Thermochimica Acta, 92 (1985) 571-574
Elsevier Science Publishers B.V., Amsterdam

STUDIES OF THE REACTIVITY OF $Fe_2/MoO_4/_3$ in the Fe_2O_3-V_2O_5-MoO_3 SYSTEM

J.Walczak, M.Kurzawa*, K.Wasążnik, Institute of Fundamental Chemistry of Politechnic University of Szczecin
Szczecin, Poland

ABSTRACT

Diagrams of phase sections of the pseudo binary $Fe_2/MoO_4/_3$-$V_9Mo_6O_{40}$ and $Fe_2/MoO_4/_3$-$FeVMoO_7$ systems of the three-component Fe_2O_3-V_2O_5-MoO_3 kind have been constructed. They were examined with the aid of X-ray and differential thermal analyses.

INTRODUCTION

The investigation of the Fe_2O_3-V_2O_5-MoO_3 system has tempted us to undertake studies on the reactivity of $Fe_2/MoO_4/_3$ in that system. Ferric molibdate is the best known of all compounds to occur in two - component systems, viz., Fe_2O_3-V_2O_5, Fe_2O_3-MoO_3, and V_2O_5-MoO_3, which build the three - component kind under investigation. There are known two forms of $Fe_2/MoO_4/_3$: α -monoclinic /space group $2 \to P_1$ [1], or $2 \to P_1/a$ [2]/, stable, according toliterature reports, up to 786 K [3], or 791 K [4], and β -orthorombic, existing above transformation temperature. By our studies, the polymorphic transformation temperature of $Fe_2/MoO_4/_3$ is 778 $\pm$ 5 K. Ferric molibdate melts congruently eithes at 1229 K [5] or at 1248 K [6], depending on the temperature reportr. We have assessed that its melting point is 1228 $\pm$ 5 K, however. In addition to this, we have stated that, in the reaction proceeding in a solid state, $Fe_2/MoO_4/_3$ forms a phase /as yet unknown in literature/ with $FeVO_4$ [7] -that of the two compounds occurring in the Fe_2O_3-V_2O_5 system [8,9],

$$Fe_2/MoO_4/_{3/s/} + 2\ FeVO_{4/s/} \longrightarrow Fe_4V_2Mo_3O_{20/s/} \qquad /1/$$

From the evidence of the reaction process between $FeVO_4$ and MoO_3 [10] we succeeded in establishing yet another phase /also unknown to date/:

$$FeVO_{4/s/} + MoO_{3/s/} \longrightarrow FeVMoO_{7/s/}$$

In the last system, i.e., V_2O_5-MoO_3, composing the three - component one, Fe_2O_3-V_2O_5-MoO_3, exists a phase for which a molecular formula; V_2MoO_8 [11], or $V_9Mo_6O_{40}$ [12] was formulated. This compo-

Proceedings of ICTA 85, Bratislava

to the ambient temperature. Compositions of those preparations and the temperatures, at which the samples were heated, are depicted in Figures1 and 2.

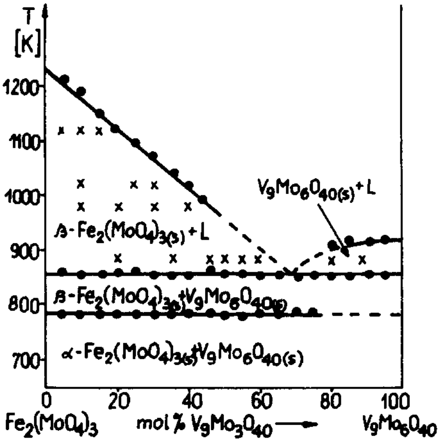

Fig.1.Phase diagram of the $Fe_2/MoO_4/_3-V_9Mo_6O_{40}$ system.

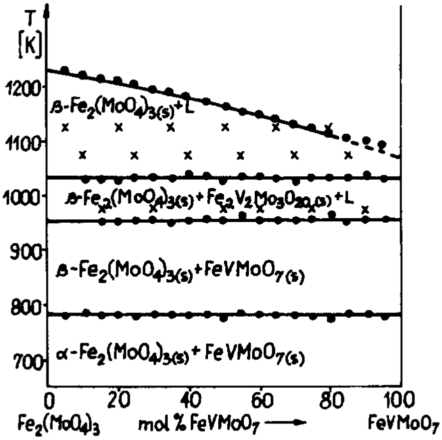

Fig.2.Phase diagram of the $Fe_2/MoO_4/_3-FeVMoO_7$ system.

x-phase identyfication after air quenching.

Fig. 1 shows a phase diagram of the $Fe_2/MoO_4/_3-V_9Mo_6O_{40}$ system. It is a simple two - component one. In a subsolidus area, up to the temperature of transformation of α $-Fe_2/MoO_4/_3$ into β $-Fe_2/MoO_4/_3$, i.e., up to 778 K coexist a monoclinic $Fe_2/MoO_4/_3$ and $V_9Mo_6O_{40}$. In the range of temperatures from 778 to 858 K, i.e., up to an eutectic temperature, β $-Fe_2/MoO_4/_3$ and $V_9Mo_6O_{40}$ are at equilibrium. An eutectic point occurs, in the system, at around 32 % mole of $Fe_2/MoO_4/_3$ and about 68 % mole of $V_9Mo_6O_{40}$. Upwards of the solidus line, the components of the system remain at equilibrium with a liquid.

