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# PHASE EQUILIBRIA IN THE SYSTEM $Fe_2(MoO_4)_3$–$V_2O_5$

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## ABSTRACT

Phase equilibria being established in the $Fe_2(MoO_4)_3$–$V_2O_5$ system in the whole range of component concentrations up to 1000 °C were studied. A phase diagram of the system was constructed on the DTA and X-ray phase powder diffraction results. The system appears not to be a true two-component system, even in the subsolidus area.

## INTRODUCTION

Ferric molybdate, a compound existing in the $Fe_2O_3$–$MoO_3$ system [1] has been a subject of extensive study for many years, primarily due to its catalytic properties. The same qualities are exhibited by the system with vanadium pentoxide. Therefore, we found it desirable to study the phase equilibria being established in the $Fe_2(MoO_4)_3$–$V_2O_5$ system in the whole range of component concentrations up to 1000 °C.

The structure and the properties of the components of the system are known. $Fe_2(MoO_4)_3$ exists in two polymorphic modifications, a low-temperature variety ($\alpha$) with monoclinic crystals and a high-temperature variety ($\beta$) crystallizing in an orthorhombic system. The temperature of the phase transition is either 499 °C [2], 513 °C [3] or 518 °C [4], whereas we have found it to be 505 ± 5 °C in each case. The structure of the two modifications of ferric molybdate is known, too. Rapposch attributes a spatial group $P2_1$ to $\alpha$-$Fe_2(MoO_4)_3$ [5], whereas Klevtsov [6], Plasova [7] and Chen [8] attribute a centrosymmetrical group $P2_{1/a}$. $\beta$-$Fe_2(MoO_4)_3$ belongs to the Pnca spatial group [2]. According to various authors, ferric molybdate melts congruently either at 956, 940 or at 975 °C [1,9,10]. We have stated that the melting temperature of $Fe_2(MoO_4)_3$ is 955 ± 5 °C.

Vanadium pentoxide is characterized by orthorhombic symmetry [11] and belongs to the space group Pmm [12]. $V_2O_5$ melts congruently, too, either at 675 [13], 690 [14] or at 675 ± 5 °C (our findings).

We have found previously that $Fe_2(MoO_4)_3$ reacts with $FeVO_4$ (a compound existing together with $Fe_2V_4O_{13}$ in the $Fe_2O_3$–$V_2O_5$ system [15]) to

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yield $Fe_4V_2Mo_3O_{20}$ [16]. Ferric orthovanadate is another compound to react with $MoO_3$, but the reaction product is $FeVMoO_7$ [17]. These two compounds—stable phases of the $Fe_2O_3$–$V_2O_5$–$MoO_3$ system—are involved in a reaction between three oxides building a three-component system [16,17]. They melt noncongruently: $FeVMoO_7$ at 680 ± 5 °C according to the equation

$$FeVMoO_{7(s)} \rightarrow Fe_4V_2Mo_3O_{20(s)} + \text{liquid} \tag{1}$$

$Fe_4V_2Mo_3O_{20}$, however, suffers decomposition to two solid phases and a liquid:

$$Fe_4V_2Mo_3O_{20(s)} \rightarrow Fe_2(MoO_4)_{3(s)} + \alpha\text{-}Fe_2O_{3(s)} + \text{liquid} \tag{2}$$

We have found that $Fe_2V_4O_{13}$, the other compound of the $Fe_2O_3$–$V_2O_5$ system, forms a solid solution with $MoO_3$, the amount of $MoO_3$ incorporated into the $Fe_2V_4O_{13}$ lattice being 18 mol% [18,19]. Molybdenum trioxide forms a solid solution with $V_2O_5$, which is illustrated in the phase diagram of the $V_2O_5$–$MoO_3$ system in which a compound, $V_9Mo_6O_{40}$, exists, and melts congruently at ~ 635 °C [20].

It is worth noting that the study of the system under consideration was presented in parts [21]; the preparations obtained from the oxides enabled us to show equilibria established in the solid state.

