

## REACTIVITY OF THE OXIDES IN THE TERNARY $V_2O_5$ – $CuO$ – $\alpha$ - $Sb_2O_4$ SYSTEM IN AIR

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In this work it has been established which compounds finally are formed in air in the two-component  $CuO$ – $V_2O_5$  and  $CuO$ – $\alpha$ - $Sb_2O_4$  systems. Unknown thermal properties of  $CuV_2O_6$ ,  $Cu_2V_2O_7$  and  $Cu_{11}V_6O_{26}$  have been established. Reactivity of the oxides and phase relations in the ternary  $V_2O_5$ – $CuO$ – $\alpha$ - $Sb_2O_4$  system in air have been studied by using XRD and DTA methods. The results have showed the reaction of  $V_2O_5$ ,  $CuO$  with  $\alpha$ - $Sb_2O_4$  does not produce any compound where all the three oxides would be involved. It has been established that the  $\alpha$ - $Sb_2O_4$  reacts and forms binary phases independently with  $CuO$  or  $V_2O_5$ . On the base of these results the investigated system was divided into subsidiary subsystem in which  $CuSb_2O_6$  remains at equilibrium in the solid state with other phases formed in corresponding binary systems.

**Keywords:** *CuO, DTA, phase relations, reactivity of oxides,  $\alpha$ - $Sb_2O_4$ ,  $V_2O_5$ , XRD*

### Introduction

The review of literature demonstrated that the  $CuO$ ,  $V_2O_5$  and  $\alpha$ - $Sb_2O_4$  oxides have been subject to research for a number of years, mostly owing to their practical application in industry. Both vanadium(V) oxide, diantimony tetroxide as well as the phases formed with their participation, are particularly attractive due to their catalytic properties [1–5]. They are the components of the active and selective catalysts of numerous chemical processes, among others, methanol oxidation to formaldehyde [1–4], the production of nitrile from the acrylic acid [3] and also the process of obtaining acrylonitrile from propane [5]. Owing to an industrial significance of the mentioned oxides, it seems that investigating their mutual reactivity in order to state whether they react by forming phases demonstrating interesting utilitarian properties, is essential. According to literature data the reactivity of these oxides has not been subject to investigation, so far.

However, the bibliographical data demonstrate that the reactivity of  $V_2O_5$  towards  $CuO$  as well as  $V_2O_5$  with  $\alpha$ - $Sb_2O_4$  has been extensively studied.

It has been established that the kind of phases formed as a result of the reaction of  $V_2O_5$  with  $\alpha$ - $Sb_2O_4$  is dependent on the synthesis conditions, mainly the temperature and the gaseous atmosphere. Until recently it was believed that during the heating of the equimolar mixture of  $V_2O_5$  oxides with  $\alpha$ - $Sb_2O_4$  in air at the temperature of  $\sim 800^\circ C$ , non-stoi-

chiometric compound with the  $Sb_{1-x}V_{1-x}O_4$  formula where  $0 < x < 0.1$ , is formed [6, 7]. According to the majority of researchers, this compound is of the  $Sb_{0.92}V_{0.92}O_4$  formula and is stable in air up to the temperature of  $810^\circ C$  [5, 8]. At this temperature  $Sb_{0.92}V_{0.92}O_4$  melts incongruently, followed by the release of the solid solution of  $V_2O_5$  in  $\beta$ - $Sb_2O_4$  [8, 9]. It has been known for some years that at the temperature not exceeding  $650^\circ C$   $V_2O_5$  reacts with  $\alpha$ - $Sb_2O_4$  in air, forming the  $SbVO_5$  compound. The  $SbVO_5$  compound is stable in air up to the temperature of  $\sim 710^\circ C$ , at which it decomposes with releasing oxygen to the phase of the rutile structure with the  $Sb_{0.9}^{5+}V_{0.1}^{3+}V_{0.8}^{4+}\square_{0.2}O_4$  formula [10], (where  $\square$ —the notation of cationic vacancies).

The literature data regarding the phases being formed as a result of a reaction between  $CuO$  and  $\alpha$ - $Sb_2O_4$  in air, is contradictory. The literature available provides the information that the  $CuSb_2O_6$  phase, containing antimony and copper on the highest accessible degree of oxidation, is formed in this system [11–16].

