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PHASE EQUILIBRIA UP TO THE SOLIDUS LINE IN THE V_2O_5-$CrVMoO_7$ SYSTEM

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The phase equilibria being established in the V_2O_5-$CrVMoO_7$ system in the solid state and the whole component concentration range have been studied by the X-ray powder diffraction and thermal analysis methods. The measurements have shown that the V_2O_5-$CrVMoO_7$ system is not a real two-component system in the subsolidus area.

Vanadium pentoxide and the systems of which it is one of their components are objects of strenuous investigations, first of all, on account of the catalytic properties of the components and the phase occurring in such systems. The cognitive studies on the three-component system: Cr_2O_3-V_2O_5-MoO_3, and the study of the $CrVO_4$-MoO_3 system have shown the occurrence of a compound to which a molecular formula, $CrVMoO_7$, has been ascribed [1, 2]. Hence, it seemed advisable to find out whether the phase of interest reacts with V_2O_5 and to establish which phases permanently coexist at equilibrium with the V_2O_5-$CrVMoO_7$ system.

The properties and structure of V_2O_5 are known well. Vanadium pentoxide is characterized by an orthorhombic symmetry [3] and belongs to the spatial group, Pmnm [4, 5]. V_2O_5 melts incongruently, according to Kubaschewski – at 675° [6], according to Burdese – at 690° [7], and by our investigation – at 675±5° [8].

$CrVMoO_7$ is a compound known since a short time, so the properties of that phase have not yet been investigated in every respect. It is only known that $CrVMoO_7$ melts incongruently at 820±5° depositing a solid Cr_2O_3. Its density and X-ray characteristics at the angle range of 2θ: 12-65° (CoK_α) are also known [2].

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Experimental

An analar V_2O_5 (a commercial product), as well as MoO_3 and Cr_2O_3 obtained by a thermal decomposition of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $(NH_4)_2Cr_2O_7$, respectively, were used for experiments. The decomposition of ammonium molybdate was carried out at 120-550° for dozen or so hours, whereas the decomposition was carried out first at 100°, then at 150° and afterwards the decomposition product was additionally calcinated at 1000° for 72 h. X-ray powder diffraction of those preparations showed the presence of respective oxides, i.e. MoO_3 or Cr_2O_3.

Weighed in given amounts the oxides were mixed by grinding, then pastilled and calcinated in air. Preparations with the contents of up to 65% mol of V_2O_5 in terms of the components of the V_2O_5-$CrVMoO_7$ system were heated in the following cycles: 400°-500° (24 h)-600° (24 h)-600° (48 h)-600°-(72 h). After each of the heating cycle the preparations were slowly cooled to ambient temperature, ground down and, analyzed by DTA and X-ray powder diffraction, and then again pastilled and heated until preparations being at equilibrium were obtained. Some of them were additionally heated for 48 h at 620° and vehemently cooled down to ambient temperature.

The thermal analysis (DTA) was made at 20-1000° in quartz crucibles at a heating rate of 10 deg/min using a derivatograph F. Paulik-J. Paulik-L. Erdey (MOM Budapest). The weight of each sample was 1000 mg. The phase composition of the preparations was established by X-ray powder diffraction (a diffractometer of type A2 with a goniometer HZG-4, CoK_α) and on the ASTM cards [9], and the publications [2, 10, 11].

In order to study the phase equilibria being established in a given system, in the solid state and the whole component concentration range 19 samples of oxides were prepared. The samples were heated under given conditions and the preparations obtained were analyzed by DTA and X-ray powder diffraction.

Results and discussion

The results from experiments prove that V_2O_5 does not remain at permanent equilibrium with $CrVMoO_7$. X-ray powder diffraction of preparations containing up to 65% mol of V_2O_5 in terms of the system components shows that they are a mixture of three phases: $CrVMoO_7$, $V_2O_{5(s.s.)}$, and $Cr_2V_4O_{13(s.s.)}$, respectively. In the other component concentration range, i.e. above 65% mol of V_2O_5, the preparations being at equilibrium were two-phase and contained $V_2O_{5(s.s.)}$ and $Cr_2V_4O_{13(s.s.)}$ respectively. It implies that at that component concentration range V_2O_5 reacts with $CrVMoO_7$ to completion, yielding two solid solutions, viz., a solid solution of MoO_3 in $Cr_2V_4O_{13}$ and a solution of a solid MoO_3 in V_2O_5, respectively. The reaction in the solid state can be written as follows:

$$2\,CrVMoO_{7(s)} + 2\,V_2O_{5(s)} = Cr_2V_4O_{13(s.s.)} + V_2O_{5(s.s.)} \qquad (1)$$

With the sample whose composition is of 65% mol of V_2O_5 (in terms of the phase components) reaction 1 is quantitative. It means, that $CrVMoO_7$ is a stable phase coexisting with $Cr_2V_4O_{13(ss)}$ and $V_2O_{5(ss)}$ only up to 65% mol of V_2O_5.

The solubility limit for MoO_3 in $Cr_2V_4O_{13}$ is cá 16% mol [11], and that for MoO_3 in V_2O_5 - cá 30 % mol [12]. The mechanism of reaction 1 is not known, but it is to be supposed that in the solid state a reaction takes place:

$$2\,CrVMoO_{7(s)} + V_2O_{5(s)} = Cr_2V_4O_{13(s)} + 2\,MoO_{3(s)} \qquad (2)$$

The resultant MoO_3, under the synthesis conditions, is being incorporated into the crystal lattice of $Cr_2V_4O_{13}$ or V_2O_5 to give the respective solid solutions:

$$Cr_2V_4O_{13(s)} + MoO_{3(s)} = Cr_2V_4O_{13(s.s.)} + V_2O_{5(s)} \qquad (3)$$

$$V_2O_{5(s)} + MoO_{3(s)} = V_2O_{5(s.s.)} \qquad (4)$$

Hence, one may consider reaction 1 to be a total reaction of reactions 2, 3 and 4. But experimental verification of such course of the reaction requires further studies.

The phase equilibria being established in the V_2O_5-$CrVMoO_7$ system in the solid state in the whole component concentration range is shown in the Fig. 1. The temperature range at which the subsolidus area exists was found by DTA of the preparations being at equilibrium and by X-ray powder diffraction of the samples vehemently cooled down to ambient temperature. The Fig. 1 shows that the V_2O_5-$CrVMoO_7$ system is not, in the subsolidus area, any real two-component system in the whole component concentration range.

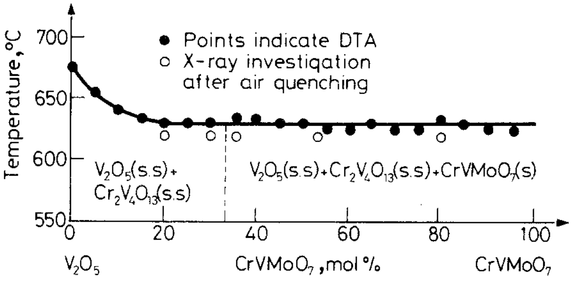

Fig. 1 The subsolidus area of the V_2O_5-$CrVMoO_7$ system

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Zusammenfassung – Mittels Thermoanalyse und Debye-Scherrer-Verfahren wurde das Phasengleichgewicht im Feststoffsystem V_2O_5-$CrVMoO_7$ im gesamten Konzentrationsbereich untersucht. Die Messungen zeigen, daß es sich bei dem System V_2O_5-$CrMoO_7$ im Bereich unter Solidus um kein echtes Zweikomponentensystem handelt.