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REACTIVITY IN AIR OF $SbVO_5$ TOWARDS MoO_3 AND PHASE EQUILIBRIA IN THE $SbVO_5$–MoO_3 SYSTEM IN THE SOLID STATE

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Abstract

The use of XRD and DTA methods has allowed studies on the interaction of the $SbVO_5$ and MoO_3, taking place in the solid state and in the medium of ambient air. The experimental results of XRD and DTA for all the samples showed the presence of a novel phase, i.e. $Sb_3V_2Mo_3O_{21}$ apart from various amounts of MoO_3 and $V_9Mo_6O_{40}$ or $SbVO_5$ and $V_2O_{5(s.s.)}$. The $SbVO_5$–MoO_3 system is not a real two-component system over the entire range of component concentrations up to the solidus line.

Keywords: DTA, phase equilibria, reactivity, $Sb_3V_2Mo_3O_{21}$, XRD

Introduction

For the past few years some systematic studies on phase equilibria being established in the V_2O_5–α-Sb_2O_4 system in air have been conducted [1]. The results obtained have allowed us to state that an equimolar V_2O_5/Sb_2O_4 mixture when heated below 650°C will give a new phase, $SbVO_5$. The phase appears stable at 710°C. Over 710°C that phase decomposes liberating oxygen to produce $Sb_2V_2O_9$ phase which possesses a rutile structure [2]. At this stage of study one could not exclude the possibility that the thermal decomposition of $SbVO_5$ would lead to a non-stoichiometric phase, $Sb_{0.92}V_{0.92}O_4$. The phase can be prepared by heating Sb_2O_3 with V_2O_5 at 800°C in air [3].

Results of other investigations of mutual reactivity in air of the oxides: α-Sb_2O_4, V_2O_5 and MoO_3 have given an indication that the oxides react in a solid phase to form a novel compound, which a formula $Sb_3V_2Mo_3O_{21}$ has been attributed [4, 5]. Formation of the compound involves the oxides V_2O_5, MoO_3 and α-Sb_2O_4 (in a molar ratio 2:6:3), its synthesis running in the presence of atmospheric oxygen. X-ray characteristic of $Sb_3V_2Mo_3O_{21}$ have been determined. The compound melts with accompanying decomposition at 740ºC, a solid product of this meritectic reaction being $Sb_2V_2O_9$ [5]. The involvement of oxygen in synthesis of the compound carried out with the use of all the three oxides, that is, V_2O_5, α-Sb_2O_4, and MoO_3 can be accounted for by the gain in mass of the samples processed and by the presence of $SbVO_5$ in the reaction mixtures [5].

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In the light of the recent experimental results it seemed interesting to establish the types and number of phases arising from a reaction in the solid state between $SbVO_5$ and MoO_3 in air atmosphere.

Experimental

MoO_3 was a commercial pure product of POCh (Gliwice, Poland) and $SbVO_5$ was prepared by heating an equimolar mixture of V_2O_5 (p.a. product, POCh, Gliwice, Poland) with α-Sb_2O_4 (obtained by heating a pure Sb_2O_3, Merck, Germany, in air) by a method described in work [1].

From a specially prepared $SbVO_5$ [1] and MoO_3 there were prepared 9 samples composed so as to present the whole component concentration range (Table 1). Accordingly, MoO_3/$SbVO_5$ mixtures were homogenised and shaped into pastilles to be then heated in a silite furnace, in the following cycles:

I: 400°C (1 h) → 500°C (24 h) → 550°C (24 h); II: 575°C (48 h);

III: 600°C (48 h); IV: 600°C (24 h).

