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SUBSOLIDUS PHASE EQUILIBRIA IN THE SYSTEM $AlVO_4$–MoO_3

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Abstract

The phase equilibria in the solid state in the system $AlVO_4$–MoO_3 were determined by DTA and XRD methods. The experimental results are presented in the form of a phase diagram. In the subsolidus area, the system $AlVO_4$–MoO_3 is a real two-component system only within the range $AlVO_4$–$AlVMoO_7$.

Keywords: phase equilibria, system $AlVO_4$–MoO_3

Introduction

Studies on the three-component system Al_2O_3–V_2O_5–MoO_3, not investigated so far, have shown that the components of the system in the solid state form a hitherto unknown compound, $AlVMoO_7$ [1]. The compound was obtained from a reaction between MoO_3 and $AlVO_4$, a compound existing in one of the two-component systems forming the system Al_2O_3–V_2O_5–MoO_3, i.e. the system Al_2O_3–V_2O_5 [1]. Accordingly, it seemed useful to undertake studies on the phase equilibria in the solid state in a binary section of the three-component system in which the compound $AlVMoO_7$ occurs, i.e. the system $AlVO_4$–MoO_3.

The properties and structures of the components of the system are known. $AlVO_4$ crystallizes in the triclinic system, with spatial group $P\bar{1}$. It does not exhibit polymorphism at ambient pressure. $AlVO_4$ melts incongruently to give solid Al_2O_3. It has been reported to melt at 695°C [2], 700°C [3], 760°C [4], and 775°C [5]. Our own finding for the melting temperature of $AlVO_4$ was 745±5°C. MoO_3 has orthorhombic symmetry [6]. Crystals of MoO_3 melt congruently at 795°C [7].

Experimental

The following reagents were used for the experiments: V_2O_5, p.a. (POCh, Gliwice, Poland); Al_2O_3, p.a., a commercial amorphous product; and MoO_3, obtained by thermal decomposition of $(NH_4)_6Mo_7O_{24}\cdot4H_2O$, at 150–450°C in

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air. $AlVO_4$ and $AlVMoO_7$, obtained separately, were used as reagents too. $AlVO_4$ was prepared by calcination an equimolar mixture of Al_2O_3 and V_2O_5 at 600°C for 72 h and at 650°C in two cycles for 48 h. $AlVMoO_7$ was obtained from a mixture of Al_2O_3, V_2O_5 and MoO_3 at the 1:1:2 molar ratio, by heating at 550°C for 72 h and then at 600°C for 48 h.

DTA was performed with Paulik-Paulik-Erdey derivatograph (MOM, Budapest), in quartz crucibles, in air, at 20–1000°C, at a heating rate of 10 $\text{deg}\cdot\text{min}^{-1}$. The mass of each sample was 1000 mg. A phase diagram was constructed, and the solidus line temperatures were determined via the DTA effect onset temperatures. The accuracy of reading established by repetition of measurements was ±5 deg.

The phase compositions of preparations were determined by X-ray diffraction (DRON-3 diffractometer, CoK_α), using the data listed in PDF cards [8] and in publications [1, 5, 9, 10].

The experiments were carried out with a basic series of 20 samples prepared from the oxides, and from a verification series composed of 5 samples; four verification samples were made from $AlVO_4$ and $AlVMoO_7$ and one from $AlVMoO_7$ and MoO_3. The compositions of the basic series samples are listed in the Table. The reagents, weighed in suitable proportions, were ground, shaped into pastilles and then heated under conditions optimal for establishment of the equilibrium state. The conditions for equilibrium were established in preliminary tests with three samples initially containing 30.00, 60.00 and 80.00 mol% of MoO_3, in terms of the system components $AlVO_4$ and MoO_3. All the samples made from the oxides were heated at 500°C for 24 h, then at

Table 1 The composition of initial mixtures, the conditions of preparation and results of XRD analysis for samples in the equilibrium state