## EXPERIMENTAL

$V_2O_5$ p.a. (Reachim), $MoO_3$ p.a. (POCh Gliwice) and $\alpha$-$Fe_2O_3$ were used for the experiments. $\alpha$-$Fe_2O_3$ was obtained by precipitating $Fe(OH)_3$, then drying and thermally decomposing the substrate at 450 °C in air during several dozen hours. $Fe_2(MoO_4)_3$ used for the tests was obtained by calcinating to a constant weight the mixture of $\alpha$-$Fe_2O_3$ with a small excess of $MoO_3$ at 700 °C, and then at 750 °C for 48 h. Diffractograms of the substrates obtained show only the diffraction lines characterizing $Fe_2O_3$ and $Fe_2(MoO_4)_3$ [22].

The DTA measurements were made with a F. Paulik–J. Paulik–L. Erdey derivatograph in quartz crucibles in air at 20–1000 °C and a heating rate of 10 °C $min^{-1}$. The weight of the specimens under investigation was 1000 mg. The phase diagram was constructed with the aid of solidus lines determined on the grounds of the DTA initial effect temperatures and with liquidus curves assigned by the apex effect temperatures. The accuracy of the temperature readings estimated on the repeatability of measurements was ±5 °C.

The phase composition of preparations was established by X-ray phase powder diffraction (DRON-3, $CoK_\alpha$) and on the data from ASTM cards [22,23] and on other works [3,4,15–17].

Two series of preparations were prepared: a basic one from oxides and the verification series made from phases building the system of interest, i.e. from $Fe_2(MoO_4)_3$ and $V_2O_5$. Substrates in weighed proportions were ground, pastilled and heated in air under experimentally determined conditions which were advantageous to the establishment of equilibrium: 400–500 ° C, 24 h; 550 ° C, 72 h; 570 ° C, 24 h. The samples prepared from oxides were cooled slowly to ambient temperature, whereas those of the verification series were cooled rapidly to ambient temperature. Specimens of both series were ground and studied by the DTA method for their phase composition. Afterwards, preparations of the basic series were additionally heated at 570 ° C for 72 h with repeated tableting and then rapidly cooled to ambient temperature, ground and analysed by X-ray phase powder diffraction. By this technique, the types of the resultant phases were established as well as the coexistence ranges of the phases at the subsolidus area. On the other hand, solid phases at equilibrium with liquid in the high-temperature area of a phase diagram were found by the study of the phase composition of selected preparations of the basic series which were additionally heated at 590–885 ° C for 2 h and then cooled rapidly to ambient temperature.

## RESULTS AND DISCUSSION

Table 1 shows the compositions of the original mixtures and the results from the X-ray phase powder diffraction of preparations at equilibrium. The results refer to both the samples of the basic and the verification series. The data from the table imply that the phase composition of preparations at equilibrium, whose original mixtures contain the same amounts of $Fe_2(MoO_4)_3$ and $V_2O_5$, is independent of the type of the substrates used.

The experimental results suggest that $V_2O_5$ does not remain at constant equilibrium with $Fe_2(MoO_4)_3$ because it is not found in the phase composition of preparations at equilibrium. X-ray phase powder diffraction of preparations whose original mixtures contain 2.5–30.0 mol% of $V_2O_5$ show that they are biphase preparations, which would indicate that $V_2O_5$ reacts with $Fe_2(MoO_4)_3$ to yield $FeVMoO_7$ only. But such a reaction course is not possible since

$$Fe_2(MoO_4)_{3(s)} + V_2O_{5(s)} = 2FeVMoO_{7(s)} + MoO_{3(s)} \tag{3}$$

thus specimens at equilibrium should indicate the presence of $MoO_3$ besides $Fe_2(MoO_4)_3$ and $FeVMoO_7$. However, there is another reaction possible

$$6Fe_2(MoO_4)_{3(s)} + 10.5V_2O_{5(s)} = 12FeVMoO_{7(s)} + V_9Mo_6O_{40(s)} + \tfrac{1}{4}O_2 \tag{4}$$

in which a compound, contained in preparations obtained from the original mixtures abundant in $V_2O_5$, arises along with $FeVMoO_7$ (see Table 1). Hence, in specimens containing up to 30 mol% of $V_2O_5$ and brought to