Table 1 Contents of initial mixtures and X-ray phase analysis of $SbVO_5$/MoO_3 mixtures made on the final heating cycle

No.	Contents of initial mixtures/mol%		Molar ratio MoO_3:$SbVO_5$	Phase composition on the final heating cycle
	MoO_3	$SbVO_5$		
1	10.00	90.00	1:9	$SbVO_5$, $Sb_3V_2Mo_3O_{21}$, $V_2O_{5(s.s.)}$
2	20.00	80.00	1:4	$SbVO_5$, $Sb_3V_2Mo_3O_{21}$, $V_2O_{5(s.s.)}$
3	30.00	70.00	3:7	$SbVO_5$, $Sb_3V_2Mo_3O_{21}$, $V_2O_{5(s.s.)}$ – traces
4	40.00	60.00	2:3	$Sb_3V_2Mo_3O_{21}$, $SbVO_5$, $V_2O_{5(s.s.)}$ – traces
5	50.00	50.00	1:1	$Sb_3V_2Mo_3O_{21}$, $V_2O_{5(s.s.)}$
6	53.85	46.15	7:6	$Sb_3V_2Mo_3O_{21}$, $V_2O_{5(s.s.)}$ – traces, $V_9Mo_6O_{40}$
7	55.00	45.00	11:9	$Sb_3V_2Mo_3O_{21}$, $V_9Mo_6O_{40}$
8	60.00	40.00	3:2	$Sb_3V_2Mo_3O_{21}$, MoO_3, $V_9Mo_6O_{40}$ – traces
9	80.00	20.00	4:1	MoO_3, $V_9Mo_6O_{40}$, $Sb_3V_2Mo_3O_{21}$

The heating was carried out in a furnace equipped with an electronic temperature regulator, permitting to keep the temperature within the range (400–1000)±2.5°C.

After each heating cycle the samples were cooled slowly to ambient temperature, weighed to find a change in their mass, ground, subjected to DTA and XRD examinations then freshly pastilled and heated to give samples in equilibrium.

The establishment of equilibrium was checked by X-ray phase analysis of chosen specimens after two successive calcining cycles. If identical diffractograms were obtained it was accepted that equilibrium has been achieved. The heating of the samples was finished and the products were then analysed.

DTA of the samples was performed with derivatograph (MOM, Budapest) in quartz crucibles in air at 20–1000°C and a heating rate of 10°C min^{-1}. The weighed amount of the samples was 500 mg in each case.

The phase compositions of the specimens were assigned by using a diffractometer of a DRON-3 type (Bourevestnik, Sankt Petersburg, Russia) with CoK_α/Fe radiation. The phases were identified with the help of appropriate PDF cards and literature data [1–3, 5].

Results and discussion

X-ray analysis of all the samples processed showed after the first heating cycle that they contained, apart from parent substances, MoO_3 and $SbVO_5$ – a phase $Sb_3V_2Mo_3O_{21}$ that is novel compound formed in air in the three-component V_2O_5–α-Sb_2O_4–MoO_3 system. The second and third heating cycles caused an increase in the amount of phase $Sb_3V_2Mo_3O_{21}$ and the formation of $V_2O_{5(s.s.)}$ or $V_9Mo_6O_{40}$ against the decreasing amount of reagents.

Table 1 shows the phase content of samples after the final heating cycle, i.e. at equilibrium state. Samples 1–5 with up to 50.00 mol% of MoO_3 in their initial mixtures content comprised apart from phases $Sb_3V_2Mo_3O_{21}$ and $SbVO_5$ various quantities of solid solution of MoO_3 in V_2O_5 on the final heating cycle. The analysis of a diffraction pattern of a sample comprising 50.00 mol% of MoO_3 after the final heating stage has shown the sample to contain the novel phase $Sb_3V_2Mo_3O_{21}$ and $V_2O_{5(s.s.)}$ only. The mechanism of the reaction between $SbVO_5$ with MoO_3 in this concentration range of components is not known and calls for special studies. Nevertheless, one can suppose that an intermediate reaction may take place in the solid state delivering free V_2O_5; the reaction could be written as follows:

$$3SbVO_{5(s)}+3MoO_{3(s)}=Sb_3V_2Mo_3O_{21(s)}+0.5V_2O_{5(s)}+0.25O_{2(g)} \quad (1)$$

