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Studies on the $V_9Mo_6O_{40}$–Cr_2O_3 system

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Abstract

The phase equilibria established in the $V_9Mo_6O_{40}$–Cr_2O_3 system over the whole component concentration range up to 1000°C have been studied by differential thermal analysis and X-ray diffractometry. The results provide a basis for the construction of a phase diagram of the system investigated.

Keywords: Binary system; DTA; Melting; Phase equilibrium, Ternary system; XRD

1. Introduction

The $V_9Mo_6O_{40}$–Cr_2O_3 system is one of the sections of the Cr_2O_3–V_2O_5–MoO_3 system. $V_9Mo_6O_{40}$ is a compound occurring in the V_2O_5–MoO_3 system which is one of the three two-component systems forming the three-component system. $V_9Mo_6O_{40}$, widely known for its catalytic properties, has stimulated considerable interest [1–6]. $V_9Mo_6O_{40}$ crystallizes in a monoclinic system [2,3] and melts congruently at a temperature that we have measured as 640 ± 10°C, while according to other investigators the melting temperature of $V_9Mo_6O_{40}$ oscillates between 635 and 677°C [1,4–6]. Its density is $3.86\ \mathrm{g\ cm^{-3}}$ [5].

In addition to $V_9Mo_6O_{40}$, the components of the V_2O_5–MoO_3 system also form a substitution solid solution of MoO_3 in V_2O_5 [4,7,8].

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The properties and the structure of chromium(III) oxide, the second component of the system under study, are known. Cr_2O_3 crystallizes in a rhombohedric system and melts congruently. The published melting temperatures of Cr_2O_3 are characterized by considerable scattering, 1990–2435°C [2,9,10]. Cr_2O_3 reacts with V_2O_5 to yield two compounds, $CrVO_4$ amd $Cr_2V_4O_{13}$, in the third two-component system, Cr_2O_3–V_2O_5 [11]. $CrVO_4$ melts incongruently at 865°C to give Cr_2O_3, a product of the melting process. However, $Cr_2V_4O_{13}$ decomposes in the solid phase to produce $CrVO_4$ and V_2O_5 [11]. Chromium(III) oxide also reacts with MoO_3 to form $Cr_2(MoO_4)_3$, the only compound formed in the Cr_2O_3–MoO_3 system. In the solid state at 810°C, chromium(III) molybdate decomposes to oxides, concurrent with the sublimation of MoO_3 [12].

At ambient temperature, molybdenum(VI) oxide forms a solid solution with $Cr_2V_4O_{13}$ with a solubility limit of 15.38 mol% of MoO_3. Such a solution is stable up to about 640°C, i.e. to the decomposition temperature of the $Cr_2V_4O_{13}$ matrix [13]. The components of the three component Cr_2O_3–V_2O_5–MoO_3 system react to form $CrVMoO_7$ [14] which crystallizes in a triclinic system and melts incongruently at 820 ± 5°C [14,15]. The solid product of the $CrVMoO_7$ melting is Cr_2O_3. $CrVMoO_7$ remains inert towards $V_9Mo_6O_{40}$ up to 600°C. This has been demonstrated by studying the phase equilibria established in the $V_9Mo_6O_{40}$–$CrVMoO_7$ system [15].

There is no information concerning the behaviour of Cr_2O_3 towards $V_9Mo_6O_{40}$. Thus, the aim of this work is to construct a phase equilibrium diagram for the $V_9Mo_6O_{40}$–Cr_2O_3 system up to 1000°C. Such a diagram has not yet been determined for this temperature range. In our previous works, we merely presented the phase equilibria established in this system in the solid state [16].

2. Experimental

Analytically pure V_2O_5, obtained commercially (POCh, Gliwice, Poland), 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 also being roasted at 1000°C for 72 h. X-ray powder diffraction analysis on the preparations obtained by this method showed only MoO_3 and Cr_2O_3, respectively.

Twenty samples were prepared to investigate the phase equillibria established in the $V_9Mo_6O_{40}$–Cr_2O_3 system over the component concentration range present up to 100°C. Mixtures of oxides of the given compositions were homogenized by grinding, shaped into pastilles and heated under conditions that ensured that the preparations were obtained at equilibrium. Thus, at up to 72.50 mol% Cr_2O_3 in terms of the components of the system under study, the samples were heated as follows: 500°C (48h) → 550°C (48 h) → 570°C (24 h) → 570°C (24 h) → 570°C (24 h). Samples consisting of 75.00–81.00 mol% Cr_2O_3 were heated in the following way: 500°C (48 h) → 550°C (48 h) → 570°C (24 h) → 590°C (24 h) → 610°C (24 h) → 610°C (24 h). In the other component concentration range, the samples were heated in the cycles: 500°C (48 h) → 550°C (48 h) → 570°C (24 h) → 570°C (48 h) → 650°C (24 h) → 700°C (24 h).

