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PHASE EQUILIBRIA IN THE $Cr_2V_4O_{13}$–$CrVMoO_7$ SYSTEM

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ABSTRACT

The phase equilibria in the $Cr_2V_4O_{13}$–$CrVMoO_7$ 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 there is a solid solution of MoO_3 in $Cr_2V_4O_{13}$ in this system. The Mo^{6+} ions are incorporated in the $Cr_2V_4O_{13}$ lattice, replacing V^{5+} ions, and this substitution gives rise to excessive positive charges the compensation of which leads to the reduction of Cr^{3+} to Cr^{2+}. All the results are shown in the form of a phase diagram.

INTRODUCTION

Studies on the Cr_2O_3–V_2O_5–MoO_3 system and studies on the phase equilibria in the $CrVO_4$–MoO_3 system [1–3] have shown that the system components react with each other in the solid state to form an unknown phase with the formula $CrVMoO_7$. The properties of this phase have not so far been studied in every respect. It is known, however, that the phase melts incongruently at 820 ± 5 °C with formation of solid Cr_2O_3. Its X-ray pattern in the 2θ range 12–65° (Co $K\alpha$) and its density are also known [3].

Investigation of another two-component system, i.e. Cr_2O_3–V_2O_5 has demonstrated that, as well as $CrVO_4$, there is another phase, $Cr_2V_4O_{13}$, whose existence has not as yet been unequivocally determined [4–6]. It has been found that $Cr_2V_4O_{13}$ is stable up to 640 °C when it starts to decompose in the solid state at a relatively slow rate yielding $CrVO_4$ and V_2O_5. The density of $Cr_2V_4O_{13}$ has been determined and its X-ray pattern is known [6].

In another investigation it was determined that MoO_3 is incorporated into the $Cr_2V_4O_{13}$ lattice to form a solid solution [7]. It has been established that the mechanism of formation of the solution consists of incorporating the Mo^{6+} ions in place of V^{5+} in the $Cr_2V_4O_{13}$ lattice, compensation of the excessive positive charges probably taking place by the reduction of an equivalent number of Cr^{3+} ions to Cr^{2+} [8]. In the three-component system, Cr_2O_3–V_2O_5–MoO_3, besides $CrVMoO_7$, there are also phases of the

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$Cr^{3+}_{2-x}Cr^{2+}_{x}V_{4-x}Mo_{x}O_{13}$-type, which are formed by the three oxides, with $0.500 < x_{max} < 0.581$.

As $CrVMoO_7$ and $Cr_2V_4O_{13}$ are recently discovered phases, it seemed expedient to establish how the phase equilibria are formed in the system composed of the components of interest. Until now, we have only determined what kinds of phase equilibria are established in the solid state [9]. The purpose of the studies presented here was to produce a complete diagram of the phase equilibria being established up to 1000 °C in the system of interest.

EXPERIMENTAL

Analytically pure V_2O_5, obtained commercially, was used in the experiments. The MoO_3 and Cr_2O_3 used were obtained by the thermal decomposition of ammonium molybdate and ammonium dichromate, respectively. The decomposition of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was carried out at 120–550 °C for over 10 h; the decomposition of $(NH_4)_2Cr_2O_7$ was first carried out at 100 °C, and then at 150 °C, the decomposition product being also roasted at 1000 °C for 72 h. X-ray powder diffraction analysis of the preparations obtained by this method showed MoO_3 and Cr_2O_3, respectively, only.

Appropriate weights of the oxides were homogenised by grinding, pastilling and roasting in air, as follows: 400 °C → 500 °C (24 h) → 600 °C (24 h) → 620 °C (9 h) → 635 °C (9 h × 3). After each heating cycle, the preparations were slowly cooled to ambient temperature, ground, examined by DTA and X-ray powder diffraction, then repastilled and reheated until the samples were obtained in the equilibrium state. The conditions necessary to attain the equilibrium state were established in separate experiments carried out during the synthesis of the preparations, verifying the model of the solid solution of MoO_3 in $Cr_2V_4O_{13}$ [7]. The attainment of equilibrium was verified by X-ray powder diffraction of selected samples following two successive roasting cycles. Two identical results indicated that equilibrium had been achieved.

The phase composition of the preparations was ascertained by X-ray powder diffraction (DRON-3, Co $K\alpha$) and from ASTM data [10], and from publications [3,6].

