

REACTIVITY OF CrVO_4 WITH FeVO_4

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It has been confirmed by DTA and X-ray powder diffraction that the components of the CrVO_4 - FeVO_4 system react with each other in the solid state yielding a compound, $\text{FeCr}(\text{VO}_4)_2$. $\text{FeCr}(\text{VO}_4)_2$ has been found to melt incongruently at $870 \pm 10^\circ\text{C}$ depositing $\text{Fe}_{2-2x}\text{Cr}_x\text{O}_3(\text{s.s.})$.

Chromium(III) orthovanadate, iron(III) orthovanadate and systems in which these compounds occur - have been objects of investigations in very respect, first of all, due to their interesting catalytic properties [1]. Hence, it seemed interesting to study how CrVO_4 and FeVO_4 react with each other in the solid state.

The literature review has shown that the structure and physico-chemical properties of CrVO_4 and FeVO_4 are well known [2-7], but informations relevant to the CrVO_4 - FeVO_4 system are few and inconsistent [8-11]. Thus, according to Vatolin, Attfield and Lavat [8, 10, 11], CrVO_4 forms with FeVO_4 a solid solution $\text{Fe}_{1-x}\text{Cr}_x\text{VO}_4$ adopt the α - MnMoO_4 structure, which is different from those of the end members of the series, but Fotiev with his associates find that a compound, $\text{FeCr}(\text{VO}_4)_2$, exists in the CrVO_4 - FeVO_4 system, and the system components do not form a solid solution.

Experimental

CrVO_4 , FeVO_4 , analar V_2O_5 (Reachim), Cr_2O_3 pure (POCh, Gliwice) and analar α - Fe_2O_3 (VEB, GDR) were used to experiments. Chromium(III) orthovanadate was obtained by heating an equimolar mixture of CrO_3 with V_2O_5 under following conditions: $500^\circ \rightarrow 24$ h; $550^\circ \rightarrow 24$ h; $600^\circ \rightarrow 24$ h; $630^\circ \rightarrow 24$ h; $700^\circ \rightarrow 24$ h; $750^\circ \rightarrow 24$ h; $800^\circ \rightarrow 24$ h. Iron(III) orthovanadate was ob-

tained by calcinating an equimolar mixture of Fe_2O_3 and V_2O_5 at $600^\circ \rightarrow 24$ h; $650^\circ \rightarrow 24$ h and $700^\circ \rightarrow 72$ h.

DTA was made with a derivatograph F. Paulik-J. Paulik-L. Erdey in air, in quartz crucibles, at $20\text{--}1000^\circ$, at a heating rate 10 deg/min. The weight of samples was 1000 mg in each case.

The phase composition of preparations was found by X-ray powder diffraction (a diffractometer A₂ with a goniometer HZG-4, $\text{CoK}\alpha$) and on the data from the ASTM cards [12] and publications [3, 9].

To experiments were used three mixtures of CrVO_4 and FeVO_4 with following molar ratios of components: 2:1, 1:1 and 1:2, which corresponds to 66.67, 50.00 and 33.33% mol of CrVO_4 in a sample. Substrates weighed in the above proportions were mixed by grinding, pastilled and heated in air, at $600^\circ \rightarrow 24$ h; $650^\circ \rightarrow 24$ h; $700^\circ \rightarrow 48$ h and $700^\circ \rightarrow 72$ h. After each roasting cycle the samples were cooled down slowly to ambient temperature, ground, examined by DTA, their phase composition having been established they were repastilled.

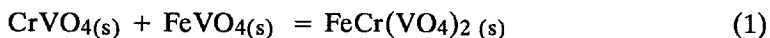
Results and discussion

Table 1 shows the compositions of initial mixtures and X-ray powder diffraction results of preparations obtained on the last stage of heating at 700° during 72 h.

Table 1 Compositions of initial mixtures and X-ray powder diffraction results of samples on the last heating cycle

No	Composition of initial mixtures, mol %		X-ray powder diffraction results
	CrVO_4	FeVO_4	
1	66.67	33.33	CrVO_4 , $\text{FeCr}(\text{VO}_4)_2$
2	50.00	50.00	$\text{FeCr}(\text{VO}_4)_2$
3	33.33	66.67	FeVO_4 , $\text{FeCr}(\text{VO}_4)_2$

X-ray powder diffraction of a sample containing 66.67% mol of CrVO_4 in its initial mixture shows that it is a mixture of CrVO_4 and $\text{FeCr}(\text{VO}_4)_2$. It applies that CrVO_4 reacts with FeVO_4 yielding $\text{FeCr}(\text{VO}_4)_2$ - a compound to existence of which pointed Fotiev only [9]. The phase composition of a preparation containing 50.00% mol of CrVO_4 in its initial mixture shows that, in the solid state, an equimolar mixture of CrVO_4 and FeVO_4 reacts to completion yielding $\text{FeCr}(\text{VO}_4)_2$ in accord an equation:



FeVO_4 and $\text{FeCr}(\text{VO}_4)_2$ were found in the third sample.

The $\text{FeCr}(\text{VO}_4)_2$ phase was obtained, too, from oxides by calcinating a mixture of Fe_2O_3 , Cr_2O_3 and V_2O_5 with a molar ratio 1:1:2 under given conditions. On the diffraction pattern of the preparation obtained a reflexion set was recorded, identical with a set recorded on the diffraction pattern of a preparation obtained by calcinating an equimolar mixture of CrVO_4 and FeVO_4 .