TABLE 1

The composition of original mixtures and the results from X-ray phase powder diffraction of preparations at equilibrium

| The composition of samples in terms of mol% $V_2O_5$ | | Phases found |
|---|---|---|
| $Fe_2O_3$, $V_2O_5$, $MoO_3$ | $Fe_2(MoO_4)_3$, $V_2O_5$ | |
| 5.0, 10.0, 15.0, 20.0, 25.0, 30.0 | 2.5, 5.0, 7.5, 10.0, 15.0, 20.0, 25.0, 30.0 | $Fe_2(MoO_4)_3$, $FeVMoO_7$ |
| 35.0, 40.0, 45.0, 50.0, 55.0, 60.0 | 35.0, 40.0, 45.0, 50.0, 55.0, 60.0 | $Fe_2(MoO_4)_3$, $FeVMoO_7$, $V_9Mo_6O_{40}$ |
| – | 63.64 | $FeVMoO_7$, $V_9Mo_6O_{40}$ |
| 65.0, 70.0, 75.0 | 65.0, 70.0, 75.0 | $FeVMoO_7$, $V_9Mo_6O_{40}$, $V_2O_{5(s\,s)}$ |
| 80.0, 82.5, 85.0 | 80.0, 85.0 | $FeVMoO_7$, $V_2O_{5(s\,s)}$, $Fe_2V_4O_{13(s\,s)}$ |
| 87.5, 90.0, 92.0, 93.5, 95.0, 96.5 | 90.0, 95.0 | $V_2O_{5(s\,s)}$, $Fe_2V_4O_{13(s\,s)}$ |
| 98.5 | 98.5 | $V_2O_{5(s\,s)}$ |

equilibrium, a third phase should be detectable, that is, either $MoO_3$ or $V_9Mo_6O_{40}$.

Equations (3) and (4) make it possible to calculate the amount of $MoO_3$ in the reaction products, which would be 23 mol% if reaction (3) took place and the original mixture contained 30 mol% $V_2O_5$. Although $V_2O_5$ did react with $Fe_2(MoO_4)_3$ by virtue of reaction (4), only 3.18 mol% of $V_9Mo_6O_{40}$ was detectable at the 30 mol% level of $V_2O_5$ in the original mixture. Additional tests have shown that despite large excessive amounts of $Fe_2(MoO_4)_3$ and $FeVMoO_7$, X-ray phase powder diffraction makes it possible to detect 2.5 mol% of $MoO_3$ with certainty, but, with $V_9Mo_6O_{40}$, the detection would not be effective until the phase amount was 5 mol%. Thus, it is $V_9Mo_6O_{40}$ that is the third phase occurring in the system at 30 mol% of $V_2O_5$ in the original mixtures.

Experimental results indicate that $V_2O_5$ in amounts of up to 63.64 mol% will react with $Fe_2(MoO_4)_3$ until completion to yield $FeVMoO_7$, and only at this component concentration range will the $Fe_2(MoO_4)_3$ phase coexist with $FeVMoO_7$ and $V_9Mo_6O_{40}$. The phase composition of a preparation of the verification series, 36.36 mol% $Fe_2(MoO_4)_3$ with 63.64 mol% $V_2O_5$, confirms that at the molar ratio of $Fe_2(MoO_4)_3$–$V_2O_5$ equal to 6 : 10.5 in the system a quantative reaction takes place (reaction (4)), i.e. both the components react till completion to yield $FeVMoO_7$ and $V_9Mo_6O_{40}$, respectively.