Still, the reactivity of  $CuO$  with  $V_2O_5$  evokes the largest amount of contradictory information [17–29]. Two versions of phase diagram of the  $CuO$ – $V_2O_5$  system have been constructed by Fleury [17], Brisi and Molinari [18] are known. According to the phase diagram constructed by Fleury [17] in this system four compounds, i.e.  $CuV_2O_6$ ,  $Cu_2V_2O_7$ ,  $Cu_3V_2O_8$  and  $Cu_5V_2O_{10}$  are formed. However Brisi and Molinari [18] claim that in this system, apart from the four

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vanadates already mentioned, the  $\text{Cu}_4\text{V}_2\text{O}_9$  phase is also formed. According to Brisi [18], the  $\text{Cu}_4\text{V}_2\text{O}_9$  compound melts at  $780^\circ\text{C}$  incongruently by releasing the solid  $\text{Cu}_5\text{V}_2\text{O}_{10}$ . Some researchers attribute the  $\text{Cu}_{11}\text{V}_6\text{O}_{26}$  formula to this phase [19]. The other phase existing in the Cu–V–O system, i.e.  $\text{Cu}_4\text{V}_{2.15}\text{O}_{9.38}$  and  $\text{Cu}_{6.78}\text{V}_6\text{O}_{18.78}$  were examined only by Christian [30] and Rea [31], respectively.

The studies on the reactivity of  $\text{V}_2\text{O}_5$ , CuO oxides with  $\alpha\text{-Sb}_2\text{O}_4$  require comprehensive knowledge regarding the number, type and the thermal properties of the phases formed with two appropriate oxides being involved. Therefore, the studies commenced within the scope of this work were begun by the verification of the literature data regarding the reactivity of  $\text{V}_2\text{O}_5$  with CuO and CuO with  $\alpha\text{-Sb}_2\text{O}_4$ . These studies allowed to finally establish which compounds are formed in air in the two-component  $\text{V}_2\text{O}_5\text{--CuO}$  and  $\text{CuO--}\alpha\text{-Sb}_2\text{O}_4$  systems.

## Experimental

The analytically pure oxides CuO (Aldrich, USA),  $\text{V}_2\text{O}_5$  (POCh, Poland) and  $\alpha\text{-Sb}_2\text{O}_4$ , obtained by means of heating the commercial pure  $\text{Sb}_2\text{O}_3$  (Merck, Germany) under the following conditions:  $400^\circ\text{C}$  (2 h)  $\rightarrow$   $500^\circ\text{C}$  (24 h)  $\rightarrow$   $550^\circ\text{C}$  (72 h), were used in the study.

These oxides have been subjects of comprehensive studies for many years. The properties and the structure of  $\text{V}_2\text{O}_5$ , CuO and  $\alpha\text{-Sb}_2\text{O}_4$  are known [32–34].  $\text{Sb}_2\text{O}_4$  occurs in two polymorphic modifications and the temperature of transformation  $\alpha\text{-Sb}_2\text{O}_4 \rightarrow \beta\text{-Sb}_2\text{O}_4$  in air is equal to  $1080^\circ\text{C}$  [32].  $\text{V}_2\text{O}_5$  melts congruently at  $675^\circ\text{C}$  [33]. Copper(II) oxide is stable in air to  $\sim 800^\circ\text{C}$  – an onset temperature of its breaking down to  $\text{Cu}_2\text{O}$ , accompanied by the releasing of  $\text{O}_2$  [34].

The DTA/TG investigations were performed by means of a Paulik–Paulik–Erdey derivatograph, product of MOM, Hungary. The measurements were conducted in the atmosphere of air, in the temperature range  $20\text{--}1000^\circ\text{C}$ , at the DTA galvanometer sensitivity of  $1/5$  and a constant heating rate of  $10^\circ\text{C min}^{-1}$ . All investigations were performed in quartz crucibles. The mass of investigated samples amounted always to 500 mg. The accuracy of temperature reading determined on the base of repetitions was established as  $\pm 5^\circ\text{C}$ .

The kind of phases contained in the samples was identified on the base of X-ray phase analysis results [35, 36] (diffractometer DRON-3 made in USSR, radiation  $\text{CoK}_\alpha$ , filter Fe) and data found in the PDF cards [37] and in the work [38].

