

Studies on the $\text{CrVMoO}_7\text{--Cr}_2(\text{MoO}_4)_3$ system

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Abstract

The phase equilibria in the $\text{CrVMoO}_7\text{--Cr}_2(\text{MoO}_4)_3$ system at temperatures up to 1000°C over the entire component concentration range have been studied by DTA and X-ray powder diffraction. It has been found that only up to the solidus line does the $\text{CrVMoO}_7\text{--Cr}_2(\text{MoO}_4)_3$ system behave like a real two-component system.

INTRODUCTION

Studies on the $\text{Cr}_2\text{O}_3\text{--V}_2\text{O}_5\text{--MoO}_3$ system and on the phase equilibria in the $\text{CrVO}_4\text{--MoO}_3$ system have shown that the system components react with each other in the solid state to form an unknown phase CrVMoO_7 , the properties of which have not so far been studied in every respect [1, 2]. It is known, however, that the phase melts incongruently at $820 \pm 5^\circ\text{C}$ with formation of solid Cr_2O_3 . Its X-ray pattern in the 2θ range $12\text{--}65^\circ$ (Co $K\alpha$), its density and its triclinic unit cell parameters are also known [2–6]. The IR spectrum [7] of the compound whose structure has not yet been determined implies that the compound is built of VO_4 and MoO_4 tetrahedra and CrO_6 octahedra. In the IR spectrum of the compound also occur absorption bands developed by stretching vibrations of the M–O–M bridge, leading to corresponding co-ordination polyhedra [7].

By contrast, the structure and properties of chromium (III) molybdate, the other compound of the studied system are well known. It is known that $\text{Cr}_2(\text{MoO}_4)_3$ occurs in two polymorphic modifications: a low-temperature form consisting of monoclinic crystals and a high-temperature form consisting of orthorhombic crystals [8]. The temperature of the $\text{Cr}_2(\text{MoO}_4)_3$ polymorphic transition determined by Sleight and Brixner is 385°C [9]. However, our investigations have proved the transformation takes place at $400 \pm 5^\circ\text{C}$, in each case. Also, two of the chromium (III) molybdate modifications are well known. Plasova and Kefeli [8] attributed the space

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group $P2_1/a$ to the low-temperature variety of $\text{Cr}_2(\text{MoO}_4)_3$, and the space group $Pnca$ to the high-temperature variety of interest. It has also been found that chromium(III) molybdate in the solid state decomposes to Cr_2O_3 and MoO_3 before reaching its melting point. The decomposition of $\text{Cr}_2(\text{MoO}_4)_3$ starts at a very slow rate at 810°C . Molybdenum trioxide is evolved from the sample due to the high rate of sublimation under these conditions [10].

Having in mind the above information and the fact that the equilibria established in the three-component system are not yet known, it seemed reasonable to investigate how the phase equilibria in one of the inter-sections of the system, viz. in the pseudobinary $\text{CrVMoO}_7\text{--Cr}_2(\text{MoO}_4)_3$ system, over the whole component concentration range and up to 1000°C are established.

EXPERIMENTAL

The samples were made from oxides V_2O_5 , MoO_3 and Cr_2O_3 , which were weighed in the appropriate amounts, ground into powder, pastilled and heated under conditions that led to the equilibrium state: $400^\circ\text{C} \rightarrow 500^\circ\text{C}$ (24 h) $\rightarrow 550^\circ\text{C}$ (48 h) $\rightarrow 600^\circ\text{C}$ (24 h) $\rightarrow 700^\circ\text{C}$ (24 h) $\rightarrow 700^\circ\text{C}$ (24 h).

The conditions under which samples were brought to the equilibrium state were established in preliminary studies where the samples contained, respectively 25.00, 50.00 and 70.00 mol% $\text{Cr}_2(\text{MoO}_4)_3$ in primary mixtures, in terms of the components of the system under study. After successive heating cycles, the test samples were slowly cooled to ambient temperature, ground down and then examined by X-ray powder diffraction and DTA. Identical results from the analyses after two heating cycles proved the equilibrium state had been established. Other samples representing the whole component concentration range were heated under fixed conditions and afterwards examined by X-ray powder diffraction and DTA.

X-Ray diffraction patterns of the samples were obtained with the help of an HZG 4/A-2 diffractometer using $\text{Co K}\alpha$ radiation. The interplanar distances of the samples were compared with the data from refs. 2 and 9 and also the Powder Diffraction File [11]. Differential thermal analysis (DTA) was performed using an F. Paulik–J. Pauliki–L. Erdey derivatography in quartz crucibles, in air, at $20\text{--}1000^\circ\text{C}$.

RESULTS AND DISCUSSION

Twelve samples, the compositions of which are shown on the phase diagram, were prepared to investigate phase equilibria in the $\text{CrVMoO}_7\text{--Cr}_2(\text{MoO}_4)_3$ system within the whole range of component concentrations. The X-ray powder diffraction of preparations remaining at equilibrium has revealed that they are a mixture of only two phases CrVMoO_7 and $\text{Cr}_2(\text{MoO}_4)_3$ over the whole concentration range. The experimental data are presented graphically in Fig. 1, in the form of a phase diagram of the $\text{CrVMoO}_7\text{--Cr}_2(\text{MoO}_4)_3$ system.