V_2O_5 released by this reaction carried out under the fixed conditions forms with molybdenum(VI) oxide a solid solution:

$$(1-x)V_2O_{5(s)}+xMoO_{3(s)} \rightarrow V_{2-2x}Mo_xO_{5-2x(s.s.)} \quad (2)$$

As MoO_3 has been totally involved in this component concentration range, i.e. up to 50.00 mol% MoO_3, $SbVO_5$ will occur in excess and remain in equilibrium with products of the reactions (1) and (2) that is with $Sb_3V_2Mo_3O_{21}$ and $V_2O_{5(s.s.)}$.

X-ray phase analysis of the diffraction pattern taken from the final thermally-induced sample 6, the initial mixture of which comprising MoO_3 and $SbVO_5$ at a molar ratio of 7:6, has shown that the sample was triphase and contains apart from the $Sb_3V_2Mo_3O_{21}$ minor quantities of $V_2O_{5(s.s.)}$ and $V_9Mo_6O_{40}$. Sample 7 being at equilibrium was of mixture $Sb_3V_2Mo_3O_{21}$ and $V_9Mo_6O_{40}$. The XRD results of the equilibrium samples with the MoO_3 content of their initial mixtures ranging form ~50.00 to 55.00 mol% MoO_3 suggest that molybdenum(VI) oxide reacts with $SbVO_5$ to completion, yielding $Sb_3V_2Mo_3O_{21}$ and $V_9Mo_6O_{40}$:

$$9SbVO_{5(s)}+11MoO_{3(s)}=3Sb_3V_2Mo_3O_{21(s)}+1/3V_9Mo_6O_{40(s)}+5/6O_{2(g)} \quad (3)$$

The total mass losses, resulting in the sample composed initially of $SbVO_5$ and MoO_3 at a molar ratio 9:11, were on all the heating cycles equal to 0.57 mass%. This confirms the course of the reaction occurring according to Eq. (3). Samples 8 and 9, covering the remaining concentration range for components of the $SbVO_5$–MoO_3 system were triphase, and contain MoO_3, $V_9Mo_6O_{40}$ and $Sb_3V_2Mo_3O_{21}$.

The thermodynamic coexistence range for the above-mentioned phases in the solid state could be inferred here from the onset temperature of the first endothermic effects, recorded on the DTA curves that were measured for the samples being in a state of equilibrium.

DTA curves of samples 1–5 with up to 50.00 mol% of MoO_3 content of their initial mixtures taken after the final heating cycle showed three endothermic effects. The first of which started at 620°C, whereas the onset temperature of the second effect was fluctuating between 690 and 710°C. The onset temperature of the last endothermic effect, recorded in the range 780–810°C. Figure 1 shows, for example, a DTA curve of a sample comprising on the last heating cycle a mixture of $Sb_3V_2Mo_3O_{21}$ with $V_2O_{5(s.s.)}$ and $SbVO_5$ (20.00 mol% of MoO_3 in the initial mixture). The DTA measurements imply that the $Sb_3V_2Mo_3O_{21}$ when in the solid state and in air coexists with $V_2O_{5(s.s.)}$ and $SbVO_5$ up to 620°C. The endothermic effect starting at ~710°C was increasing with the increase of $SbVO_5$, accompanied by the change in mass noticed on TG curves, its values making up from 1.2 to 2.4% by mass. This effect is bound with the decomposition of $SbVO_5$ taking place in the solid state and starting at 710°C [1]. The product of decomposition of $SbVO_5$, i.e. $Sb_2V_2O_9$ (or $Sb_{0.92}V_{0.92}O_4$) melts at ~810°C.