In order to verify the literature data, particularly determining which phases are formed as a result of the reaction of  $\text{V}_2\text{O}_5$  with CuO and CuO with  $\alpha\text{-Sb}_2\text{O}_4$ , 6 samples were prepared from appropriate oxides. These samples corresponded with their compositions to the following compounds, i.e.  $\text{CuSb}_2\text{O}_6$ ,  $\text{CuV}_2\text{O}_6$ ,  $\text{Cu}_2\text{V}_2\text{O}_7$ ,  $\text{Cu}_3\text{V}_2\text{O}_8$ ,  $\text{Cu}_5\text{V}_2\text{O}_{10}$  and  $\text{Cu}_{11}\text{V}_6\text{O}_{26}$ . These compounds were synthesized in air, under the conditions described in literature [20–26]. In the cases when no data regarding the thermal properties of the obtained compounds was available or it was clearly contradictory, the temperature and the manner of melting were established. For this reason the samples were heated for 3 h at the temperature of maximum of the first effect recorded on their DTA curves, not resulting from the polymorphous transition, and next rapidly cooled down to ambient temperature, ground and examined by XRD. Such course of activities has been described in works [39, 40].

The next stage was concerned with the proper studies, i.e. examining the reactivity of CuO,  $\text{V}_2\text{O}_5$  and  $\alpha\text{-Sb}_2\text{O}_4$ , for which 15 samples were prepared from the oxides. The composition of the samples was demonstrated in Table 1. The reacting substances for the verification studies as well as for the proper ones were weighed in appropriate quantities, subjected to homogenisation by grinding, pelletizing and heating in air, under the conditions ensuring that the reaction would run in the solid phase. The samples Nos 1, 2, 3, 12, 13, 14 were heated over the following cycles: I– $575^\circ\text{C}$  (24 h), II– $600^\circ\text{C}$  (24 h), III– $625^\circ\text{C}$  (24 h), IV– $625^\circ\text{C}$  (24 h); the samples Nos 4, 10, 11, 15: I– $575^\circ\text{C}$  (24 h), II– $600^\circ\text{C}$  (24 h), III– $625^\circ\text{C}$  (24 h), IV– $650^\circ\text{C}$  (24 h), V– $650^\circ\text{C}$  (24 h); Nos 5–9: I– $575^\circ\text{C}$  (24 h), II– $600^\circ\text{C}$  (24 h), III– $625^\circ\text{C}$  (24 h), IV– $650^\circ\text{C}$  (24 h), V– $700^\circ\text{C}$  (24 h), VI– $700^\circ\text{C}$  (24 h).

Within the scope of this work additional studies on the phase equilibria establishing in the  $\text{V}_2\text{O}_5\text{--CuO--}\alpha\text{-Sb}_2\text{O}_4$  system in air, have been conducted, 15 samples made up of oxides were prepared for the studies and the state of equilibrium was declared when the results of the tests examined with the XRD and DTA after two consecutive heating cycles were identical, and the number of the phases corresponded with the extended rule of Gibb's phases.

## Results and discussion

### Verification studies

The studies whose aim was to establish which phases are formed as a result of the reaction of CuO with  $\text{V}_2\text{O}_5$  in air, were begun by the preparation of

**Table 1** The composition of the initial mixtures and XRD phase analysis results after the selected heating stage of the samples

