7$ bis zu 1000 °C im gesamten Konzentrationsbereich der Komponenten untersucht. Die experimentellen Ergebnisse werden in Form von Phasendiagrammen dargestellt.

Резюме — Используя ДТА и порошковый рентгенофазовый анализ изучено взаимодействие V_2O_5 с $FeVMoO_7$ в широкой области концентраций исходных компонент при температурах до 1000 °. Экспериментальные результаты представлены в форме фазовой диаграммы.