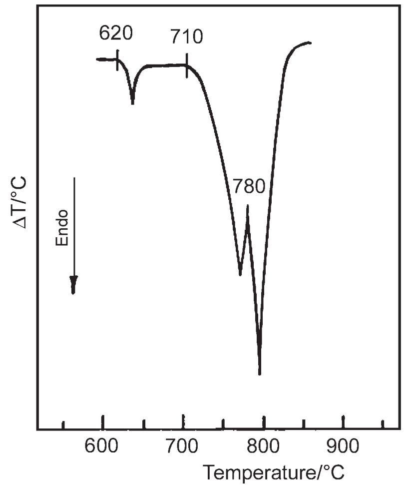

Fig. 1 DTA curve of mixture $Sb_3V_2Mo_3O_{21}$ and $V_2O_{5(s.s.)}$ with $SbVO_5$

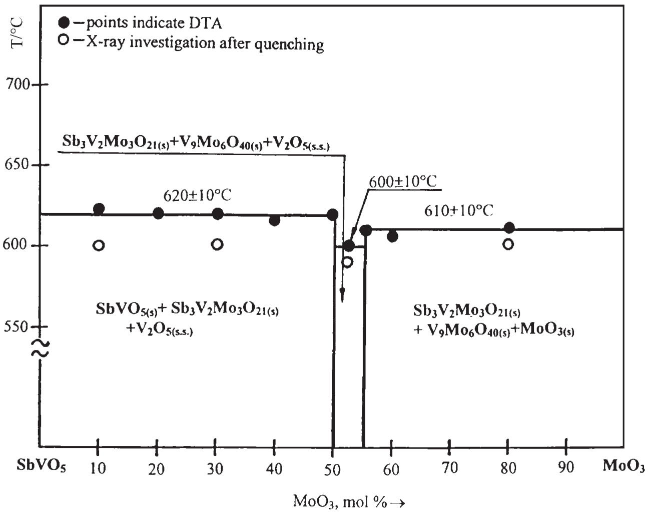

Fig. 2 Phase diagram of the $SbVO_5$–MoO_3 system in the solid state

DTA curves of samples 6 and 7 showed one strong endothermic effect with its onset temperature ~735°C and a weak effect recorded at 600°C, which may be accounted by the presence of $V_2O_{5(s.s.)}$ or $V_9Mo_6O_{40}$, both compounds occurring in minute quantities. The effect recorded at ~735°C corresponds of melting $Sb_3V_2Mo_3O_{21}$ [5]. DTA measurements of the samples covering the remaining concentration range of components of the $SbVO_5$–MoO_3 system at equilibrium have also shown that the melting temperature of the mixtures comprising the $Sb_3V_2Mo_3O_{21}$ together with MoO_3 and $V_9Mo_6O_{40}$ is ~610°C.

Figure 2 shows a phase diagram of the $SbVO_5$–MoO_3 system up to the solidus line. The diagram has been constructed from the DTA and XRD results of all the samples being in equilibrium. The solidus line temperatures have been determined based on the temperature onset of the first effect recorded from the DTA curves. The $SbVO_5$–MoO_3 system is not a real two-component system over the entire range of component concentration up to the solidus line, because $SbVO_5$ does not remain in equilibrium with MoO_3. In the solid state the components react at a molar ratio of ~1:1 to yield $Sb_3V_2Mo_3O_{21}$ and solid solution of MoO_3 in V_2O_5. At a molar ratio of 9:11 ($SbVO_5$:MoO_3), on the other hand, the components react to produce $Sb_3V_2Mo_3O_{21}$ and $V_9Mo_6O_{40}$.

Conclusions

The investigations permit the following conclusions:

– $SbVO_5$ and MoO_3 are not inert but reactive towards each other in air in the solid state,

– depending on the molar proportion $SbVO_5$/MoO_3 mixture, the phases into a reaction giving rise to a number of solid phases, viz. $Sb_3V_2Mo_3O_{21}$ and $V_2O_{5(s.s.)}$; $Sb_3V_2Mo_3O_{21}$ and $V_9Mo_6O_{40}$,

– the $SbVO_5$– MoO_3 system is not a real two-component system up to the solidus line in the all component concentration range (Fig. 2).

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