No.	Samples comp. in terms of oxides/mol%			Phase comp. of the samples after the heating at 600°C	Phase comp. of the samples after the heating at 650°C	Phase comp. of the samples after the next to last and last heating stage
	CuO	$V_2O_5$	$\alpha$ -Sb $_2$ O $_4$			
1	33.33	33.34	33.33	CuSb $_2$ O $_6$ $V_2O_5$ , $\alpha$ -Sb $_2$ O $_4$	Last heating at 625°C	CuSb $_2$ O $_6$ $V_2O_5$
2	50.00	25.00	25.00	$\alpha$ -CuV $_2$ O $_6$ $\alpha$ -Sb $_2$ O $_4$ CuSb $_2$ O $_6$	Last heating at 625°C	CuSb $_2$ O $_6$ $\alpha$ -CuV $_2$ O $_6$
3	60.00	20.00	20.00	$\alpha$ -Sb $_2$ O $_4$ , CuO $\alpha$ -Cu $_2$ V $_2$ O $_7$	Last heating at 625°C	CuSb $_2$ O $_6$ $\alpha$ -Cu $_2$ V $_2$ O $_7$
4	66.66	16.67	16.67	$\alpha$ -Sb $_2$ O $_4$ Cu $_{11}$ V $_6$ O $_{26}$ CuSb $_2$ O $_6$	CuSb $_2$ O $_6$ Cu $_3$ V $_2$ O $_8$	CuSb $_2$ O $_6$ Cu $_3$ V $_2$ O $_8$
5	70.00	15.00	15.00	$\alpha$ -Sb $_2$ O $_4$ Cu $_5$ V $_2$ O $_{10}$ Cu $_{11}$ V $_6$ O $_{26}$	$\alpha$ -Sb $_2$ O $_4$ , CuSb $_2$ O $_6$ Cu $_5$ V $_2$ O $_{10}$ Cu $_{11}$ V $_6$ O $_{26}$	CuSb $_2$ O $_6$ Cu $_{11}$ V $_6$ O $_{26}$
6	75.00	12.50	12.50	$\alpha$ -Sb $_2$ O $_4$ , CuO Cu $_5$ V $_2$ O $_{10}$	$\alpha$ -Sb $_2$ O $_4$ , CuO Cu $_5$ V $_2$ O $_{10}$	CuSb $_2$ O $_6$ Cu $_5$ V $_2$ O $_{10}$
7	80.32	9.84	9.84	$\alpha$ -Sb $_2$ O $_4$ , CuO	$\alpha$ -Sb $_2$ O $_4$ , CuO	Cu $_5$ V $_2$ O $_{10}$
8	82.62	8.69	8.69	Cu $_5$ V $_2$ O $_{10}$	Cu $_5$ V $_2$ O $_{10}$	CuSb $_2$ O $_6$ CuO
9	67.50	8.75	23.75	$\alpha$ -Sb $_2$ O $_4$ , CuO Cu $_{11}$ V $_6$ O $_{26}$	$\alpha$ -Sb $_2$ O $_4$ , CuO Cu $_5$ V $_2$ O $_{10}$	Cu $_5$ V $_2$ O $_{10}$ CuSb $_2$ O $_6$
10	33.33	16.67	50.00	$V_2O_5$ , $\alpha$ -Sb $_2$ O $_4$	CuSb $_2$ O $_6$	CuSb $_2$ O $_6$
11	25.00	25.00	50.00	CuSb $_2$ O $_6$	SbVO $_5$	SbVO $_5$
12	25.00	50.00	25.00	$V_2O_5$ , $\alpha$ -Sb $_2$ O $_4$ CuSb $_2$ O $_6$ $\alpha$ -CuV $_2$ O $_6$	Last heating at 625°C	CuSb $_2$ O $_6$ $V_2O_5$
13	40.00	40.00	20.00	$V_2O_5$ , $\alpha$ -Sb $_2$ O $_4$ CuSb $_2$ O $_6$ , CuO $\alpha$ -CuV $_2$ O $_6$	Last heating at 625°C	CuSb $_2$ O $_6$ $\alpha$ -CuV $_2$ O $_6$ $V_2O_5$
14	58.24	28.82	12.94	$V_2O_5$ , $\alpha$ -Sb $_2$ O $_4$ CuSb $_2$ O $_6$ $\alpha$ -CuV $_2$ O $_6$ , CuO	Last heating at 625°C	$\alpha$ -CuV $_2$ O $_6$ CuSb $_2$ O $_6$ $\alpha$ -Cu $_2$ V $_2$ O $_7$
15	64.29	28.57	7.14	$\alpha$ -Sb $_2$ O $_4$ , CuO $\alpha$ -Cu $_2$ V $_2$ O $_7$	CuSb $_2$ O $_6$ $\alpha$ -Cu $_2$ V $_2$ O $_7$	CuSb $_2$ O $_6$ $\alpha$ -Cu $_2$ V $_2$ O $_7$