Such preparation conditions were established by screening tests which determined that after the given heating cycles the preparations achieved the equilibrium state. Equilibrium was demonstrated by X-ray phase powder diffractiometry of selected samples after two successive heating cycles. Identical results confirmed that equilibrium had been attained. Samples comprising in their initial mixtures the following amounts of Cr_2O_3 in terms of the components of the $V_9Mo_6O_{40}$–Cr_2O_3 system were subjected to screening tests: 50.00, 75.00, 80.00, 85.00 and 90.00 mol%, respectively.

Differential thermal analysis (DTA) was carried out using a Paulik–Paulik–Erdey (MOM Budapest) derivatograph in the range 20–1000°C. The samples (1000 mg) were each heated at a constant rate of $10\ K\ min^{-1}$.

Diffraction patterns of the preparations were made using an HZG-4/A_2 diffractometer and Co Kα radiation. The phase compositions of the preparations were established by X-ray phase analysis, from data listed in the PDF index cards [17] and from published data [1,11,14].

In constructing a phase diagram, the solidus lines were fixed using the onset temperatures of the first effects recorded on the DTA curves of preparations at equilibrium. The liquidus lines were drawn when possible, from the onset temperature of the successive effects, and, in other cases, from the nodes of those effects. The accuracy of the temperature reading, fixed by repetition, was ±5°C. The types of phases remaining at equilibrium with the liquid were established by a further heating of selected equilibrium samples for 3 h at 600, 610, 625, 650, 700, 750, 810, 850 and 900°C, the samples then being cooled rapidly to ambient temperature and then analyzed by XRD.

3. Results and discussion

The experimental results are presented in the form of a phase equilibria diagram for the system under consideration in Fig. 1 which also includes components of the samples heated further and cooled rapidly to ambient temperature.

The diagram shows that Cr_2O_3 does not remain in permanent equilibrium with $V_9Mo_6O_{40}$, not even in the sub-solidus area. X-ray phase powder diffractometry of the equilibrium preparations, which contained in their initial mixtures up to 72.50 mol% Cr_2O_3 in terms of the components of the system of interest, has shown that the preparations are mixtures of three phases: $V_9Mo_6O_{40}$, $CrVMoO_7$ and V_2O_5(s.s). This shows that Cr_2O_3 with this content limit reacts totally to $CrVMoO_7$, and that MoO_3, despite reaction with $CrVMoO_7$ leading to $V_9Mo_6O_{40}$, is incorporated in the crystal lattice resulting in a substitution solid solution. A preparation with 72.50 mol% Cr_2O_3 and 27.50 mol% $V_9Mo_6O_{40}$ in the equilibrium state is diphasic and contains, in addition to $CrVMoO_7$, a solid solution of MoO_3 in V_2O_5 (Fig. 1).

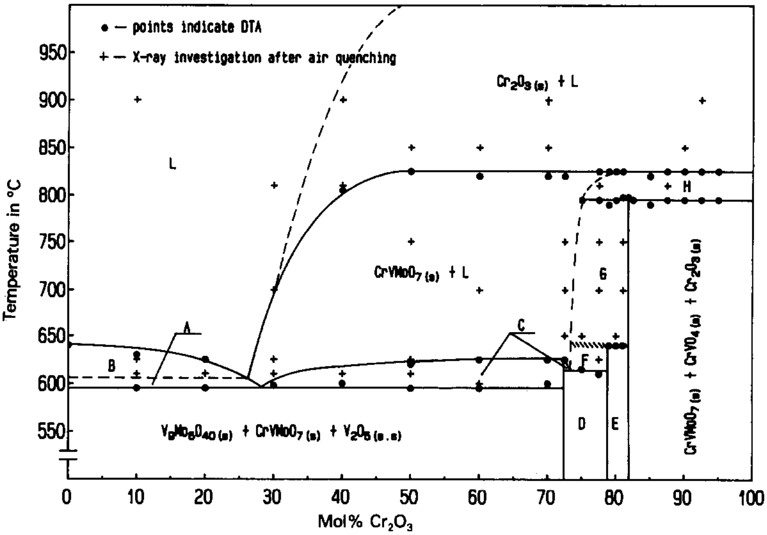

Fig. 1. The phase diagram of the $V_9Mo_6O_{40}$–Cr_2O_3 system: A, $V_9Mo_6O_{40}(s) + CrVMoO_7(s) + L$; B, $V_9Mo_6O_{40}(s) + L$; C, $CrVMoO_7(s) + V_2O_5(s.s.) + L$; D, $CrVMoO_7(s) + V_2O_5(s.s.) + Cr_2V_4O_{13}(s.s.)$; E, $CrVMoO_7(s) + Cr_2V_4O_{13}(s.s) + CrVO_4(s)$; F, $CrVMoO_7(s) + Cr_2V_4O_{13}(s.s.) + L$; G, $CrVMoO_7(s) + CrVO_4(s) + L$; H, $CrVMoO_7(s) + Cr_2O_3(s) + L$.

