

STUDIES ON THE SYSTEM $\text{AlVMoO}_7\text{-V}_2\text{O}_5$

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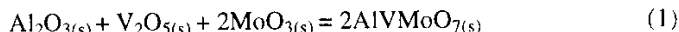
Abstract

The phase equilibria in the system $\text{AlVMoO}_7\text{-V}_2\text{O}_5$ were investigated over the whole component concentration range up to 1000°C. A phase diagram was constructed from the results of DTA and XRD methods.

Keywords: AlVMoO_7 , phase equilibria, vanadium(V)oxide

Introduction

Vanadium(V) oxide and the phases occurring in systems which include the oxide as one of the components have long been subject to intensive study, mainly because of the widely exploitable catalytic properties of V_2O_5 and the phases arising from it [1-3]. The other component of the title system, AlVMoO_7 , is formed in the three-component system $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5\text{-MoO}_3$ by a reaction taking place in the solid state between the following oxides [4]:



This compound may also be a product of another reaction [4]:



Hence, it seemed reasonable to undertake detailed studies on the phase relations in a system involving V_2O_5 as one of the components, the other being AlVMoO_7 formed in a system of active catalytic oxides [5, 6]. The structure and basic properties of the system components have been well recognized. AlVMoO_7 crystallizes in an orthorhombic system and belongs in the space group Pmnc ; the parameters of its unit cell are: $a=0.53812(1)$ nm, $b=0.81788(1)$ nm, $c=1.27488(2)$ nm [7]. The compound melts incongruently at $690\pm 10^\circ\text{C}$, depositing two solid phases: $\text{Al}_2(\text{MoO}_4)_3$ and Al_2O_3 [8].

Vanadium(V) oxide occurs in two polymorphic forms. The commonly-known high-temperature modification crystallizes in an orthorhombic system and belongs in the space group Pmnm [9]. The other form, $\gamma\text{-V}_2\text{O}_5$, discovered quite recently as a low-temperature modification also crystallizes in an orthorhombic system, but within the space group Pnma [10]. At 340°C , $\gamma\text{-V}_2\text{O}_5$ undergoes irreversible trans-

formation into the thermodynamically stable orthorhombic V_2O_5 [10]. Our measurements indicated that V_2O_5 melts congruently at $675 \pm 10^\circ\text{C}$.

It is known that in the solid state vanadium(V) oxide reacts with Al_2O_3 to give $AlVO_4$ [11, 12]. V_2O_5 also reacts with MoO_3 , the reaction products being a compound, $V_9Mo_6O_{40}$, and a substitutional solid solution of MoO_3 in V_2O_5 ; the solubility limit of MoO_3 in solid V_2O_5 is about 30 mol% at the eutectic temperature [13, 14]. We have found in work on the system Al_2O_3 - V_2O_5 - MoO_3 that V_2O_5 also reacts with $Al_2(MoO_4)_3$, a compound that occurs in the system Al_2O_3 - MoO_3 [15]. Depending upon the molar proportion $V_2O_5/Al_2(MoO_4)_3$ the products of the reaction are various solid phases, such as $AlVMoO_7$ and $V_9Mo_6O_{40}$; $AlVMoO_7$ and $V_2O_5(s.s.)$; or $AlVO_4$ and $V_2O_5(s.s.)$. On the other hand, aluminium molybdate reacts with $AlVO_4$ to give $AlVMoO_7$ and Al_2O_3 . We have also found that in the solid state $AlVMoO_7$ reacts with MoO_3 to result in the formation of $Al_2(MoO_4)_3$ and $V_9Mo_6O_{40}$.

Experimental procedure

The following reagents were used for the experiments: V_2O_5 , p.a., (POCh, Gliwice, Poland) and $AlVMoO_7$ obtained by heating a mixture of Al_2O_3 , V_2O_5 and MoO_3 at a molar ratio of 1:1:2 at 550°C for 24 h, then at 550°C for 24 h and finally at 600°C for 72 h.