5 samples from oxides. The composition of the samples corresponded to the CuV $_2$ O $_6$ , Cu $_2$ V $_2$ O $_7$ , Cu $_3$ V $_2$ O $_8$ , Cu $_5$ V $_2$ O $_{10}$  and Cu $_{11}$ V $_6$ O $_{26}$  compounds. The mixtures of the oxides were heated in the 24-h stages at the temperatures within the range from 550 to 950°C. The obtained results proved that  $V_2O_5$  reacts with CuO, forming all the mentioned compounds. Considering the fact that the literature information is contradictory [23, 26, 28], the test which proved that the compound CuV $_2$ O $_6$  melts incongruently at the temperature of 650°C, followed by the release of  $\alpha$ -Cu $_2$ V $_2$ O $_7$ , was carried out. This result confirms the literature data provided by Mercurio-Lavaud [23] and Prokofiev [26]. However, Fleury [28] according to whom CuV $_2$ O $_6$  melts congruently at the temperature of 650°C, was of an adverse opinion. In our studies two endothermic effects with the temperature of the start at 650 and

760°C were recorded on the DTA curve of CuV $_2$ O $_6$ . The temperature of the second effect corresponds to the melting temperature of  $\alpha$ -Cu $_2$ V $_2$ O $_7$ . The solid product of the CuV $_2$ O $_6$  melting, i.e.  $\alpha$ -Cu $_2$ V $_2$ O $_7$  was identified by XRD after the sample was heated at the temperature of 680°C, that is the temperature corresponding to the maximum of the first endothermic effect recorded on the DTA curve of the studied compound.

Similar studies were conducted in reference to the Cu $_2$ V $_2$ O $_7$  and Cu $_{11}$ V $_6$ O $_{26}$  compounds. They proved that Cu $_2$ V $_2$ O $_7$  melts congruently at 760°C. The way of melting Cu $_2$ V $_2$ O $_7$  established in these studies, is in agreement with the data according to Mercurio-Lavaud and Frit [21] as well as Fleury [28], as opposed to Cirilli and Burdese [29] who claim that the compound melts incongruently with the release of Cu $_3$ V $_2$ O $_8$  and Cu $_4$ V $_2$ O $_9$ .

Moreover, the lack of information regarding the thermal properties of the  $\text{Cu}_{11}\text{V}_6\text{O}_{26}$  compound has been supplemented. It was found that this compound melts incongruently at the temperature of  $780^\circ\text{C}$  with a deposition of solid  $\text{Cu}_5\text{V}_2\text{O}_{10}$ .

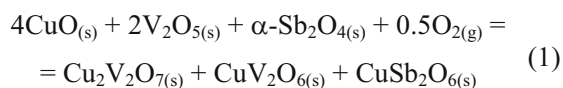
The studies conducted in this part of the work allowed to state that only one compound, namely  $\text{CuSb}_2\text{O}_6$ , is formed as a result of a reaction between  $\text{CuO}$  and  $\alpha\text{-Sb}_2\text{O}_4$  proceeding in air.

The  $\text{CuSb}_2\text{O}_6$  compound examined by DTA and XRD turns out to be stable up to the temperature of  $1200^\circ\text{C}$ , then it decomposes to  $\text{Cu}_2\text{O}$ , which confirms the data included in the work of Scarlat *et al.* [15]. However, Prokofiev *et al.* [16] stated that the  $\text{CuSb}_2\text{O}_6$  compound demonstrates the solid structure in air up to  $\sim 1213^\circ\text{C}$ . At this temperature it decomposes to  $\text{CuO}$ .

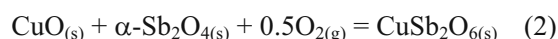
#### *Reactivity of the oxides in the $\text{V}_2\text{O}_5\text{-CuO-}\alpha\text{-Sb}_2\text{O}_4$ system*

Table 1 presents the compositions of the samples that were prepared with the view to examining the reactivity of the oxides in the  $\text{V}_2\text{O}_5\text{-CuO-}\alpha\text{-Sb}_2\text{O}_4$  system.