DTA studies were carried out on a F. Paulik–J. Paulik–L. Erdey derivatograph in quartz crucibles, in air at 20–1000 °C at a heating rate of 10 °C min^{-1}. The weight of the samples was 1000 mg in each case. When the phase diagram was constructed, the solidus lines were determined on the basis of the temperatures at which the effect begins to be recorded on the DTA curves, whereas the liquidus lines were marked, where possible, based on the temperatures at which a suitable effect starts, or else, in other cases, on the temperatures of the apex of these effects. The accuracy of the temperature reading, determined by repetitions, was found to be ±5 °C.

RESULTS AND DISCUSSION

Table 1 shows the compositions of the initial oxide mixtures and the compositions in terms of the components of the system under consideration, as well as the results from X-ray powder diffraction of the products obtained from the final roasting cycle. X-ray powder diffraction showed that in the initial mixtures with MoO_3 up to 15.38%, the equilibrium products were mono-phase containing a solid solution of MoO_3 in $Cr_2V_4O_{13}$ only. The diffraction patterns showed that, apart from the absence of MoO_3, the reflection set characterizing the solid solution was shifted, from the position of lines related to the matrix, towards smaller angles, corresponding, therefore, to higher interplanar distances. This fact is also proved by the existence of the solid solution MoO_3 in $Cr_2V_4O_{13}$.

TABLE 1

The composition of starting mixtures and the X-ray powder diffraction results of the preparations at equilibrium

Composition of samples				Phase composition at equilibrium
Mol% oxides in starting mixtures			In terms of components of the system, mol% $CrVMoO_7$	
Cr_2O_3	V_2O_5	MoO_3		
1	2	3	4	5
33.05	65.25	1.70	5.00	$Cr_2V_4O_{13}$(s.s.)
32.76	63.80	3.44	10.00	$Cr_2V_4O_{13}$(s.s.)
32.46	62.28	5.26	15.00	$Cr_2V_4O_{13}$(s.s.)
32.14	60.71	7.15	20.00	$Cr_2V_4O_{13}$(s.s.)
31.82	59.09	9.09	25.00	$Cr_2V_4O_{13}$(s.s.)
31.48	57.41	11.11	30.00	$Cr_2V_4O_{13}$(s.s.)
31.13	55.66	13.21	35.00	$Cr_2V_4O_{13}$(s.s.)
30.77	53.85	15.38	40.00	$Cr_2V_4O_{13}$(s.s.)
30.39	51.96	17.65	45.00	$Cr_2V_4O_{13}$(s.s.), $CrVMoO_7$ (v. little)
30.00	50.00	20.00	50.00	$Cr_2V_4O_{13}$(s.s.), $CrVMoO_7$ (little)
29.59	47.96	22.45	55.00	$Cr_2V_4O_{13}$(s.s.), $CrVMoO_7$ (little)
29.17	45.83	25.00	60.00	$Cr_2V_4O_{13}$(s.s.), $CrVMoO_7$
28.72	43.62	27.66	65.00	$Cr_2V_4O_{13}$(s.s.), $CrVMoO_7$
28.26	41.30	30.43	70.00	$CrVMoO_7$, $Cr_2V_4O_{13}$, (s.s.)
27.78	38.89	33.33	75.00	$CrVMoO_7$, $Cr_2V_4O_{13}$(s.s.)
27.27	36.36	36.36	80.00	$CrVMoO_7$, $Cr_2V_4O_{13}$(s.s.)
26.74	33.72	39.54	85.00	$CrVMoO_7$, $Cr_4V_4O_{13}$(s.s.)
26.19	30.95	42.86	90.00	$CrVMoO_7$, $Cr_2V_4O_{13}$(s.s.) (v. little)
25.61	28.05	46.34	95.00	$CrVMoO_7$, $Cr_2V_4O_{13}$ (s.s.) (traces)

At over 15.38 mol% MoO_3 in the initial mixtures, as well as $Cr_2V_4O_{13}$(s.s.), the equilibrium preparations contained another phase in the $CrVMoO_7$ system.

In order to determine whether the solubility of MoC_3 in $Cr_2V_4O_{13}$ increases at higher temperatures, i.e. close to the temperatures of the solidus lines, equilibrium samples containing 15.38 mol% and 17.65 mol% MoO_3 in the initial mixtures were, in addition, heated for 3 h at 590 °C and then rapidly cooled to ambient temperature. X-ray powder diffraction of the preparations obtained in this way showed that their compositions are not essentially different from those of the slowly cooled samples at equilibrium. However, the intensity of the diffraction lines characterising $Cr_2V_4O_{13}$(ss) was increased, whereas the intensity of the reflections characterising the $CrVMoO_7$ phase was decreased. This indicates that the solubility of MoO_3 in $Cr_2V_4O_{13}$ is slightly higher at 590 °C than at ambient temperature and does not exceed 17.65 mol% in the initial mixture.