A series of 12 samples consisting of $AlVMoO_7/V_2O_5$ mixtures was prepared. The reagents were weighed in the given amounts, then homogenized by grinding and afterwards pelleted. The pellets were placed in porcelain crucibles and heated in air under conditions ensuring the establishment of equilibrium. Information on the state of equilibrium was acquired by the XRD method, which was used to monitor the compositions of the samples after each of the heating cycles. If the results were identical after at least two successive stages of heating, the equilibrium was considered stable, the heating was interrupted, and the temperatures were chosen depending on the final DTA results. All the samples were heated at 550°C for 24 h, at 570°C for 24 h and at 585°C over two 24 h cycles. Next, the furnace and the samples inside them were cooled down slowly to ambient temperature. Finally, the samples were again shaped into pastilles, heated at 590°C for 72 h, and quenched to ambient temperature, and the pellets were ground and examined by DTA and XRD.

In order to ascertain that the types of solid phases occurring in the subsolidus area of the system under study were correct, several selected samples of the basic series were additionally heated for 48 h at 580°C . The samples were then quenched to ambient temperature, ground and examined by XRD. In this way, all the arising phases and the ranges of their co-existence in the solid state were established.

In turn, the solid phases in equilibrium with liquid in the high-temperature area of the phase diagram were determined from the results of XRD analysis on selected samples additionally heated for 2–3 h at chosen temperatures within the range 610 – 820°C and then quenched to ambient temperature.

The phases occurring in the samples were identified by XRD using a DRON-3 diffractometer with CoK_α radiation and a Fe filter, the data compiled in the JC PDF cards [16] and certain publications [4, 7, 12] being utilized.

The DTA investigations were made with a Paulik-Paulik-Erdey derivatograph (MOM, Budapest). All measurements were performed in air, at 20–1000°C and a constant heating rate of 10°C min⁻¹. The mass of each sample was 1000 mg. The measurements were made in quartz crucibles.

Results and discussion

Table 1 shows the compositions of the initial mixtures and the results of XRD analysis of the samples obtained after the last stage of heating of AlVMoO₇/V₂O₅ mixtures. XRD analysis of samples whose initial mixtures contained up to 70 mol% of V₂O₅ showed that they include three solid phases: AlVMoO₇, AlVO₄ and a solid solution of MoO₃ in V₂O₅. For the other samples, only AlVO₄ and V₂O_{5(s.s.)} were identified. The formation V₂O_{5(s.s.)} was evidenced by gradual shifts in most of the V₂O₅ diffraction lines and their increasing in intensity. Thus, the compositions of samples at equilibrium in the solid-state prove that the components of the title system interact to produce two phases: AlVO₄ and V₂O_{5(s.s.)}. The contents of a sample whose initial mixture is composed of 30 mol% of AlVMoO₇ and 70 mol% of V₂O₅ reveal that the reaction proceeds quantitatively, i. e. at a 3:7 molar ratio of the AlVMoO₇/V₂O₅ mixture, the compounds interact completely to yield AlVO₄ and V₂O_{5(s.s.)}. The mechanism of the reaction is not known and calls for detailed studies. In the component concentration range up to 70 mol% of V₂O₅, the solid solution formed is saturated, i. e. the content of MoO₃ is maximum, at ~30 mol% [3,14]. For other component concentration ranges in the system, the solid solutions formed are not saturated.

Table 1 Compositions of initial mixtures and results of XRD analysis for all samples

| Composition of samples mol% of V ₂ O ₅ | Phases found |
|--------------------------------------------------------------|-------------------------------------------------------------------------------|
| 5.0; 10.0; 15.0; 20.0; 30.0; 40.0; 50.0; 60.0 | AlVMoO ₇ , AlVO ₄ , V ₂ O _{5(s.s.)} |
| 70.0; 80.0; 90.0; 95.0 | AlVO ₄ , V ₂ O _{5(s.s.)} |