The samples' diffraction patterns, after the first stage of their calcination, next to the lines characterizing the oxides included in the initial mixtures, demonstrated the reflexes that could be attributed to the compounds formed with the participation of appropriate two oxides. For instance, sample 14 was subjected to four stages of calcination. As early as after the first stage of calcination, namely at  $575^\circ\text{C}$  (24 h), the sample's diffraction pattern showed, apart from the XRD lines of the  $\text{CuO}$ ,  $\text{V}_2\text{O}_5$  and  $\alpha\text{-Sb}_2\text{O}_4$  oxides, the diffraction lines typical of the  $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$  compound. After the next stage, i.e.  $600^\circ\text{C}$  (24 h), besides the previously identified phases, the  $\alpha\text{-CuV}_2\text{O}_6$  phase appeared as well. Also a significant increase in the intensity of the lines characterizing  $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$  was noted. Three compounds, namely  $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ ,  $\alpha\text{-CuV}_2\text{O}_6$  and  $\text{CuSb}_2\text{O}_6$  appeared in the sample as a result of the next stage of heating at the temperature of  $625^\circ\text{C}$  (24 h). The last stage of heating the sample failed to influence its phase composition, which indicates that in the solid state the phases remain at equilibrium with each other. This means that the oxides contained in the mixture of 58.24 mol%  $\text{CuO}$ , 28.82 mol%  $\text{V}_2\text{O}_5$  and 12.94 mol%  $\alpha\text{-Sb}_2\text{O}_4$  react forming  $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ ,  $\alpha\text{-CuV}_2\text{O}_6$  and  $\text{CuSb}_2\text{O}_6$ , according to the reaction equation:



The mass gain of the examined samples, i.e. 2, 10, 11, 14 and 15, fluctuating from 1.1 to 2.05 mass%, proves that oxygen participated in this and other reactions between the  $\text{CuO}$ ,  $\text{V}_2\text{O}_5$  and  $\alpha\text{-Sb}_2\text{O}_4$  oxides, which resulted in the formation of the  $\text{CuSb}_2\text{O}_6$  compound. These mass gains are the consequence of an indirect reaction taking place in the oxides mixtures, that is the reaction of forming  $\text{CuSb}_2\text{O}_6$ :



The XRD analysis results of the remaining tested samples after the selected stage of heating have been demonstrated in Table 1. It follows from the presented data that no phase is formed as a result of a reaction between the  $\text{V}_2\text{O}_5$ ,  $\text{CuO}$  oxides with  $\alpha\text{-Sb}_2\text{O}_4$  in air, which would involve all the oxides. In all the cases the examined oxides respond with making the compounds which are formed as a result of the reaction between  $\text{V}_2\text{O}_5$  with  $\text{CuO}$ ,  $\alpha\text{-Sb}_2\text{O}_4$  with  $\text{CuO}$  and  $\text{V}_2\text{O}_5$  with  $\alpha\text{-Sb}_2\text{O}_4$  in air.

#### *Phase equilibria in the $\text{V}_2\text{O}_5\text{-CuO-}\alpha\text{-Sb}_2\text{O}_4\text{-air}(\text{O}_2)$ system*

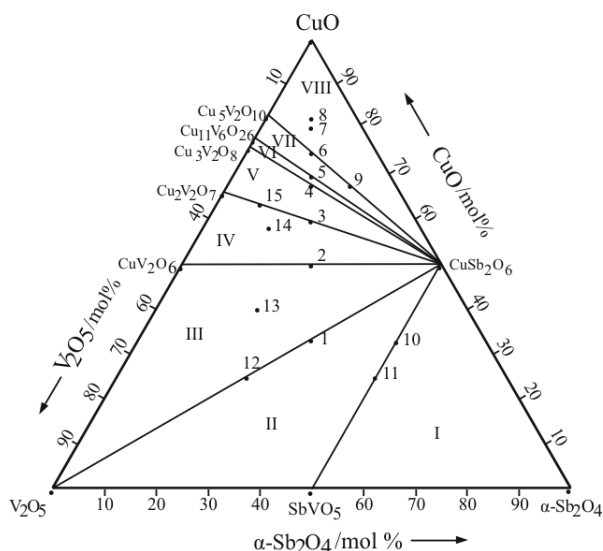
The phase composition of the examined samples after the last stage of heating, that is in the state of equilibrium, allowed to run a preliminary division of the  $\text{V}_2\text{O}_5\text{-CuO-}\alpha\text{-Sb}_2\text{O}_4\text{-air}(\text{O}_2)$  system into eight partial systems (Fig. 1), namely:

