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STUDIES OF $Fe_2V_4O_{13}$ AND ITS REACTIONS WITH MoO_3

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ABSTRACT

A substitutional solid solution has been found to arise in the $Fe_2V_4O_{13}$-MoO_3 system, in which Mo6+ ions incorporate, in place of V+5 ions, into the crystal lattice of $Fe_2V_4O_{13}$. A maximum solubility of MoO_3 in $Fe_2V_4O_{13}$ makes up at least 35 % mole of MoO_3.

INTRODUCTION

It has been established that two compounds: $FeVO_4$ and $Fe_2V_4O_{13}$ [1,2,3] occur in the Fe_2O_3-V_2O_5 system, being one of the binary systems of the three-component Fe_2O_3-V_2O_5-MoO_3 kind. Although $FeVO_4$ is rather a well known compound, the structure and properties of $Fe_2V_4O_{13}$ are,in fact, not yet known. Until quite lately there have been some doubts whether this compound is really a stable phase. Such a state of investigations of $Fe_2V_4O_{13}$ seems to arise from difficulties in synthetizing the compound 2 . At present, however, $Fe_2V_4O_{13}$ is known to melt incongruently with throwing down $FeVO_4$/s/ [1,2,3]. The melting point of $Fe_2V_4O_{13}$, by our study, is 938 K, acc. [3] - 965 K, acc. [1] - 988 K. Fotier at al. think the melting point of $Fe_2V_4O_{13}$ to depend upon the oxygen content in a gaseous phase, in which the compound is produced. Provided $Fe_2V_4O_{13}$ is synthesized in oxygen /Po_2 = 1 atm/, its melting point is 993 K [3]. The density of $Fe_2V_4O_{13/s/}$ is 3,13 ± 0,05 g/cm^3 [2]. The X-ray powder pattern is also known [1,2].

MEASURING METHODS

The samples were prepared from α-Fe_2O_3, V_2O_5 /commercial products of p.a. grade/, and MoO_3, obtained by thermal decomposition of $/NH_4/_6Mo_7O_{24} \cdot 4\,H_2O$, in air, at 423 - 823 K. The oxides were weighed, pelletized, and heated in air, in the following cycles: 673 ⟶ 773 K - 1 h, 773 K - 24 h, 823 K - 24 h, 823 K - 72 h, 853 K - 24 h, 853 K - 24 h. The preparations produced were slowly cooled to ambient temperature, and then grinded.

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The phase compositions of the preparations were determined by X-ray diffraction /DRON-3, Co K_α /, and on data of ASTM Cards [4] as well on those of publications [5-7].

Thermal analysis was accomplished with the aid of a derivatograph /MOM Budapest/, in quartz crucibles, at the heating rate 10°/min., at the temperature range 293 - 1073 K. The weights of the samples were 1000 mg. The accuracy of the effect temperature readings from DTA curves was estimated on repetitions made for ± 5 K.

RESULTS AND DISCUSSION

Results of X-ray diffraction and those of melting start temperatures with their readings taken from the DTA curves of 26 samples containing an increasing MoO_3 content in the original mixtures are given in the Table.

Table.

Results of X-ray diffraction and solidus line temperatures

The MoO_3 content in the original mixture % mole	Detected phase	Solidus line temperatures K
1	2	3
2,5; 5,0; 7,5; 10,0; 12,5; 15,0; 20,0; 25,0; 30,0; 35,0;	$Fe_2V_4O_{13}$/s,s/ V_2O_5	873
40,0; 45,0; 50,0; 55,0; 60,0; 65,0;	$Fe_2V_4O_{13}$/s.s/, V_2O_5, $FeVMoO_7$	873
67,5; 70,0; 72,5; 75,0;	$FeVMoO_7$, V_2O_5, $V_9Mo_6O_{40}$	843
77,5; 80,0; 82,5;	$V_9Mo_6O_{40}$, $FeVMoO_7$, $Fe_2/MoO_4/_3$	853
85,0; 90,0; 95,0;	$Fe_2/MoO_4/_3$, MoO_3, $V_9Mo_6O_{40}$	868