Preparation conditions	MoO_3 concentration in the initial mixtures / mol%	Phases detected
500°C (24 h)+ 550°C (48 h)+ 570°C (72 h)+ 600°C (72 h)+	5.0, 10.0, 15.0, 20.0, 25.0, 30.0, 35.0, 40.0, 45.0	$AlVO_4$, $AlVMoO_7$
	50	$AlVMoO_7$
500°C (24 h)+ 550°C (48 h)+ 570°C (72 h)+	55.0, 60.0, 65.0	$AlVMoO_7$, $Al_2(MoO_4)_3$ $V_9Mo_6O_{40}$
	68.48	$Al_2(MoO_4)_3$, $V_9Mo_6O_{40}$
	70.0, 75.0, 80.0 85.0, 90.0, 95.0	$Al_2(MoO_4)_3$, $V_9Mo_6O_{40}$ MoO_3

550°C for 48 h and finally at 570°C for 72 h. The samples whose initial mixtures contained over 50 mol% of $AlVO_4$ were additionally heated at 600°C for 72 h. The preparations obtained were slowly cooled to ambient temperature, ground and afterwards examined for their phase composition and by DTA. In this way, the natures of the resultant phases and the range of their coexistence in the subsolidus area were established.

Results and discussion

The Table shows the compositions of the initial mixtures, the conditions of synthesis and the results of XRD analysis for all the preparations. The results in the Table imply that MoO_3 does not remain in equilibrium with $AlVO_4$. XRD analysis of preparations initially containing 5.0 to 45.0 mol% of MoO_3 reveals a mixture of two phases: $AlVO_4$ and $AlVMoO_7$. MoO_3 contents of up to 45.00 mol% react with $AlVO_4$ to completion to yield $AlVMoO_7$. Only in this concentration range is $AlVO_4$ a phase coexisting with $AlVMoO_7$. It also suggests a reaction leading to $AlVMoO_7$ in the system:

$$AlVO_{4(s)}+MoO_{3(s)}=AlVMoO_{7(s)} \tag{1}$$

The phase composition of a preparation made from an initial mixture containing 50 mol% of MoO_3 implies that the reaction between MoO_3 and $AlVO_4$ goes to completion, giving $AlVMoO_7$. This means that reaction (1) is quantitative when the molar ratio of $AlVO_4$ to MoO_3 is 1:1.

The phase composition of the subsolidus $AlVO_4$–MoO_3 area in the component concentration range up to 50 mol% of MoO_3 was ascertained by preparing an additional four mixtures from $AlVO_4$ and $AlVMoO_7$, corresponding to MoO_3 contents of 10.0, 20.0, 30.0 and 40.0 mol%. The mixtures were heated at 650°C for 72 h, rapidly cooled to ambient temperature, and examined in respect of their phase composition. X-ray phase diffraction showed that, in spite of calcination for many hours at a temperature merely 15 deg lower than the solidus line temperature, the phase composition of the verification samples remained unchanged, i.e. $AlVO_4$ and $AlVMoO_7$ could be detected in the samples. This implies that, in the range up to 50 mol% MoO_3, $AlVO_4$ and $AlVMoO_7$ remain in equilibrium in the subsolidus area.

In preparations formed from initial mixtures containing over 50.0 mol% of MoO_3, i.e. whenever they contained excess MoO_3 in comparison with that required by reaction (1), two further solid phases appeared: $Al_2(MoO_4)_3$ and $V_9Mo_6O_{40}$. This phase composition may be indicative of the following reaction in the system:

$$18AlVMoO_{7(s)}+21MoO_{3(s)}=9Al_2(MoO_4)_{3(s)}+2V_9Mo_6O_{40(s)}+1/2O_2\uparrow \tag{2}$$

Reaction (2) accounts for the coexistence of three phases in the solid state: $AlVMoO_7$, $Al_2(MoO_4)_3$ and $V_9Mo_6O_{40}$.