- I –  $\text{SbVO}_5\text{-}\alpha\text{-Sb}_2\text{O}_4\text{-CuSb}_2\text{O}_6$ ;
- II –  $\text{V}_2\text{O}_5\text{-SbVO}_5\text{-CuSb}_2\text{O}_6$ ;
- III –  $\text{V}_2\text{O}_5\text{-CuSb}_2\text{O}_6\text{-CuV}_2\text{O}_6$ ;
- IV –  $\text{CuV}_2\text{O}_6\text{-CuSb}_2\text{O}_6\text{-Cu}_2\text{V}_2\text{O}_7$ ;
- V –  $\text{Cu}_2\text{V}_2\text{O}_7\text{-CuSb}_2\text{O}_6\text{-Cu}_3\text{V}_2\text{O}_8$ ;
- VI –  $\text{Cu}_3\text{V}_2\text{O}_8\text{-CuSb}_2\text{O}_6\text{-Cu}_{11}\text{V}_6\text{O}_{26}$ ;
- VII –  $\text{Cu}_{11}\text{V}_6\text{O}_{26}\text{-CuSb}_2\text{O}_6\text{-Cu}_5\text{V}_2\text{O}_{10}$ ;
- VIII –  $\text{Cu}_5\text{V}_2\text{O}_{10}\text{-CuSb}_2\text{O}_6\text{-CuO}$

From a formal point of view, the  $\text{CuSb}_2\text{O}_6$  and  $\text{SbVO}_5$  compounds belong to the  $\text{CuO-Sb}_2\text{O}_5$  and  $\text{V}_2\text{O}_5\text{-Sb}_2\text{O}_5$  systems, respectively. Thus the examined  $\text{V}_2\text{O}_5\text{-CuO-}\alpha\text{-Sb}_2\text{O}_4$  system of oxides in air can be treated as the  $\text{V}_2\text{O}_5\text{-CuO-Sb}_2\text{O}_5$  system or  $\text{V}_2\text{O}_5\text{-CuO-}\alpha\text{-Sb}_2\text{O}_4\text{-air}(\text{O}_2)$ . The latter entry is strengthened by the fact that no presence of  $\text{Sb}_2\text{O}_5$  was detected in the reaction mixtures.

In order to verify the subsolidus area of the  $\text{V}_2\text{O}_5\text{-CuO-}\alpha\text{-Sb}_2\text{O}_4\text{-air}(\text{O}_2)$  system, the samples comprising the mixtures of the phases, which on the basis of the results of the earliest tests were considered equimolar in particular partial systems,

were prepared. Additionally, the samples, which converted into the system's components, corresponded to the compositions of the samples earlier produced from oxides, were prepared from the ready-made phases. Their composition was presented in Table 2. These mixtures were subjected to long-standing heating at temperatures slightly lower than



**Fig. 1** The scheme of phase diagram of the CuO-V<sub>2</sub>O<sub>5</sub>- $\alpha$ -Sb<sub>2</sub>O<sub>4</sub> system in air up to the solidus line