Three endothermic effects were recorded in the DTA curves of the preparations at equilibrium. With monophase preparations, i.e. containing up to 15.38 mol% MoO_3 in the initial mixtures, the effects recorded were analogous with those observed in the DTA curve of pure $Cr_2V_4O_{13}$, the matrix solution (Fig. 1). It has been found from published investigations [6], that the $Cr_2V_4O_{13}$ phase is stable only up to 640 °C (below the melting point) at which temperatures it starts to decompose in the solid state

$$Cr_2V_4O_{13}(s) \rightarrow CrVO_4(s) + V_2O_5(s) \qquad (1)$$

The decomposition products form a eutectic mixture melting as low as at 650 °C [6], although the initial velocity of the decomposition is not high and the $Cr_2V_4O_{13}$ which has not decomposed melts incongruently at 740 °C. This

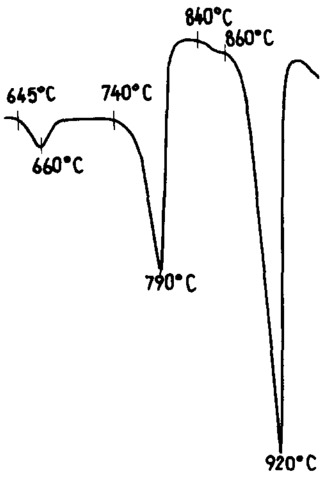

Fig. 1. The DTA curve of $Cr_2V_4O_{13}$(s.s.) containing 11.11 mol% MoO_3 in the initial mixture.

is confirmed by the second thermal effect recorded in the DTA curve (Fig. 1).

$$Cr_2V_4O_{13}(s) \rightarrow CrVO_4(s) + \text{liquid} \qquad (2)$$

The third thermal effect is related to the melting of $CrVO_4$, the solid product of reaction (2).

With $Cr_2V_4O_{13}$(s.s.), as well as $CrVO_4$(s) and V_2O_5(s), free MoO_3 appears in the decomposition products. However, this molybdenum(VI) oxide can also form a solid solution with V_2O_5 by being incorporated into its crystal lattice [11,12]. The solubility limit of MoO_3 in V_2O_5 is considerable; according to Bielański and Najbar, it is 30 mol% [11]. Hence, the decomposition of $Cr_2V_4O_{13}$(s.s.) seems to involve the formation of another solid solution, i.e. of MoO_3 in V_2O_5, as well as $CrVO_4$. However, this could not be confirmed experimentally due to the very small temperature range in which the areas comprising V_2O_5(s.s.), one of the stable equilibrium phases, occur.

In preparations whose X-ray powder diffraction pattern has shown that at equilibrium up to 640 °C two phases remain, i.e. $Cr_2V_4O_{13}$(s.s.) and $CrVMoO_7$, $Cr_2V_4O_{13}$(s.s.) is responsible for the first two effects; on the other hand, the third unsymmetrical effect is related to the incongruent melting of $CrVMoO_7$ [3]

$$CrVMoO_7(s) \rightarrow Cr_2O_3(s) + \text{liquid} \qquad (3)$$

Figure 2 shows a phase diagram of the $Cr_2V_4O_{13}$–$CrVMoO_7$ system. The ranges of coexistence of solid phases with liquid have been determined on the basis of the thermal effects recorded on the DTA curves, whereas the phases remaining at equilibrium with liquid were established experimentally: samples chosen from particular diagram areas were, in addition, heated for 3 h at 600 °C, 700 °C, 720 °C, 750 °C, 800 °C, 850 °C, 900 °C and 950 °C, then cooled rapidly to ambient temperature and analysed by X-ray powder diffraction. The compositions of samples subjected to such an examination are marked on the diagram (Fig. 2).

It follows from the phase diagram that $Cr_2V_4O_{13}$–$CrVMoO_7$ is a real two-component system over the entire component concentration range until the decomposition temperature of $Cr_2V_4O_{13}$(s.s.), i.e. up to 640 °C. The range of existence of solid solution at ambient temperature is at least 15.38 mol% MoO_3 in the initial mixture. Above 640 °C, $Cr_2V_4O_{13}$(s.s.) ceases to be a thermodynamically stable phase and, at equilibrium in the solid state in a very small temperature range, either the products of its decomposition ($CrVO_4$(s) and V_2O_5(s.s.) or three solid phases ($CrVO_4$(s), V_2O_5(s.s.) and $CrVMoO_7$(s)) remain. Both $CrVO_4$ and $CrVMoO_7$ melt incongruently and Cr_2O_3, being a solid product of both reactions, finally remains at equilibrium with the liquid (Fig. 2).

