PHASE EQUILIBRIA IN THE SOLID STATE IN THE $V_9Mo_6O_{40}$-Cr_2O_3 SYSTEM

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Phase equilibria have been established in the solid state in the $V_9Mo_6O_{40}$-Cr_2O_3 system. The results obtained have permitted to state that the system of interest, in the subsolidus area, is not a real two-component system in the whole component concentration range.

Introduction

$V_9Mo_6O_{40}$, a compound existing in the V_2O_5-MoO_3 system is well known, first of all, for its catalytic properties [1]. These properties account for an exhaustive study of the system [1–6]. The other component of the system under study – Cr_2O_3 is a well-known catalyst, too [7]. No reliable information on the behaviour of Cr_2O_3 towards $V_9Mo_6O_{40}$ has been found in the available literature so far, and this has induced us to undertake a study on the system. It seemed interesting to find out, in the first place, what kind of phase remains at equilibrium in the solid state in the $V_9Mo_6O_{40}$-Cr_2O_3 system.

$V_9Mo_6O_{40}$ crystallizes in the monoclinic system [2, 3] and, structurally, it belongs to a homologous series, M_nO_{3n-1} [2]. In that phase, 1/9 of the vanadium atoms occur in the form of V^{4+} [4]. $V_9Mo_6O_{40}$ melts congruently, its melting point, as given by different authors, is within the range 635°–677°C [1, 4–6]. According to our findings, $V_9Mo_6O_{40}$ melts at 640°±10°C. Its density is 3.86 g/cm^3 [5]. The components of the V_2O_5-MoO_3 system, beside $V_9Mo_6O_{40}$, form, as well, an α phase, iso-structural with V_2O_5 and being a substitution solid solution of MoO_3 in V_2O_5, with a general formula $(V_{1-x}Mo_x)_2O_5$, where $0 < x < 0.3$ [4, 8, 9].

The properties and structure of chromium(III) oxide are known well, too. Cr_2O_3 crystallizes in the rhombohedral system, it is isomorphous with α-Al_2O_3

and forms solid solutions with the latter. It, too, is a compound melting congruently. The melting temperatures published for Cr_2O_3 are rather scattered, from 1990° to 2435°C [2, 11, 12]. The oxide reacts with V_2O_5 to form two compounds, $CrVO_4$ and $Cr_2V_4O_{13}$. $CrVO_4$ melts incongruently at 865°C, whereas $Cr_2V_4O_{13}$ is decomposed in the solid phase into $CrVO_4$ and V_2O_5 at 640°C [13]. Cr_2O_3 reacts with MoO_3, giving rise to $Cr_2(MoO_4)_3$ to be decomposed in the solid state into oxides with simultaneous sublimation of MoO_3 [14]. The decomposition starts at 810°C.

The components of the Cr_2O_3-V_2O_5-MoO_3 system have the ability to form a solid solution in which the matrix is $Cr_2V_4O_{13}$ whereas MoO_3 is incorporated into the crystal lattice of the compound in the place of V^{5+}. The charge compensation takes place, in all probability, through reduction of an equivalent number of Cr^{3+} ions to Cr^{2+}, thus the formation of phases of the type

$$Cr_{2-x}^{3+}Cr_x^{2+}V_{4-x}Mo_xO_{13}, \text{ where } 0.500 < x_{max} < 0.581 \text{ [15]}$$
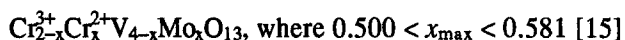
can be accounted for.

The system components react with each other to yield $CrVMoO_7$ – a compound melting incongruently at 820°C [16].

Experimental

In order to study phase equilibria being established in the $V_9Mo_6O_{40}$-Cr_2O_3 system, 20 samples of oxides with compositions corresponding to the whole component concentration range were prepared (Table 1). The oxide mixtures with the given composition were homogenized by grinding, then pelletized and calcined under conditions depending on the Cr_2O_3 content in the samples. Thus, up to a content of 72.50 mol% of Cr_2O_3 in terms of the components of the system under investigation, the samples were heated as follows:

500°C (48 h) → 550°C (48 h) → 570°C (24 h) → 570°C (48 h) → 570°C (24 h).

On the other hand, samples containing $75.00 - 81.00$ mol% of Cr_2O_3 were heated as follows:

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 other ranges of the component concentration, the samples were heated in the following 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).

