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STUDIES ON THE SYSTEM $CrVO_4$-$Fe_2(MoO_4)_3$

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X-RPD and DTA revealed that $CrVO_4$ reacts with $Fe_2(MoO_4)_3$ in the solid state to form $Fe_2Cr_2V_2Mo_3O_{20}$. The thermal and X-ray characteristics of this phase have been established.

It is known from studies on the phase equilibria in the system $FeVO_4$-$Fe_2(MoO_4)_3$ and $CrVO_4$-$Cr_2(MoO_4)_3$ that $FeVO_4$ reacts with iron(III) molybdate to yield the phase $Fe_4V_2Mo_3O_{20}$ [1]. Chromium(III) orthovanadate does not remain in permanent equilibrium with chromium(III) molybdate, though a compound analogous to $Fe_4V_2Mo_3O_{20}$ [2] does not arise in the $CrVO_4$-$Cr(MoO_4)_3$. On the other hand, a reaction takes place in the solid state in this system:

$$3\,CrVO_{4(s)} + Cr_2(MoO_4)_{3(s)} = 3\,CrVMoO_{7(s)} + Cr_2O_{3(s)} \qquad (1)$$

It seemed of interest to investigate how $CrVO_4$ behaves towards $Fe_2(MoO_4)_3$.

The structures and properties of the system components, i.e. $CrVO_4$ and $Fe_2(MoO_4)_3$, are well known [3-11].

Experimental

α-Fe_2O_3, Cr_2O_3, MoO_3, $CrVO_4$ and $Fe_2(MoO_4)_3$ were used in the experiments.

The DTA studies were performed with a Paulik-Paulik-Erdey derivatograph, in quartz crucibles, in air, at 20-1000°, at heating rate of 10 deg/min. The sample weight was 1000 mg in each case.

The phase compositions of preparation were established by means of X-ray powder diffraction (an A_2 diffractometer with an HZG-4 goniometer,

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and CoK_α radiation), via the data from the ASTM cards [12] and literature publications [1-4, 8].

Three mixtures of the appropriate oxides corresponding to 75 mol% of $CrVO_4$ and 25 mol% of $Fe_2(MoO_4)_3$, 66.67 mol% of $CrVO_4$ and 33.33 mol% of $Fe_2(MoO_4)_3$ and 50 mol% $CrVO_4$ and 50 mol% of $Fe_2(MoO_4)_3$, and three mixtures of $CrVO_4$ and $Fe_2(MoO_4)_3$ with the same compositions, were used in the experiments. The substrates in weighed proportions were ground, pastilled and calcined in air under the following conditions: $400^\circ \rightarrow 500^\circ$ (24 h); 550° (72 h); 600°(24 h); 650° (24 h); 700° (48 h); 700° (72 h). From 550° the samples were cooled down slowly to ambient temperature after each roasting cycle, ground and examined by DTA. After their compositions had been established, they were repastilled.

Results and discussion

The diffraction patterns of preparations obtained by calcining at 550° substrates corresponding to 66.67 mol% of $CrVO_4$ and 33.33 mol% of $Fe_2(MoO_4)_3$, irrespective of the kind of substrates used, contained not only the diffraction lines of the substrates, but also a set of lines imperceptibly differing from the diffraction lines characteristic of $Fe_4V_2Mo_3O_{20}$ [1]. The intensities of these lines successively increased in the diffraction patterns of preparations calcined at 600 and 650°, respectively, whereas the intensities of the lines characteristic of the substrates decreased. Substrates were not found in the preparation obtained on calcination at 700°. On the other hand, preparations corresponding to 75 mol% of $CrVO_4$, obtained on calcination at 700°, contained $CrVO_4$ and a phase characterized by a new reflexion set, while preparations corresponding to 50 mol% of $CrVO_4$ contained not only this phase, but also $Fe_2(MoO_4)_3$.

Thus, X-ray powder diffraction shows that $CrVO_4$ does not remain in permanent equilibrium with $Fe_2(MoO_4)_3$. It also reveals that a reaction takes place in the solid state in the system $CrVO_4$-$Fe_2(MoO_4)_3$:

$$2\,CrVO_{4(s)} + Fe_2(MoO_4)_{3(s)} = Fe_2Cr_2V_2Mo_3O_{20(s)} \qquad (2)$$

giving rise to a new phase, not previously reported in the literature.

The interplanar distances of the phase $Fe_2Cr_2V_2Mo_3O_{20}$ and the relative intensities of the relevant reflexions are given in (Table 1).

Table 1 Interplanar distances of $Fe_2Cr_2V_2Mo_3O_{20}$ and relative intensities for relevant reflexions

d, Å	I, %
4.75	10
4.57	5
4.34	40
4.26	20
4.14	25
3.89	40
3.80	35
3.65	50
3.40	30
3.36	75
3.29	100
3.21	25
3.17	15
3.11	20
3.04	90
3.01	10
2.96	15
2.89	10
2.77	10
2.72	5
2.66	5
2.62	5
2.51	5
2.48	5
2.45	10
2.39	15
2.36	20
2.28	20
2.24	5
2.17	5
2.14	5
2.11	10

Two endothermic effects were recorded in the DTA curve (Fig. 1). The first, with a peak start temperature of 775±10°, is attributed to the incongruent melting of $Fe_2Cr_2V_2Mo_3O_{20}$, and the other, with a peak maximum temperature of about 910°, to solid products deposited during melting of the phase. X-ray powder diffraction on the phase $Fe_2Cr_2V_2Mo_3O_{20}$, heated additionally for 4 h at 790, 850 and 910°, respectively, and then cooled down rapidly to ambient temperature, demonstrated that incongruent melting of

$Fe_2Cr_2V_2Mo_3O_{20}$ occurs, with the deposition of two solid solutions: a continuous solid solution of $Fe_{2-2x}Cr_{2x}O_3$ [13] and a solid solution of $Fe_{2-2x}Cr_{2x}(MoO_4)_3$ [14], according to the equation:

$$Fe_2Cr_2V_2Mo_3O_{20(s)} = Fe_{2-2x}Cr_{2x}O_{3(s.s.)} + Fe_{2-2x}Cr_{2x}(MoO_4)_{3(s.s.)} + \text{liquid} \qquad (3)$$

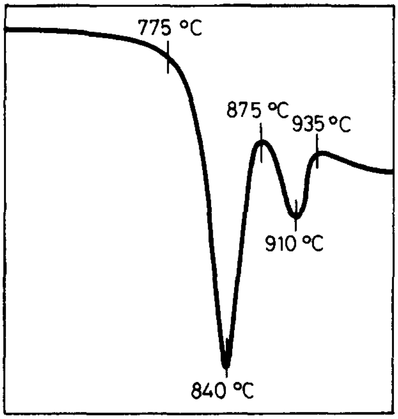

Fig. 1 DTA curve of $Fe_2Cr_2V_2Mo_3O_{20}$

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Zusammenfassung — Mittels DTA und Debye-Scherrer-Untersuchungen wurde festgestellt, daß $CrVO_4$ und $Fe_2(MoO_4)_3$ im festen Zustand miteinander reagieren und $Fe_2Cr_2V_2Mo_3O_{20}$ bilden. Thermische und röntgenographische Eigenschaften dieser Phase wurden ermittelt.