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# SUBSOLIDUS AREA OF THE $AlVO_4$–$Al_2(MoO_4)_3$ SYSTEM

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## Abstract

The behaviour of $Al_2(MoO_4)_3$ towards $AlVO_4$ in the subsolidus area, over the whole component concentration range, has been studied using the DTA and XRD methods. The experimental results have been presented in the form of a phase diagram. It has been found that components of the system of interest do not remain in equilibrium, and $AlVO_4$–$Al_2(MoO_4)_3$ system is not a real two-component system, even in the subsolidus area.

**Keywords:** aluminium molybdate, aluminium orthovanadate, phase equilibria

## Introduction

Aluminium orthovanadate and aluminium molybdate, and the systems in which the compounds exist, viz. $Al_2O_3$–$V_2O_5$ and $Al_2O_3$–$MoO_3$, have been subjects of comprehensive studies for many years, mainly on account of their interesting catalytic properties [1–3]. Accordingly, we thought it would be well to investigate whether $Al_2(MoO_4)_3$ and $AlVO_4$ would react with each other in the solid state and, what kind of phases could coexist in the equilibrium state in the $AlVO_4$–$Al_2(MoO_4)_3$ system in the whole concentration range.

Survey of publications has shown that the structure and the basic properties of components of the system are known. $AlVO_4$ was described in details in a publication covering $AlVO_4$–$MoO_3$ system, the work being presented at this Conference as well [4].

Aluminium molybdate forms two polymorphic modifications: a monoclinic form stable below the phase transformation temperature and an orthorhombic form occurring at temperatures higher than the temperature of transformation [5–10]. Basing on the results obtained from differential scanning calorimetry (DSC) and those from the conductivity measurement, Forzatti and his associates showed that transformation of aluminium molybdate took place at about 200°C, and the thermal effect was 1.3 J/g [3]. The structure of both polymorphs was recognized. The monoclinic modification belongs to a spatial group P21/a [5, 7, 9, 10] whereas the orthorhombic modification – to Pnca [7, 8]. $Al_2(MoO_4)_3$ melts congruently at 940°C [6].

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## Experimental

The following reagents were used for the experiments: $Al_2O_3$, p.a. – a commercial amorphous product, (POCh Gliwice, Poland); $V_2O_5$, p.a., (POCh Gliwice, Poland) and $MoO_3$ which was prepared by thermal decomposition of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ at 150–450°C. For the experiments were also used $AlVO_4$ and $Al_2(MoO_4)_3$ prepared by calcination of oxide mixtures. Accordingly $AlVO_4$ was prepared by calcination of an equimolar mixture of $Al_2O_3$ and $V_2O_5$ at 600°C for 48 h and then at 650°C for 72 h. $Al_2(MoO_4)_3$ was prepared by heating a mixture of $Al_2O_3$ with $MoO_3$, at a molar ratio of 1:3, at 550°C for 24 h, then at 650°C for 48 h and finally at 700°C for 24 h.

DTA was made using a derivatograph of a Paulik-Paulik-Erdey type (MOM Budapest). The samples, in quartz crucibles, were heated in air from 20 to 1000°C, at a heating rate of 10 $\mathrm{deg\cdot min^{-1}}$. The weight of each sample examined was 1000 mg.

The phase composition of preparations was determined by X-ray diffraction (diffractometer DRON-3, $CoK_\alpha$) using the data listed in the ASTM cards [11] and those included in publications [12, 13].

Two series of samples were prepared for experiments: a basic series comprising 23 samples was prepared from oxides, the other to be a verification series was prepared from phases building the system under study, viz. from $AlVO_4$ and $Al_2(MoO_4)_3$. The reagents in weighed proportions were ground, shaped into pastilles and then heated in air under conditions ensuring establishment of the equilibrium state. The conditions were fixed through introductory experiments which consisted in heating the samples at 550°C for 72 h, then at 600°C for 48 h, and finally at 620°C for 48 h. After the final heating cycle, all the samples were ground, analyzed by the DTA method and examined for their phase composition. Afterwards, the preparations of the basic series were shaped into pastilles again, additionally heated at 620°C for 48 h, then rapidly cooled to ambient temperature, ground and examined for their phase composition. In this way, there were found the kinds of the resultant phases and the range of their coexistence in the subsolidus area.