In preparations with their original mixtures containing 63.64 mol% $V_2O_5$, that is, an excessive amount of $V_2O_5$ with respect to reaction (4), there appears a solid solution of $MoO_3$ in $V_2O_5$, considered to be an equilibrium phase [20,24]. At the same time a reaction starts to deliver free $MoO_3$. One can infer from the phase composition of preparations that the reaction runs in agreement with the equation:

$$V_9Mo_6O_{40(s)} + \tfrac{1}{4}O_2 = 4.5V_2O_{5(s)} + 6MoO_{3(s)} \qquad (5)$$

Decomposition of $V_9Mo_6O_{40}$ is nearing completion when the $V_2O_5$ content of an original mixture does not exceed 80 mol%, the decomposition yielding $MoO_3$ and additional amount of $V_2O_5$. A further increase in the $V_2O_5$ content of the substrates hinders identification of the compound, but a new stable phase containing iron appears in the system. $V_2O_5$ not involved in formation of the solid solution is not a stable phase and, in consequence, a reaction starts in the system when 80 mol% $V_2O_5$ contributes to the composition of the original mixture:

$$2FeVMoO_{7(s)} + V_2O_{5(s)} = Fe_2V_4O_{13(s)} + 2MoO_{3(s)} \qquad (6)$$

The resultant $Fe_2V_4O_{13}$ also forms a solid solution with $MoO_3$ [18,19].

In the original mixtures with 87.5–96.5 mol% $V_2O_5$, only two solid solutions remain at equilibrium, viz. $V_2O_{5(s\,s)}$ and $Fe_2V_4O_{13(s\,s)}$. At other concentration ranges the equilibrium phase is a sole solid solution with the $V_2O_5$ structure. It is not unlikely that, at the concentration range mentioned above, $Fe_2O_3$ will be incorporated in the $V_2O_5$ lattice to form a solid solution [15].

Figure 1 shows a phase diagram of the $Fe_2(MoO_4)_3$–$V_2O_5$ system constructed with the help of the DTA curves and with X-ray phase powder diffraction results of preparations of the basic and verification series. The coexistence ranges of the solid phase with liquid were assigned on the results from DTA of preparations being at equilibrium, whereas the types of these phases were established on the results from X-ray phase powder diffraction of samples of selected diagram areas, the specimens being additionally heated for 2 h at 590, 600, 620, 640, 670, 690, 710, 740, 800 and 850 ° C, respectively, and then cooled rapidly to ambient temperature. The compositions of the samples investigated in this way are shown in the figure.

The diagram shown in the figure suggests that the $Fe_2(MoO_4)_3$–$V_2O_5$ system is not a true two-component phase, either in the whole component concentration range or in the subsolidus area. This fact indicates the presence of areas in this region where three solid phases are equilibrium. Above the solidus line, in the given phase diagram areas, solid phases are at equilibrium with liquid, the presence of which was not stated in the subsolidus area. The phases $Fe_4V_2Mo_3O_{20}$ and $FeVO_4$ occur in a high-temperature area of the phase diagram due to noncongruent melting of $FeVMoO_7$ (reaction (1)) and of

$Fe_2V_4O_{13(s.s)}$ [17,18]