Figure 1 shows a phase diagram of the system AlVMoO₇-V₂O₅ over the whole component concentration range up to 850°C. The phase diagram was drawn on the basis of the XRD results and the DTA curves of all the samples prepared. The DTA curves of selected samples are shown in Fig. 2. Solidus line temperatures were determined from the onset temperatures of the first endothermic effects observed in the DTA curves of the samples examined. Liquidus curves, in turn, were also assigned from the onset temperatures of the effects recorded as the final ones in the DTA curves. The limits of coexistence of solid phases with liquid were established by taking the DTA results on samples in an equilibrium state, while the types of the phases were established by XRD analysis of some of the samples that had been additionally heated for 2–3 h at 610–820°C and afterwards rapidly cooled to ambient temperature. The compositions of the samples and the temperatures of 'freezing' are indicated in the phase diagram.

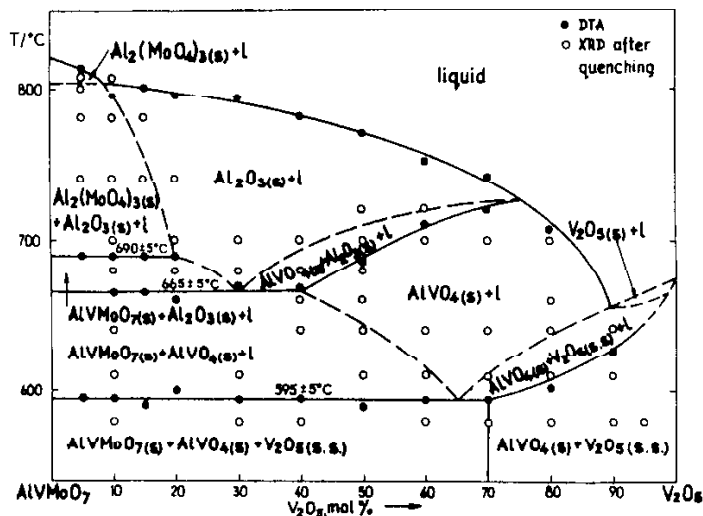
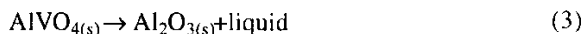


Fig. 1 Phase diagram of the system $\text{AlVMoO}_7\text{-V}_2\text{O}_5$

The phase diagram in Fig. 1 demonstrates that the system $\text{AlVMoO}_7\text{-V}_2\text{O}_5$ is not a real two-component system within the whole component concentration range, not even in the subsolidus area. This is indicated by the phase relations in the subsolidus area, viz. the presence of a field where three solid phases coexist in equilibrium, $[\text{AlVMoO}_{7(s)}+\text{AlVO}_{4(s)}+\text{V}_2\text{O}_{5(s.s.)}]$, and another field where AlVO_4 is in equilibrium with a solid solution of MoO_3 in V_2O_5 . In consequence, the system $\text{AlVMoO}_7\text{-V}_2\text{O}_5$ appears to be only a section of the three-component system $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5\text{-MoO}_3$ (Fig. 3), crossing two subsidiary systems of the three-component one, i. e. the systems $\text{AlVMoO}_7\text{-AlVO}_4\text{-V}_2\text{O}_{5(s.s.)}$ and $\text{AlVO}_4\text{-V}_2\text{O}_{5(s.s.)}$. The phase diagram of the system $\text{AlVMoO}_7\text{-V}_2\text{O}_5$ shows that the subsidiary system $\text{AlVMoO}_7\text{-AlVO}_4\text{-V}_2\text{O}_{5(s.s.)}$ is an eutectic; the temperature of the ternary eutectic is $595\pm 5^\circ\text{C}$. The melting temperature of the other subsidiary system, $\text{AlVO}_4\text{-V}_2\text{O}_{5(s.s.)}$ in the section $\text{AlVMoO}_7\text{-V}_2\text{O}_5$, is between $595\pm 5^\circ\text{C}$ and $675\pm 10^\circ\text{C}$, due to the occurrence of solid solutions of MoO_3 in V_2O_5 with different contents of MoO_3 .