## Results and discussion

The Table 1 shows the composition of initial mixtures and the results of XRD analysis for both the basic and verifying series of the preparations obtained. By the XRD analysis, all the samples of the basic series contain, beside other phases, a metastable modification of aluminium oxide, $\gamma$-$Al_2O_3$. The presence of $\gamma$-$Al_2O_3$ in samples of this series can be accounted, for by the use of an amorphic aluminium oxide, as one of the reagents. It is known from the literature that transformation of amorphic aluminium oxide into $\gamma$-modification takes

Table 1 The composition of original mixtures and the results from XRD analysis for all the samples made

| The composition of samples in terms of mol% $Al_2(MoO_4)_3$ | Reagents | Phases found |
|---|---|---|
| 5.0; 7.5; 10.0; 12.5; 15.0; 17.5; 20.0; 22.5 | $Al_2O_3$, $V_2O_5$, $MoO_3$ | $AlVO_4$, $AlVMoO_7$, γ-$Al_2O_3$ |
| 10.0; 20.0 | $Al_2(MoO_4)_3$, $AlVO_4$ | $AlVO_4$, $AlVMoO_7$, α-$Al_2O_3$ |
| 25.0 | $Al_2O_3$, $V_2O_5$, $MoO_3$ | $AlVMoO_7$, γ-$Al_2O_3$ |
| 25.0 | $Al_2(MoO_4)_3$, $AlVO_4$ | $AlVMoO_7$, α-$Al_2O_3$ |
| 30.0; 35.0; 40.0; 45.0; 50.0; 55.0; 60.0; 65.0; 70.0; 75.0; 80.0; 85.0; 90.0; 95.0 | $Al_2O_3$, $V_2O_5$, $MoO_3$ | $AlVMoO_7$, $Al_2(MoO_4)_3$,γ-$Al_2O_3$ |
| 50.0; 75.0 | $Al_2(MoO_4)_3$, $AlVO_4$ | $AlVMoO_7$, $Al_2(MoO_4)_3$,α-$Al_2O_3$ |

place at 400–700°C, whilst the transformation of $\gamma$-$Al_2O_3$ into thermodynamically stable form of aluminium oxide, $\alpha$-$Al_2O_3$, needs a long-term heating at above 1000°C [14]. Consequently, a quantitative transformation of $\gamma$-$Al_2O_3$ into $\alpha$-$Al_2O_3$ was unfeasible under the conditions of preparation of samples. The final conclusion about formation of $\alpha$-$Al_2O_3$ in the system studied has been reached by investigation of phase composition of the verifying samples which were made of $AlVO_4$ and $Al_2(MoO_4)_3$ and heated in conditions similar to those applied to the samples of the basic series. XRD analysis has supported the occurrence of, apart from other phases, a thermodynamically stable modification of aluminium oxide, $\alpha$-$Al_2O_3$ (Table 1). Thus, it is the $\alpha$-modification of aluminium oxide, but $\gamma$-$Al_2O_3$, which is the phase being formed in the system studied.

The data of the Table 1 imply that the components of $AlVO_4$–$Al_2(MoO_4)_3$ system do not remain in equilibrium with each other. X-ray diffraction patterns of the preparations whose initial mixtures contained from 5.0 to 22.5 mol% of $Al_2(MoO_4)_3$ has shown that they are a mixture of three phases: $AlVO_4$, $AlVMoO_7$ and $Al_2O_3$. Absence of aluminium molybdate in these preparations indicates that $Al_2(MoO_4)_3$ with contents of up to 25.0 mol% reacts with $AlVO_4$ to completion giving $Al_2O_3$ and $AlVMoO_7$ – the compound whose existence in the three-component system, $Al_2O_3$–$V_2O_5$–$MoO_3$, has been ascertained recently [12]. The fact is indicative of a reaction taking place in $AlVO_4$–$Al_2(MoO_4)_3$ system in the solid state:

$$3AlVO_{4(s)}+Al_2(MoO_4)_{3(s)}=3AlVMoO_{7(s)}+Al_2O_{3(s)} \qquad (1)$$

Both the phase composition of the preparation corresponding to the $Al_2(MoO_4)_3$ content of 25.0 mol% in its initial mixture, the preparation being obtained from oxides, and the phase composition of a preparation obtained from a reaction of the mixture of $AlVO_4$ with $Al_2(MoO_4)_3$, at the 3:1 molar ratio, prove that reaction (1) runs to completion.

In the other preparations, viz. in those comprising over 25.0 mol% of $Al_2(MoO_4)_3$ in their initial mixtures, in the system occurs, beside $AlVMoO_7$ and $Al_2O_3$, a stable phase, $Al_2(MoO_4)_3$. It means that within that component concentration range reaction (1) keeps running yet it is $Al_2(MoO_4)_3$ that is in excess. And also in that component concentration range, $Al_2(MoO_4)_3$ remains in equilibrium with $AlVMoO_7$ and $Al_2O_3$.