The phase diagram of the $Fe_2/MoO_4/_3-FeVMoO_7$ system in shown in Fig. 2. In the subsolidus area, up to 778 K, coexist α $-Fe_2/MoO_4/_3$ and $FeVMoO_7$. By the contrast, above this temperature up to 953 K, viz., up to the temperature at which a liquid appears, resultant from the incongruent melting of $FeVMoO_7$ [10],

$$4\ FeVMoO_{7/s/} \longrightarrow Fe_4V_2Mo_3O_{20/s/} + \text{liquid} \qquad /3/$$

β $-Fe_2/MoO_4/_{3/s/}$ and $FeVMoO_{7/s/}$ are being at equilibrium with each other.

und is also considered to belong to the homologeous series, M_nO_{3n-1}, its final composition depending on the preparation temperature [13]. Provided the process is carried out at the range of temperatures from 773 to 873 K, $V_9Mo_6O_{40}$ is obtained [13].

Accordingly, it seemed to be of interest to start with examination of the phase equilibrium being established between $Fe_2/MoO_4/_3$ and a phase to occur in the V_2O_5-MoO_3 system, viz., $V_9Mo_6O_{40}$, and that between $Fe_2/MoO_4/_3$ and $FeVMoO_7$.

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 $/NH_4/_6Mo_7O_{24} \cdot 4\ H_2O$ at 423 - 823 K, in air, by a method and under conditions described in [14].

The phase compositions of the preparations were determined by X-ray diffraction /DRON-3, CoK_α /, and on data included in ASTM cards [15] and on those enclosed in publications [3,7,10].

The thermal analysis /DTA/ was performed with the use of a derivatograph J.Paulik, J.Paulik, L.Erdey /MOM Budapest/, in quartz crucibles, in air, in the region of temperatures from 293 to 1273 K, and at the heating rate of 10^o/min.; the weight of a sample being, in each case, 1000 mg. The solidus lines were determined on the first effect temperatures, DTA, and the liquidus curves - on the temperatures of the vertex effects. The accuracy of temperature readings was evaluated on the basis of repetitions accomplished for $\pm$ 5 K.

RESULTS AND DISCUSSION

In order to get knowledge of phase equilibria being established in systems: $Fe_2/MoO_4/_3$-$V_9Mo_6O_{40}$ and $Fe_2/MoO_4/_3$-$FeVMoO_7$, respectively, two series of samples were prepared from Fe_2O_3, V_2O_5 and MoO_3, each comprising 19 preparations which corresponded with the $Fe_2/MoO_4/_3$ content increased by 5 % mole. The preparations produced were analysed by X-ray diffraction and DTA.

In consequence, both the kinds of resultant phases and the range of their coexistence were determined in the subsolidus areas of the two systems. But on the other hand, the ranges of coexistence of solid phases with a liquid, and their kinds, were determined on the results from experiments with preparations which had been additionally heated at suitable temperatures and, afterwards, cooled rapidly

The section of $Fe_2/MoO_4/_3$-$FeVMoO_7$ is a two-component system, true only up to the temperature of the solidus line.

REFERENCES

1 M.H.Rapposch, J.B.Anderson, E.Kostiner, Inorg.Chem., 19 /1980/ 3531
2 Horng-yih Chen, Mat.Res.Bull., 14 /1979/ 1583
3 V.Massarotti, G.Flor, A.Marini, J.Appl.Cryst., 14 /1981/ 64
4 L.M.Plasova, Zh.Strukt.Khim., 17 /1958/ 738
5 W.Jager, A.Rahmel, K.Becker, Arch.Eisenhuttenwesen, 30 /1959/ 1971
6 N.P.Burmistrova, R.M.Tzetzetkin, L.A.Segova, Zh.Prikl.Khim., 5 /1969/ 1166
7 J.Walczak, J.Ziolkowski, M.Kurzawa, L.Trzesniowska, J.Therm. Anal., 29. In the press.
8 J.Walczak, J.Ziolkowski, M.Kurzawa, J.Osten-Sacken, M.Łysio, Pol.J.Chem., /Formerly Rocz.Chem./. In the press
9 J.Otsubo, K.Utsumi, J.Chem.Soc.Japan, Pure Chem.Sec., 92, /1971/ 737
10 J.Walczak, M.Kurzawa, E.Filipek, The Third Polish Seminar to the memory of St.Bretsznajder, Płock, 14-16.IX.1983
11 N.Strupler, A.Morette, 260 /1965/ 1971
12 A.Bielański, K.Dyrek, J.Pozniczek, E.Wenda, Bull.Acad.Pol.Scie., Ser.Scie.Chim., 19 /1971/ 507
13 R.H.Jarman, A.K.Cheetham, Mat.Res.Bull., 17 /1982/ 1011
14 M.Kurzawa, 8 th Internat.Conf.Therm.Anal., Bratislava, Czechoslovakia, August 19-23,1985
15 Joint Committee of Powder Diffraction File 5-508, 9-387, 13-543, 18-851, 19-813, 20-526