Reaction (2) is quantitative at 68.48 mol% of MoO_3 in terms of the components of the system $AlVO_4$–MoO_3. The quantitative course of the reaction can be accounted for by the phase composition of the preparation obtained from the oxide mixture comprising 68.48 mol% of MoO_3 and by that of the verification sample prepared by calcination a 6:7 mixture of $AlVMoO_7$ and MoO_3 at a molar ratio 6:7 under identical conditions for both preparations.

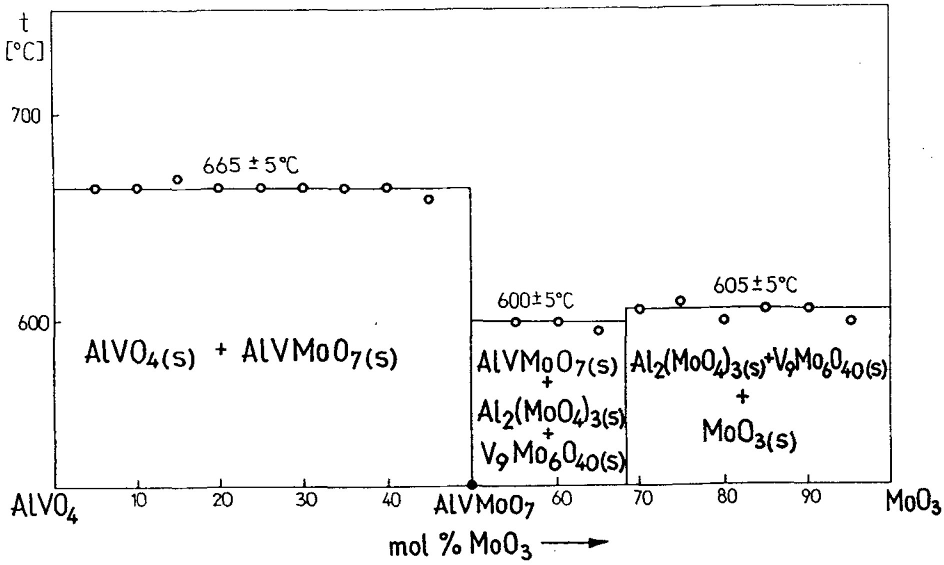

Fig. 1 Phase diagram of $AlVO_4$ – MoO_3 system in the subsolidus area

In the concentration range of MoO_3 contents higher than 68.48 mol%, MoO_3 appears in the system as a stable phase, (reaction (2)) involving complete utilization of $AlVMoO_7$ in the formation of $Al_2(MoO_4)_3$ and $V_9Mo_6O_{40}$. For such a component concentration range, three phases: MoO_3, $Al_2(MoO_4)_3$ and $V_9Mo_6O_{40}$, coexist in equilibrium in the system $AlVO_4$–MoO_3.

The Figure shows the phase equilibria in the solid state of the system $AlVO_4$–MoO_3 over the whole component concentration range. It can be inferred from the diagram that, within the subsolidus area, the system $AlVO_4$–MoO_3 is a real two-component system only in the range $AlVO_4$–$AlVMoO_7$. For the concentration range of over 50.0 mol% of MoO_3, the system $AlVO_4$–MoO_3 is no longer a two-component system. This is demonstrated by the occurrence of fields in which three solid phases remain in equilibrium.

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Zusammenfassung — Mittels DTA und Röntgendiffraktion wurde das Phasengleichgewicht im festen Zustand des Systemes $AlVO_4$-MoO_3 ermittelt. Die experimentelen Ergebnisse werden in Form eines Phasendiagrammes dargestellt. Im subsoliden Bereich ist das System $AlVO_4$-MoO_3 nur im Bereich $AlVO_4$-$AlVMoO_7$ ein echtes Zweikomponentensystem.