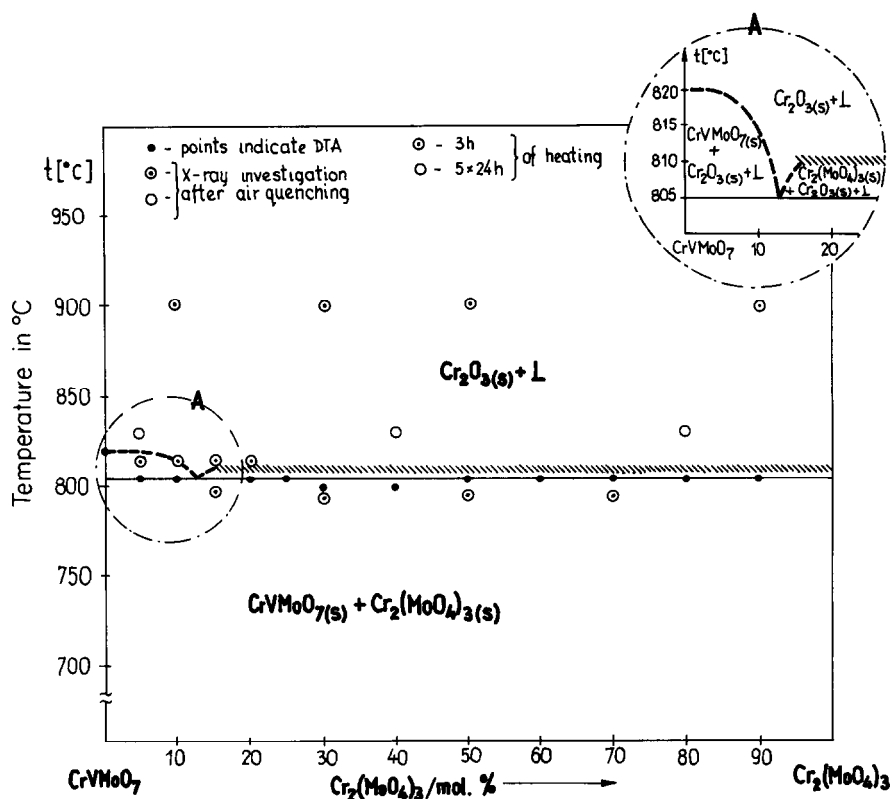


Fig. 1. Phase diagram of the CrMoO_7 - $\text{Cr}_2(\text{MoO}_4)_3$ system.

On the DTA curves of the samples which were at equilibrium and contained 15.00 mol% or more $\text{Cr}_2(\text{MoO}_4)_3$, was recorded the first, quite small, endothermic effect starting at 395–400 $^\circ\text{C}$. Such an effect failed to appear on the DTA curves of preparations containing less than 15.00 mol% $\text{Cr}_2(\text{MoO}_4)_3$. The endothermic effect was also recorded on DTA curves of all the preparations, its start temperature being confined within 795–805 $^\circ\text{C}$. The experimental results for another system Cr_2O_3 - MoO_3 , have shown that the polymorphic transformation temperature is $400 \pm 5^\circ\text{C}$. Accordingly, the first effect recorded on DTA curves of the preparations which contained 15.00 mol% or more $\text{Cr}_2(\text{MoO}_4)_3$ was attributed to this type of transformation. Lack of the effect on the DTA curves of preparations containing less than 15.00 mol% $\text{Cr}_2(\text{MoO}_4)_3$ could be accounted for by insufficient chromium(III) molybdate content, which makes the transformation effect unrecordable at the sensitivity of the apparatus at our disposal.

The solidus line was marked with help of DTA results, i.e. it was based on the temperature at which the DTA effect begins, recorded on the DTA curves of all preparations. The types of solid phase at equilibrium with

liquid were established by investigating the phase composition of selected preparations, which were additionally heated at 805, 815, 830 and 900°C for 3 h and then cooled rapidly to ambient temperature. Some of the samples were additionally heated at 830°C in five 24 h cycles. After each cycle of heating the samples were cooled rapidly, homogenized by grinding, and again heated. In this way we want to check if chromium(III) molybdate, present in the samples would be decomposed to oxides after a succeeding heating cycle during this procedure. The compositions of the samples subjected to such examinations have been denoted on the phase diagram.

The results of the DTA and X-ray phase analysis of the preparations remaining at equilibrium revealed that up to 805°C, the components of the system remained in permanent equilibrium in the solid state. The system behaves like a real two-component system. Above the solidus line temperature, the system is not a true two-component system, primarily due to incongruent melting of CrVMoO_7 .

To confirm the range of the subsolidus area, samples remaining at equilibrium and containing 15.00, 30.00, 50.00 and 70.00 mol% $\text{Cr}_2(\text{MoO}_4)_3$ were additionally heated for 3 h at 795°C, somewhat below the solidus line temperature, and after that rapidly cooled to ambient temperature. The phase composition of the samples obtained in this way did not differ from the phase composition of samples remaining at equilibrium.

With the range of component concentrations above 10.00 mol% $\text{Cr}_2(\text{MoO}_4)_3$, above 810°C, i.e. the temperature of chromium(III) molybdate decomposition in our previous studies [10], only solid Cr_2O_3 with liquid should remain at equilibrium. This has been confirmed by the experimental data presented in this work. Accordingly, selected preparations containing more than 10 mol% $\text{Cr}_2(\text{MoO}_4)_3$ were heated additionally at 830°C for 144 h in total. After this time of heating, X-ray phase powder diffraction showed a lack of $\text{Cr}_2(\text{MoO}_4)_3$, simultaneous with the presence of Cr_2O_3 .

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