These conditions of preparation were established in preliminary studies, which revealed that after the heating cycles assumed, the preparations achieved

the equilibrium state. During the preliminary study, after each heating cycle, a mass loss check was made, yet no substantial change in the weight of the samples was found and consequently record of it was relinquished in the main investigations. Samples subjected to preliminary studies contained in their initial mixtures: 50.00; 75.00; 80.00; 85.00 and 90.00 mol% of Cr_2O_3 in terms of the components of the system.

Table 1 The $V_9Mo_6O_{40}$-Cr_2O_3 system
Results from the X-ray phase analysis of samples at equilibrium and their colours

No	The Cr_2O_3 content/ mol%	The phases found[*]	Colour
1	2	3	4
1	10.00	$V_9Mo_6O_{40}$, $CrVMoO_7$, $V_2O_{5(s.s.)}$ – v. little	of graphite
2	20.00	$V_9Mo_6O_{40}$, $CrVMoO_7$, $V_2O_{5(s.s.)}$ – v. little	of graphite
3	30.00	$V_9Mo_6O_{40}$, $CrVMoO_7$, $V_2O_{5(s.s.)}$	brown
4	40.00	$CrVMoO_7$, $V_9Mo_6O_{40}$, $V_2O_{5(s.s.)}$	brown
5	50.00	$CrVMoO_7$, $V_9Mo_6O_{40}$, $V_2O_{5(s.s.)}$	dark olive
6	60.00	$CrVMoO_7$, $V_9Mo_6O_{40}$, $V_2O_{5(s.s.)}$	dark olive
7	70.00	$CrVMoO_7$, $V_2O_{5(s.s.)}$, $V_9Mo_6O_{40}$	brown-olive
8	72.50	$CrVMoO_7$, $V_2O_{5(s.s.)}$	brown-olive
9	75.00	$CrVMoO_7$, $V_2O_{5(s.s.)}$, $Cr_2V_4O_{13(s.s.)}$	brown-olive
10	77.50	$CrVMoO_7$, $Cr_2V_4O_{13(s.s.)}$, $V_2O_{5(s.s.)}$	brown-olive
11	78.95	$CrVMoO_7$, $Cr_2V_4O_{13(s.s.)}$	yellow-brown
12	80.00	$CrVMoO_7$, $Cr_2V_4O_{13(s.s.)}$, $CrVO_4$ – little	yellow-brown
13	81.00	$CrVMoO_7$, $CrVO_4$, $Cr_2V_4O_{13(s.s.)}$	yellow-brown
14	81.82	$CrVMoO_7$, $CrVO_4$	yellow-brown
15	82.50	$CrVMoO_7$, $CrVO_4$, Cr_2O_3 – little	brown-olive
16	85.00	$CrVMoO_7$, $CrVO_4$, Cr_2O_3	brown-olive
17	87.50	$CrVMoO_7$, $CrVO_4$, Cr_2O_3	brown-olive
18	90.00	$CrVMoO_7$, Cr_2O_3, $CrVO_4$	olive
19	92.50	$CrVMoO_7$, Cr_2O_3, $CrVO_4$	green-olive
20	95.00	$CrVMoO_7$, Cr_2O_3, $CrVO_4$	green

* The sequence of recording the phases results from their decreasing contents in a given sample.

Differential thermal analysis (DTA) of the samples at equilibrium was accomplished with a derivatograph of F. Paulik-J. Paulik-L. Erdey type (MOM Budapest) in the temperature range 20°–1000°C.

X-ray powder diffraction studies were made with the aid of a diffractometer HZG-4/A$_2$ using a cobalt tube as a source of radiation. X-ray phase analysis was made using data included in the ASTM cards [17] and in references [1, 13, 16].

