Thermochimica Acta, 92 (1985) 563-566
Elsevier Science Publishers B.V., Amsterdam

PHASE EQUILIBRIA IN THE SUBSOLIDUS AREA OF THE Fe_2O_3-V_2O_5-MoO_3 SYSTEM

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ABSTRACT

A subsolidus phase diagram of the Fe_2O_3-V_2O_5-MoO_3 system has been constructed. X-ray phase and differential thermal analyses /DTA/ were applied as the primary techniques of measurement.

INTRODUCTION

A review of publications revealed that the phase diagram of the Fe_2O_3-V_2O_5-MoO_3 system, in which some phases of catalytic interest are expected to occur, has not yet been developed. Nevertheless, both the features of components and the phase diagrams of binary systems: Fe_2O_3-V_2O_5 [1,2], Fe_2O_3-MoO_3 [3], V_2O_5-MoO_3 [4,5] appear to be known. The hitherto studies of the Fe_2O_3-V_2O_5-MoO_3 system [6,7] have shown the components to form two new phases, viz., $FeVMoO_7$ and $Fe_4V_2Mo_3O_{20}$, melting incongruently at 953 ± 5 K and 1033 ± 5 K, respectively:

$$4\ FeVMoO_{7/s/} \longrightarrow Fe_4V_2Mo_3O_{20/s/} + \text{liquid} \qquad /1/$$

$$Fe_4V_2Mo_3O_{20/s/} \longrightarrow Fe_2/MoO_4/_{3/s/} + \alpha\text{-}Fe_2O_{3/s/} + \text{liquid} \qquad /2/$$

It was also stated, that MoO_3 incorporates into the $Fe_2V_4O_{13}$ crystall lattice being one of two phases to exist in the Fe_2O_3-V_2O_5 system, forming a solid solution of a limited solubility, not exceeding 18 % mole of MoO_3, at ambient temperature [8].

MEASURING METHODS

As experimental materials were used α-Fe_2O_3, V_2O_5 /commercial products of p.a. grade/, and MoO_3 obtained by thermal decomposition $/NH_4/_6Mo_7O_{24} \cdot 4\ H_2O$ in air at 423 - 823 K. The oxides in weighed proportions were grinded, pelletized and heated, in air, in following cycles: 673 ⟶ 773 K - 1 h + 773 K - 24 h + 823 K - 24 h + 823 K - 72 h. Samples containing 50 - 80 % mole of MoO_3 in the original mixtures were additionally heated at 843 K for 6 hours, and then grinded.

Proceedings of ICTA 85, Bratislava

The phase compositions of the preparations were determined by X-ray diffraction /DRON-3, CoK$_{\alpha}$/, and on the data from ASTM cards [9], and on those of publications [2,6,7].

Thermal analysis was performed with a derivatograph /J.Paulik-J.Paulik-L.Erdey, MOM Budapest/, in air, at the heating rate 10°/min, at 293 - 1273 K. Measurements were performed in quartz crucibles. The weights of samples were 1000 mg each. The accuracy of readings of the effect temperatures from DTA curves was estimated on the evidence of repetitions made for ± 5 K.

RESULTS AND DISCUSSION

Two series of preparations were prepared: the main series comprising 36 samples and an additional one consisting of 16 samples. The compositions of the original mixtures of 36 samples from the main series assigned, in the Gibbs triangle, isoconcentration lines, i.e., lines indicated by the compositions of samples in which the contens of one component were constant while those of the others were ranging by 10 % mole, each of the preparations from the main series lying, at the same time, on three isoconcentration lines. The compositions of the original mixtures of additional samples were such, that each of them lied only on one isoconcentration line.

The preparations obtained were examined by X-ray diffraction and DTA. The results from examinations are given in Fig. 1.

The phase analysis showed, that in the subsolidus area of this system occur nine phases: α-Fe_2O_3, V_2O_5 /or a solid solution of MoO_3 in V_2O_5/, MoO_3, $Fe_2V_4O_{13}$/s.s/, $FeVO_4$, $Fe_2/MoO_4/_3$, $V_9Mo_6O_{40}$, $FeVMoO_7$, $Fe_4V_2Mo_3O_{20}$. 11 areas, in which appropriate phases had been at equilibrium were determined. The temperatures of solidus areas and of lines were taken as the first effect start temperatures /the effect is not a polymorphic transition/, indicated on the DTA curves of samples which were lying in a given area, or in given pseudo two - component sections. A subsolidus phase diagram of the Fe_2O_3-V_2O_5-MoO_3 system was constructed on the results from X-ray diffraction and DTA /Fig. 1/.