The Fig. 1 shows a phase diagram of $AlVO_4$–$Al_2(MoO_4)_3$ system in the subsolidus area, constructed on the basis of the DTA curves and X-ray diffraction patterns of 23 preparations being in the equilibrium state. The solidus line temperatures have been determined basing on the first effect onset temperatures recorded on the DTA curves of the preparations under study. It follows from the Fig. 1 that $AlVO_4$–$Al_2(MoO_4)_3$ system in the subsolidus area is not a real two-

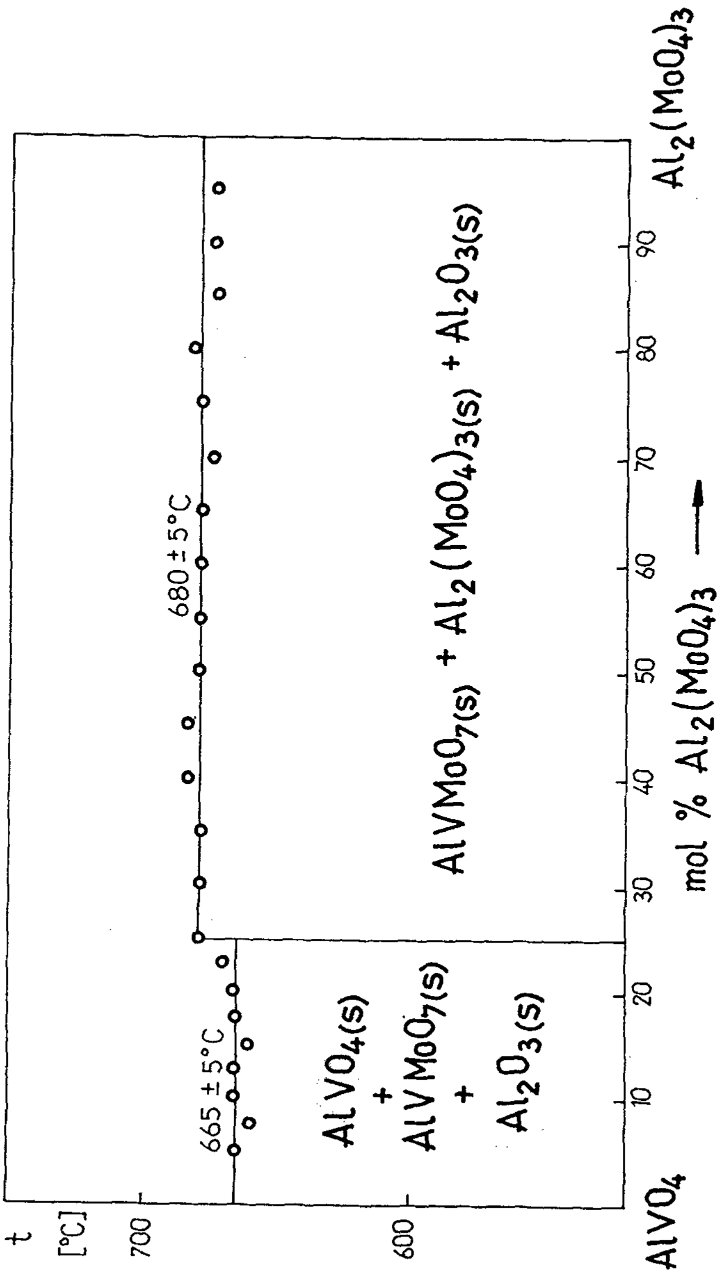

**Fig. 1** Phase equilibria in subsolidus area of $AlVO_4$-$Al_2(MoO_4)_3$ system

component system over the whole component concentration range. The fact can be supported by presence of fields in that area, in which three phases remain in equilibrium, the fields being $AlVO_{4(s)}+AlVMoO_{7(s)}+\alpha\text{-}Al_2O_{3(s)}$ and $AlVMoO_{7(s)}+Al_2(MoO_4)_{3(s)}+\alpha\text{-}Al_2O_{3(s)}$. Hence the diagram shown in the Fig. 1 *de facto* displays phase equilibria being established in the subsolidus area of the intersection of the three-component $Al_2O_3$–$V_2O_5$–$MoO_3$ system.

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**Zusammenfassung** — Mittels DTA und Röntgenmethoden wurde das Verhalten von $Al_2(MoO_4)_3$ gegenüber $AlVO_4$ im Bereich unterhalb der Soliduskurve im gesamten Konzentrationsbereich untersucht. Die experimentellen Ergebnisse wurden in einer Art Phasendiagramm dargestellt. Man fand, daß die Komponenten des untersuchten Systemes nicht im Gleichgewicht verbleiben und daß das System $AlVO_4$-$Al_2(MoO_4)_3$ gerade im Bereich unter Soliduskurve kein echtes Zweikomponentensystem ist.