Results and discussion

Table 1 shows the results of the X-ray phase analysis of all the preparations being at equilibrium as well as their colours. The results indicate that Cr$_2$O$_3$ does not remain at permanent equilibrium with V$_9$Mo$_6$O$_{40}$. X-ray phase analysis of preparations containing up to 72.50 mol% of Cr$_2$O$_3$, in terms of components of the system under study, has shown that the preparations were a mixture of three phases, i.e. V$_9$Mo$_6$O$_{40}$, CrVMoO$_7$ and V$_2$O$_{5(s.s.)}$, respectively. It implies that Cr$_2$O$_3$ with contents up to 72.50 mol% reacts to completion yielding CrVMoO$_7$, while excessive MoO$_3$, besides forming the compound, V$_9$Mo$_6$O$_{40}$ in a reaction with V$_2$O$_5$, is incorporated in the V$_2$O$_5$ lattice to form a solid solution. It means that V$_9$Mo$_6$O$_{40}$ is a phase which remains at permanent equilibrium with CrVMo-O$_7$ and V$_2$O$_{5(s.s.)}$ only in that concentration range.
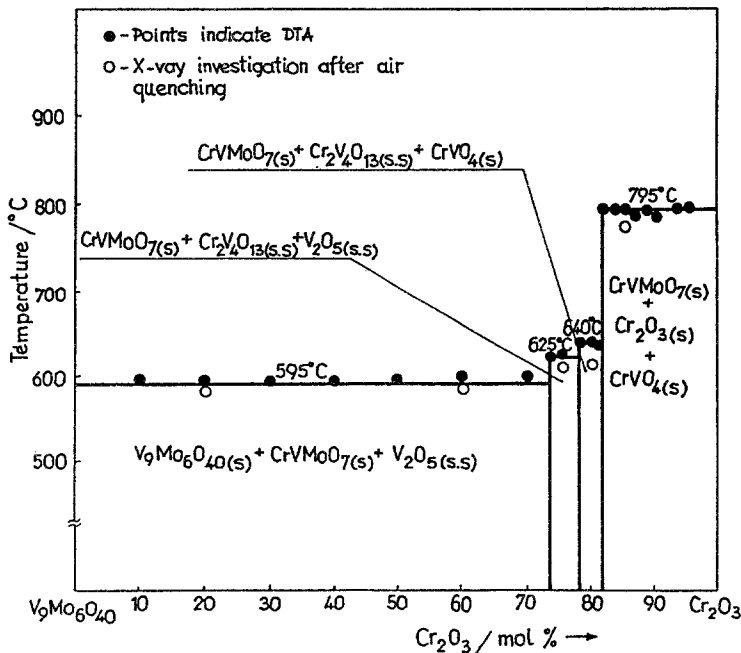
Fig. 1 Diagram of phase equilibria at the solid state in the V$_9$Mo$_6$O$_{40}$-Cr$_2$O$_3$ system

In preparations containing above 72.50 mol% of Cr_2O_3 there appears, beside $CrVMoO_7$ and $V_2O_{5(s.s.)}$ as a stable phase, a solid solution of MoO_3 in $Cr_2V_4O_{13}$. The three phases remain at equilibrium only at Cr_2O_3 contents up to 78.95 mol%.

Further increase in the Cr_2O_3 content in the system leads to $CrVO_4$ as a phase being at equilibrium. In that component concentration range, i.e. to 81.82 mol% of Cr_2O_3, the following phases remain at equilibrium: $CrVMoO_7$, $Cr_2V_4O_{13(s.s.)}$ and $CrVO_4$, respectively.

In the other component concentration range, i.e. above 81.82 mol% of Cr_2O_3 it is $CrVMoO_7$, $CrVO_4$ and Cr_2O_3 that remain at permanent equilibrium.

Figure 1 shows phase equilibria being established in the solid state in the $V_9Mo_6O_{40}$-Cr_2O_3 system. The temperature range of subsolidus area has been established on the basis of the onset temperature of the first effect recorded on the DTA curves of the preparations at equilibrium. For further confirmation of the existence range of the subsolidus area, the samples at equilibrium with 20.00; 60.00; 75.00; 80.00 and 85.00 mol% of Cr_2O_3 were additionally heated for 3 hours at a temperature somewhat lower than the temperature of the solidus line to be suddenly quenched to ambient temperature. The phase composition of the preparations obtained in this way did not deviate from the phase composition of samples being at equilibrium, gradually cooled to ambient temperature.

The experimental results show that the system $V_9Mo_6O_{40}$-Cr_2O_3, in the subsolidus area, is not a real two-component system in the whole component concentration range. This fact is confirmed by the presence of fields in the area in which three solid phases remain at equilibrium.

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Zusammenfassung — Im Festzustand des Systemes $V_9Mo_6O_{40}$-Cr_2O_3 wurden Phasengleichgewichte ermittelt. Die erhaltenen Resultate lassen darauf schließen, daß das fragliche System im Subsolidus-Gebiet über den gesamten Konzentrationsbereich kein reelles Zweikomponentensystem ist.