Above the solidus line and in a high-temperature area of the phase diagram, peritectic reactions take place, involved in the incongruent melting of AlVO_4 and AlVMoO_7 [8, 11, 17]:



It can be read from the diagram that reaction (3), starting at 745°C in the two-component system $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5$, takes place at 725 to 665°C in the section $\text{AlVMoO}_7\text{-V}_2\text{O}_5$ of the three-component system $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5\text{-MoO}_3$.

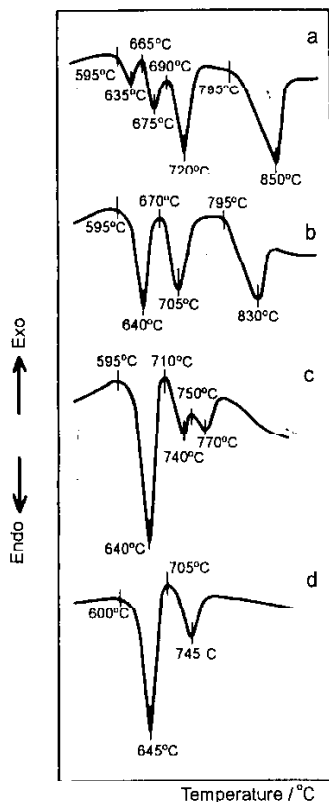


Fig. 2 DTA curves of selected samples after the final heating stage, a) 10 mol% of V_2O_5 ; b) 30 mol% of V_2O_5 ; c) 60 mol% of V_2O_5 ; d) 80 mol% of V_2O_5

The experimental results do not always furnish precise temperature ranges and concentration ranges for fields in which the solid phases coexist in equilibrium with liquid. Thus, the positions of the fields $Al_2O_3(s)+l$, $AlVO_4(s)+Al_2O_3(s)+l$, $AlVO_4(s)+l$, and $AlVO_4(s)+V_2O_5(s,s)+l$ were determined not only from the DTA curves, XRD analysis on samples 'frozen' at appropriate temperatures were also taken into consideration. However, the boundaries of a field where $V_2O_5(s,s)+l$ occurs could not be determined because the ranges of the basic parameters describing the field, i.e. the temperature and the concentrations of the components, were too small to delimit the field. However, the existence of the field can be inferred from the adjoining fields, whose presence in the phase diagram of the title system is undisputed. Some of the curves which demarcate certain fields have therefore been indicated with dotted lines.

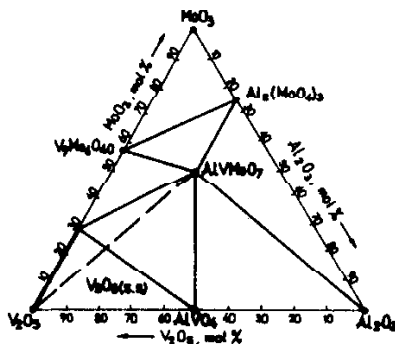


Fig. 3 Position of the section $\text{AlVMoO}_7\text{-V}_2\text{O}_5$ in the three-component system $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5\text{-MoO}_3$

Conclusions

The investigations made lead to the following conclusions:

- The system $\text{AlVMoO}_7\text{-V}_2\text{O}_5$ is not a real two-component system, not even in the subsolidus area, and forms a section of the three-component system $\text{Al}_2\text{O}_3\text{-V}_2\text{O}_5\text{-MoO}_3$ (Fig. 3)
- The section crosses two subsidiary systems that coexist in equilibrium: $\text{AlVMoO}_7\text{-AlVO}_4\text{-V}_2\text{O}_5(\text{s.s.})$ and $\text{AlVO}_4\text{-V}_2\text{O}_5(\text{s.s.})$ (Fig. 3).
- The phase diagram (Fig. 1) demonstrates phase equilibria established in the section $\text{AlVMoO}_7\text{-V}_2\text{O}_5$ over the whole component concentration range up to 1000°C .

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