The area mapping of a subsolidus phase in a parallel perspective is shown in Fig. 1b. This mapping separates the area of coexistence of appropriate phases, whose unequivocal positions are indicated by a full line, whereas the sections, whose transitions in the light of the hitherto studies, are disputable, are indicated by a broken line.

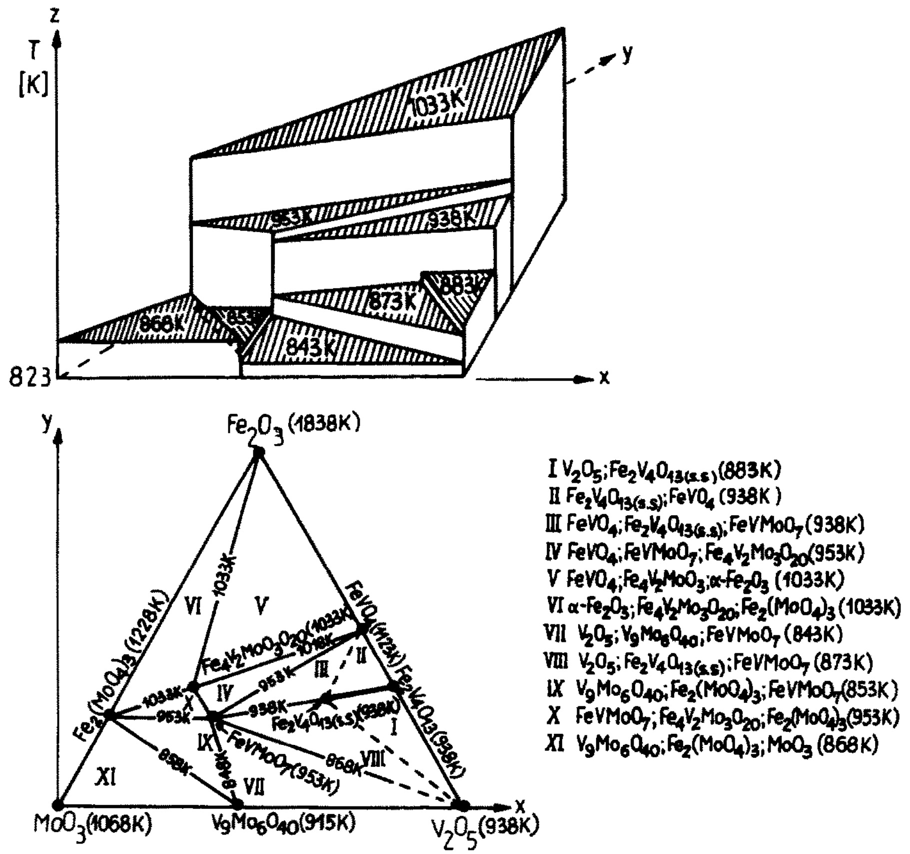

Fig.1. Subsolidus phase diagram of Fe_2O_3 - V_2O_5 - MoO_3 system
a/ Oblique projection on the Gibbs triangle.
b/ Mapping of the orthogonal projection in a parallel perspective.

Unfortunatelly, the results of X-ray diffraction have not furnished unquestionable information in respect to equilibria which are being established between the solid solutions, existing in systems Fe_2O_3-V_2O_5 [2] and V_2O_5-MoO_3 [4,5] , and the solid solution of MoO_3 in $Fe_2V_4O_{13}$ [8].

REFERENCES

1 A.A.Fotiev, S.M.Cheshnitskii, L.L.Surat, Zh.Neorg.Khim., 28 /1983/ 988

2 J.Walczak, J.Ziolkowski, M.Kurzawa, J.Osten-Sacken, M.Lysio, Pol.J.Chem., /Formely Rocz.Chem./ In the press.

3 W.Jäger, A.Rahmel, K.Becker, Arch.Eisenhüttenwesen, 30 /1959/ 435

4 N.Strupler, A.Morette, 260 /1965/ 1971

5 A.Bielański, M.Najbar, Pol.J.Chem., /Formely Rocz.Chem./ 52 /1978/ 883

6 J.Walczak, M.Kurzawa, E.Filipek, The Third Polish Seminar to the memory of St.Bretsznajder, Plock, 14-16.IX.1983

7 J.Walczak, J.Ziolkowski, M.Kurzawa, L.Trzesniowska, J.Therm. Anal., 29 In the press.

8 J.Walczak, M.Kurzawa, L.Trzesniowska, 8-th Internat.Conf.Therm. Anal., Bratislava, Czechoslovakia, August 19-23, 1985

9 Joint Committee of Powder Diffraction File 5-508, 9-387, 13-543, 18-851, 19-813, 20-526, 24-541, 25-418