In preparations comprising greater than 72.50 mol% of Cr_2O_3, in addition to V_2O_5 and V_2O_5(s.s.), a solid solution of MoO_3 in $Cr_2V_4O_{13}$ appears as a stable phase. The three phases remain in mutual equilibrium only to 78.95 mol% content of Cr_2O_3. A preparation comprising 78.95 mol% contains two phases at equilibrium, $CrVMoO_7$ and $Cr_2V_4O_{13}$(s.s.). Further increase in the Cr_2O_3 content leads to chromium(III) orthovanadate, a phase which is at equilibrium. At this component concentration range, namely up to 81.82 mol%, there are phases that remain at equilibrium: $CrVMoO_7$, $Cr_2V_4O_{13}$(s.s.) and $CrVO_4$. A sample comprising in its initial mixture 82.82 mol% Cr_2O_3 in tests of the components of the system of interest, is a mixture of two phases, in the equilibrium state, namely $CrVMoO_7$ and $CrVO_4$.

Over the other component concentration range of the $V_9Mo_6O_{40}$–Cr_2O_3 system, there are three phases at equilibrium in the solid state: $CrVMoO_7$, $CrVO_4$ and Cr_2O_3.

Above the solidus line, in appropriate fields of the phase diagram, the presence of the solid phases coexisting with liquid has not been determined over the component concentration range in the sub-solidus area. Accordingly, $CrVO_4$ is one of the decomposition products of $Cr_2V_4O_{13}$(s.s.). Decomposition of the solid solution of MoO_3 in $Cr_2V_4O_{13}$ starts at a very low rate at the decomposition temperature of the solution matrix, i.e. at 640°C [11]. The very small decomposition rate for $Cr_2V_4O_{13}$(s.s.) has made it impossible to confirm the process by X-ray analysis of the preparations which contained $Cr_2V_4O_{13}$(s.s.) at equilibrium, on further heating at 650°C and rapid cooling to ambient temperature.

The presence of Cr_2O_3, a phase remaining at equilibrium with the liquid, results from the incongruent melting of $CrVMoO_7$ and $CrVO_4$, and also because the oxide remains at equilibrium with the compounds (Fig. 1).

Because of a very narrow temperature range, it was impossible to determine experimentally the existence range for the $V_9Mo_6O_{40}(s) + CrVMoO_7(s) +$ liquid field. Likewise, the fragment of the $CrVMoO_7(s) + V_2O_5(s) +$ liquid field lying on the right of the two-component preparation with 72.50 mol% Cr_2O_3 has not been proved experimentally due to both the very small temperature range of its existence and the narrow concentration interval of the components of the $V_9Mo_6O_{40}$–Cr_2O_3 system in which the field exists. However, the existence of the fields is accounted for by the position of the adjacent fields, that undoubtedly occur in the $V_9Mo_6O_{40}$–Cr_2O_3 system. Therefore, the curves bordering those fields have been marked by a dotted line on the phase diagram.

4. Conclusions

The phase diagram shows that the $V_9Mo_6O_{40}$–Cr_2O_3 system (Fig. 1) is not a real two-component system over the whole component concentration range, not even in the sub-solidus area. This is supported by the presence of fields in the area in which three solid phases remain at equilibrium.

The presented phase diagram of the $V_9Mo_6O_{40}$–Cr_2O_3 system confirms the results of our previous studies on the phase equilibria established in the following systems V_2O_5–$CrVMoO_7$ [18], $V_9Mo_6O_{40}$–$CrVMoO_7$ [15], $Cr_2V_4O_{13}$–$CrVMoO_7$ [13], $CrVO_4$–MoO_3 [14] and $CrVO_4$–$Cr_2(MoO_4)_3$ [12]. Fig. 2 shows the position of

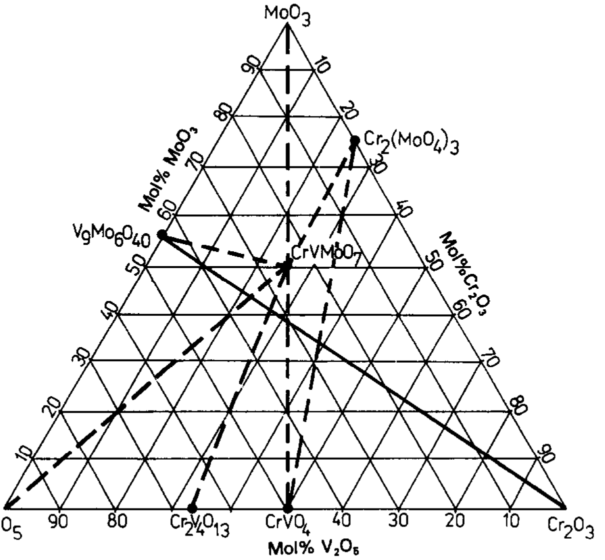

Fig. 2. Component concentration triangle of the Cr_2O_3–VO_5–MoO_3 system: – – –, sections studied previously; —, $V_9Mo_6O_{40}$–Cr_2O_3 section.

the $V_9Mo_6O_{40}$–Cr_2O_3 section on the component concentration triangle of the Cr_2O_3–V_2O_5–MoO_3 system. Sections of previously investigated systems are also marked.

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