$$Fe_2V_4O_{13(s.s)} \rightarrow FeVO_{4(s)} + \text{liquid} \qquad (7)$$

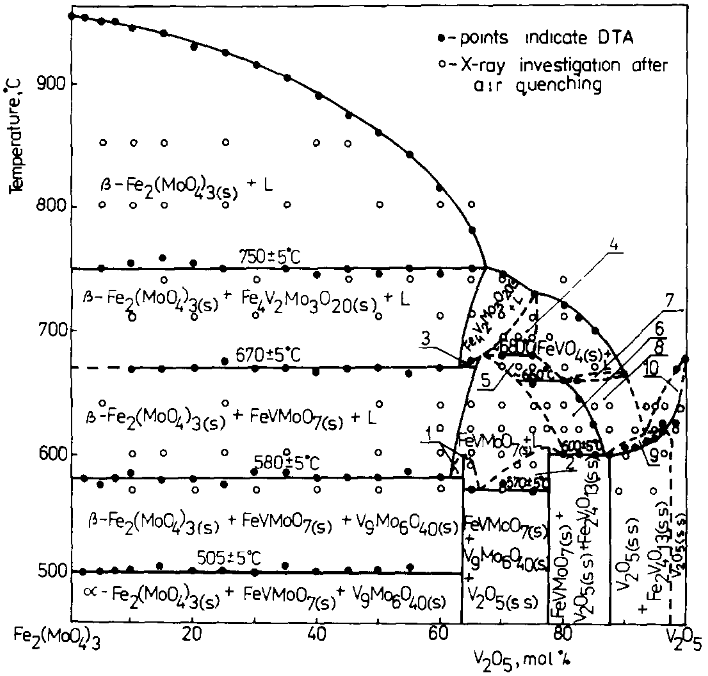

Fig. 1. Phase diagram of the $Fe_2/MoO_4/_3$-$V_2O_5$ system: 1, $FeVMoO_{7(s)} + V_9Mo_6O_{40(s)}$ + liquid; 2, $FeVMoO_{7(s)} + V_2O_{5(s\,s)}$ + liquid; 3, $FeVMoO_{7(s)} + Fe_4V_2Mo_3O_{20(s)}$ + liquid; 4, $Fe_4V_2Mo_3O_{20(s)} + FeVO_{4(s)}$ + liquid; 5, $FeVMoO_{7(s)} + FeVO_{4(s)}$ + liquid; 6, $FeVMoO_{7(s)} + Fe_2V_4O_{13(s\,s)}$ + liquid; 7, $FeVO_{4(s)} + Fe_2V_4O_{13(s\,s)}$ + liquid; 8, $Fe_2V_4O_{13(s\,s)}$ + liquid; 9, $Fe_2V_4O_{13(s\,s)} + V_2O_{5(s\,s)}$ + liquid; 10, $V_2O_{5(s\,s)}$ + liquid.

Above 750 ± 5 °C, the phase at equilibrium with liquid is $Fe_2(MoO_4)_{3(s)}$. The phase diagram shows that $Fe_4V_2Mo_3O_{20}$ melts at 750 ± 5 °C to give only one solid product, $Fe_2(MoO_4)_3$. This suggests that the $Fe_2(MoO_4)_3$–$V_2O_5$ system crosses the line of a reversible meritectic reaction,

$$\text{liquid} + Fe_2(MoO_4)_{3(s)} \rightleftharpoons Fe_4V_2Mo_3O_{20(s)} \qquad (8)$$

taking place in a three-component system, $Fe_2O_3$–$V_2O_5$–$MoO_3$. This proves that reaction (8) takes place in a three-component system at temperatures below the noncongruent melting point of $Fe_4V_2Mo_3O_{20}$, say, at temperatures lower than 760 °C.

The results obtained give little opportunity to establish coexistence ranges for all the areas in which solid phases would remain at equilibrium with liquid. Thus, the maximum temperature range of coexistence of areas 1 and 2 (Fig. 1) was assessed on the results of our other investigations, viz. on the phase diagram of the systems $FeVMoO_7$–$V_9Mo_6O_{40}$ and $FeVMoO_7$–$V_2O_{5(s.s)}$ [15]. The coexistence ranges for areas 4, 5, 6 and 10 were established exclusively from the results of the X-ray phase powder diffraction of preparations additionally heated to temperatures higher than the temperature of the solidus line and then cooled rapidly to ambient temperature. On the other hand, attempts to experimentally determine the existence bounds for areas 3, 7, 9 (Fig. 1) ended in failure because of the narrow range of parameters, i.e. temperature and concentration of the components, which define the bounds. However, the site of neighbouring areas, whose existence on the phase diagram of the $Fe_2(MoO_4)_3$–$V_2O_5$ system is believed to be unquestionable, gives evidence for the existence of the bounds under consideration. Therefore, some curves which bound areas 1–10 on the diagram have been drawn with dotted lines.

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