The experimental results could not always precisely fix the existence range for all areas, because of the small temperature ranges within which they are

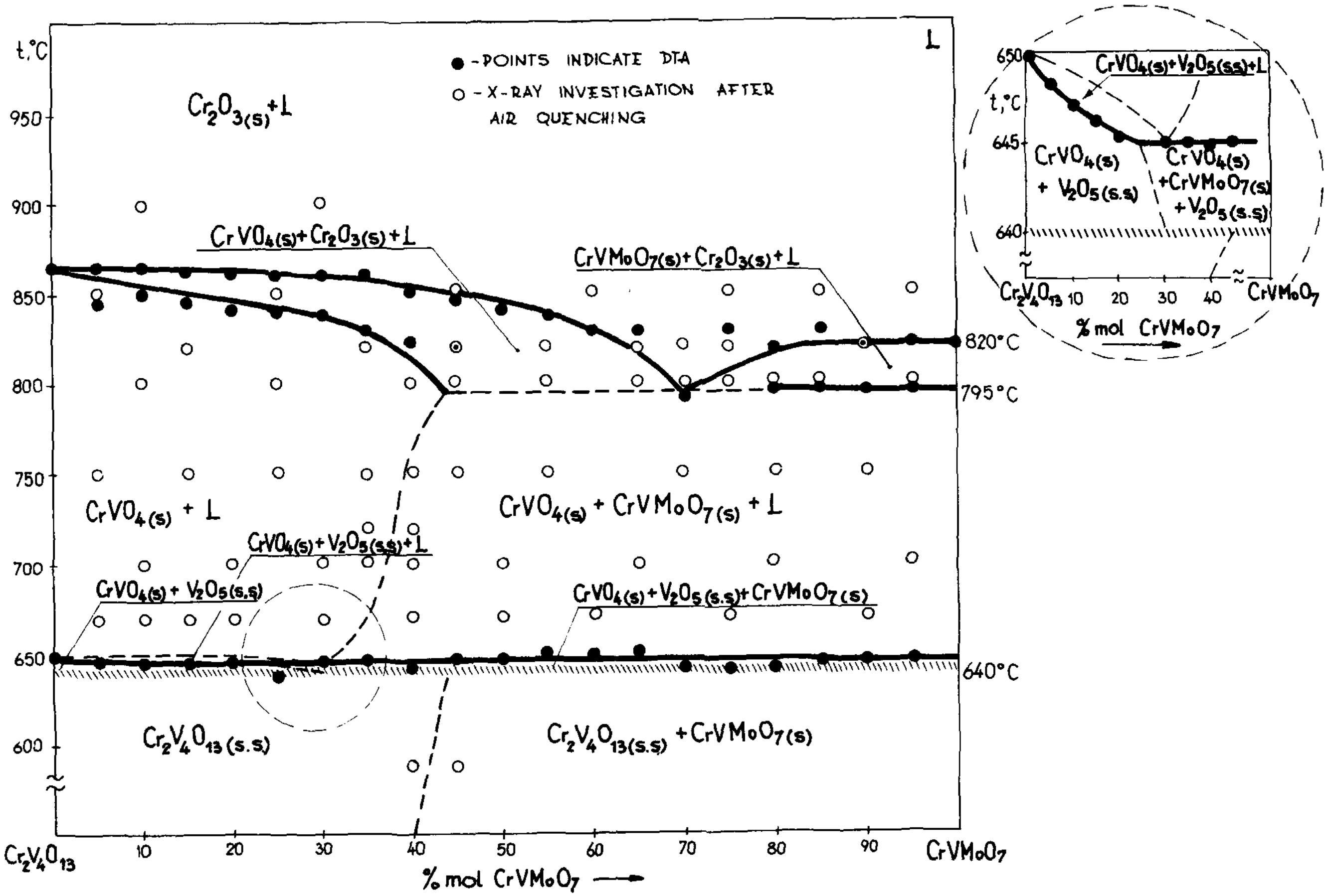

Fig. 2. Phase diagram of the $Cr_2V_4O_{13}$–$CrVMoO_7$ system.

confined. Nevertheless, the position of neighbouring areas and the results of our other investigations [3,6,13] enable the extent of these areas to be deduced. The curves outlining these areas are marked in the diagram with dotted lines.

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