Data in Table 2 show that on the diffraction pattern of $\text{FeCr}(\text{VO}_4)_2$ there are, beside lines whose X-ray characteristics gave Fotiev [9], other diffraction lines, starred in the Table 2. Fotiev [9] has found that $\text{FeCr}(\text{VO}_4)_2$ melts incongruently at $890 \pm 5^\circ$. The figure shows a DTA curve of $\text{FeCr}(\text{VO}_4)_2$ on which, at 20-1000°, has been recorded only the melting effect of the phase at $875 \pm 10^\circ$. Presence of only one effect on the DTA curve of $\text{FeCr}(\text{VO}_4)_2$ implies that the melting effect of a solid depositing during incongruent melting of $\text{FeCr}(\text{VO}_4)_2$ lies above 1000°. In order to establish the kind of a solid depositing during melting of $\text{FeCr}(\text{VO}_4)_2$, the $\text{FeCr}(\text{VO}_4)_2$ phase was heated during 4 h at 880° and on vehemently cooling down it was analyzed by X-ray

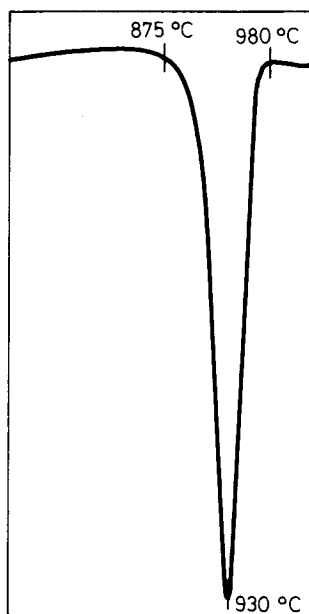


Fig. 1 DTA curve of $\text{FeCr}(\text{VO}_4)_2$

powder diffraction. The analysis has shown that a solid depositing during melting of $\text{FeCr}(\text{VO}_4)_2$ is the solid solution $\text{Fe}_{2-2x}\text{Cr}_{2x}\text{O}_3$.

Table 2 Interplanar distances for $\text{FeCr}(\text{VO}_4)_2$ and relative intensities of the corresponding reflexions

d , Å	I , %
6.47	25
5.15	5
3.66	5
3.39	5
3.36	5
3.27	30
3.23	100
3.19	30
3.17	25
3.09	5
3.04	20
2.79	5
2.69	15
2.63	10
2.58	15
2.51	5
2.46	5
2.35	5
2.22	5
2.17	5
2.15	40
2.08	5
2.01	10
1.942	5
1.926	5
1.855	5
1.839	5
1.709	10

The studies confirm that, in the solid state, CrVO_4 reacts with FeVO_4 to form $\text{FeCr}(\text{VO}_4)_2$. It has also been found that $\text{FeCr}(\text{VO}_4)_2$ can be obtained from a reaction in the solid state, both from CrVO_4 and FeVO_4 and an appropriate oxide mixture. X-ray characteristics of the phase at the angle range $2\theta:10-65^\circ$ $\text{CoK}\alpha$ has been given, in which the existence of reflexions overlooked by Fotiev [9] have been shown.

References

- 1 N. Pernicone, *J. Less-Common Met.*, **36** (1974) 289.
- 2 M. J. Isasi, R. Saez-Puche and M. L. Veiga, *Mater. Res. Bull.*, **23** (1988) 595.
- 3 J. Walczak and E. Filipek, *J. Thermal Anal.* in press.
- 4 J. Amiel, D. Coleifis and D. Olivier, *C. R. Acad. Sci., Paris*, **263** (1966) 224.
- 5 R. C. Kerby and J. R. Wilson, *Can. J. Chem.*, **51** (1973) 1032.
- 6 B. Robertson and K. Kostiner, *J. Solid State Chem.*, **4** (1972) 29.
- 7 J. Walczak, J. Ziólkowski, M. Kurzawa, J. Osten-Sacken and M. Lysio, *Pol. J. Chem.*, **29** (1985) 255.
- 8 N. A. Vatolin, N. G. Moleva, P. I. Volkova and T. V. Sanozhnikova, *Okislenie vanadievyykh schlakov*, Izd. Nauka, 1978.
- 9 A. A. Fotiev, L. L. Surat, G. A. Korablev and A. I. Tretiakov, *Zh. Neorg. Khim.*, **26** (1981) 242.
- 10 J. P. Attfield, *J. Solid State Chem.*, **67** (1987) 58.
- 11 A. E. Lavat, M. C. Grasselli and E. J. Baran, *J. Solid State Chem.* **78** (1989) 206.
- 12 Joint Committee of Powder Diffraction File: 6-504, 9-389, 13-543, 24-541, 25-418.

Zusammenfassung — Mittels DTA und Debye-Scherrer-Untersuchungen konnte bewiesen werden, daß die Komponenten des Systemes $\text{CrVO}_4\text{-FeVO}_4$ im festen Zustand miteinander reagieren und die Verbindung $\text{FeCr}(\text{VO}_4)_2$ bilden. $\text{FeCr}(\text{VO}_4)_2$ schmilzt inkongruent bei $870 \pm 10\text{C}$ und scheidet dabei $\text{Fe}_{2-2x}\text{Cr}_{2x}\text{O}_3(\text{s.s.})$ ab.