A solid solution of MoO_3 in $Fe_2V_4O_{13}$ has been proved, on the experimental evidence, to occur in the $Fe_2V_4O_{13}$-MoO_3 system. This fact was concluded from the lach of MoO_3 as well of other compounds of molibdenum in the final preparations, which had been comprised in the original samples, in amounts not exceeding 40 % mole. Consequently, a maximum solubility of MoO_3 in $Fe_2V_4O_{13}$ amounts to, at the very least, 35 % mole of MoO_3, and it does not exceed 40 % mole of MoO_3. The phase compositions of the preparations indicate, as well, that MoO_3 incorporates into the $Fe_2V_4O_{13}$ crystal lattice, to displace V_2O_5 from it:

$$Fe_2V_4O_{13/s/} + MoO_{3/s/} \longrightarrow Fe_2V_4O_{13/s.s./} + V_2O_{5/s/}$$

With the aim of proving the formation of solid solutions, which is accounted for by the incorporation of Mo^{+6} ions, in place of V^{+5}, into the $Fe_2V_4O_{13}$ crystal lattice; investigations were carried out by means of $Fe_2V_4O_{13}$ and MoO_3 as starting materials, each of the compounds having been prepared individually. The experimental results were identical with those attained from experiments brought about with oxide mixtures as starting materials. MoO_3 having reached its solubility limit in respect to $Fe_2V_4O_{13}$, $FeVMoO_7$ is arising in the system - a phase which remains at equilibrium with $Fe_2V_4O_{13}$ /s.s./ till about 67,5 % mole of MoO_3.
Its contents increase rapidly with increasing MoO_3 content in preparations, the $Fe_2V_4O_{13}$ /s.s/ content decreasing quickly. Above the 67,5 % mole contents of MoO_3, X-ray diffraction does not indicate the presence of $Fe_2V_4O_{13}$ at all, whereas $FeVMoO_7$, $V_9Mo_6O_{40}$ and V_2O_5 are at equilibrium in the system. Hence, $Fe_2V_4O_{13}$ is a phase stable only when the MoO_3 content does not exceed 67,5 % mole. Phase equilibria being established in subsolidus area of the component concentrations are drafted in Fig. 1.

Solidus line temperatures were determined on the first effect start temperatures /the effects are not polymorphic transformations/ recorded on the DTA curves of the preparations. Fig. 1 shows that the $Fe_2V_4O_{13}$-MoO_3 system is not a true two - component system, even in the subsolidus area. This evidence is supported by the presence of, in this region, areas in which three solid phases are at equilibrium.

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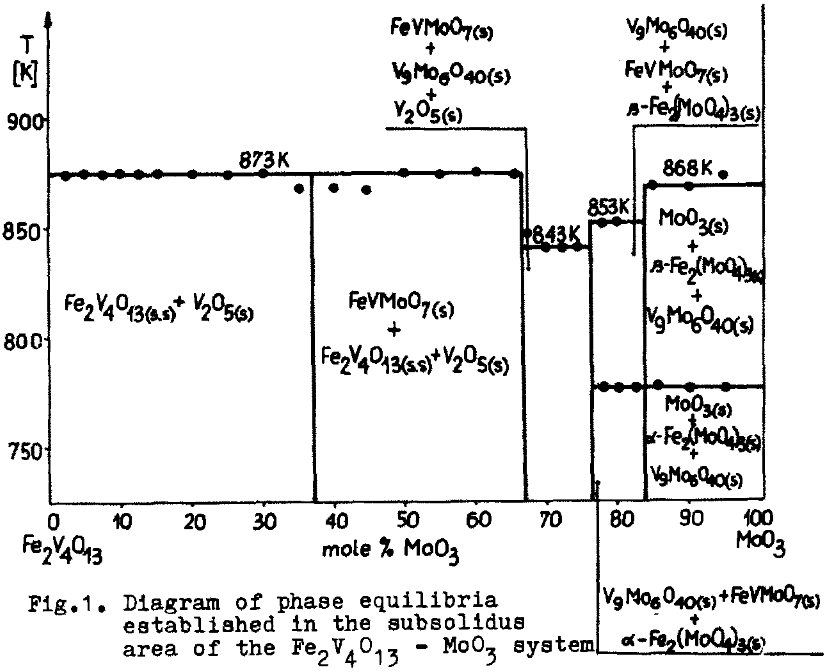

Fig.1. Diagram of phase equilibria established in the subsolidus area of the $Fe_2V_4O_{13}$ - MoO_3 system