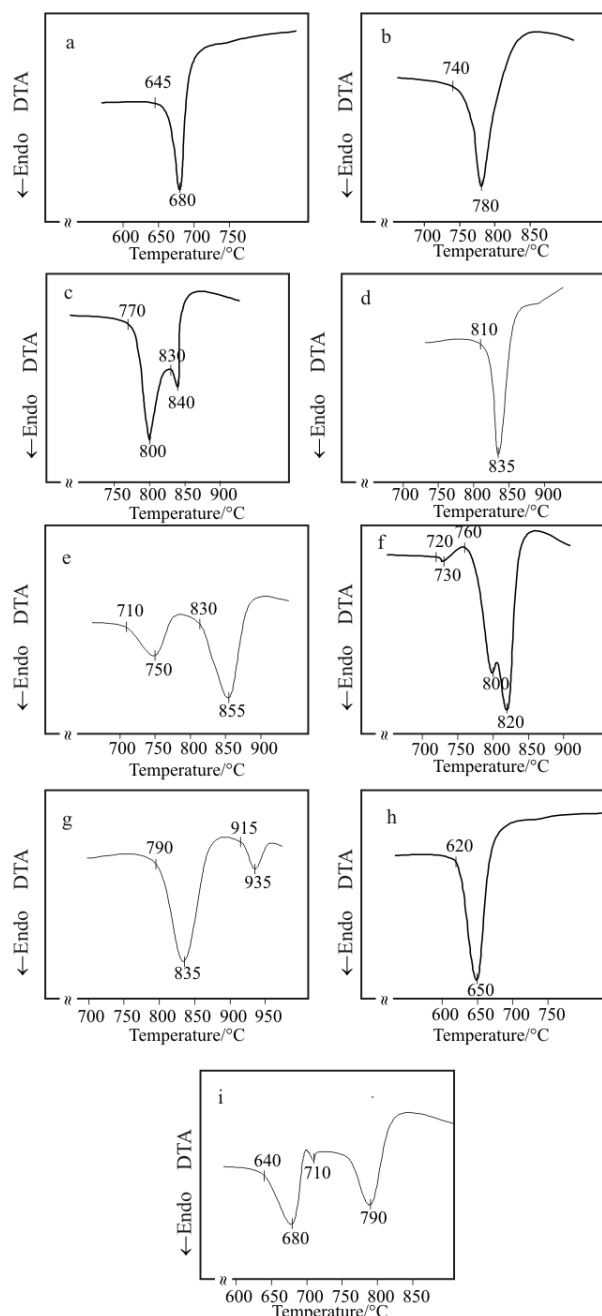
that of the corresponding solidus plane and next cooled to the ambient temperature. The analysis of the preparations by XRD demonstrated that despite the lasting many hours heating at the temperatures close to the ones of the start of melting, the composition of the samples did not undergo any changes. That proves that the initial mixtures corresponded with their composition to the phases determined earlier, coexisting in the state of equilibrium in particular fields of the subsolidus area.

On the basis of the DTA tests carried out on the samples, representing particular partial systems, after the last stage of heating, the melting temperatures of all the mixtures coexisting in the given partial system, were determined. These temperatures matched the temperatures of the beginning of the first endothermic effect, recorded on the DTA curves on the preparations in the state of equilibrium and corresponding to a particular partial system. Thus, the phases of CuSb<sub>2</sub>O<sub>6</sub>, CuV<sub>2</sub>O<sub>6</sub> with V<sub>2</sub>O<sub>5</sub> (III partial system) remain in the state of equilibrium in the solid state up to the temperature of 620±5°C. The phases of CuSb<sub>2</sub>O<sub>6</sub>, CuV<sub>2</sub>O<sub>6</sub> with Cu<sub>2</sub>V<sub>2</sub>O<sub>7</sub> (IV partial system) remain at equilibrium in the solid state up to 640±5°C. However, the phases: CuSb<sub>2</sub>O<sub>6</sub>, CuO with Cu<sub>5</sub>V<sub>2</sub>O<sub>10</sub> (VIII partial system) maintain their equilibrium in the solid state up the temperature of 795±5°C. The melting

**Table 2** The composition of the initial mixtures, XRD phase analysis after final heating cycle of the samples prepared for verifying investigations

No.	Kind of comp.	mol%	Sample composition in terms of oxides/mol%			Phase comp. of the samples in equilibrium state	Melting temp.
1	2	3	4	5	6	7	8
1	SbVO <sub>5</sub>	42.42	17.50	17.5	65.0	SbVO <sub>5</sub> $\alpha$ -Sb <sub>2</sub> O <sub>4</sub> CuSb <sub>2</sub> O <sub>6</sub>	750±5°C
	$\alpha$ -Sb <sub>2</sub> O <sub>4</sub>	36.37					
	CuSb <sub>2</sub> O <sub>6</sub>	21.21					
2	V <sub>2</sub> O <sub>5</sub>	37.50	20.00	45.0	35.0	V <sub>2</sub> O <sub>5</sub> SbVO <sub>5</sub> CuSb <sub>2</sub> O <sub>6</sub>	650±5°C
	SbVO <sub>5</sub>	37.50					
	CuSb <sub>2</sub> O <sub>6</sub>	25.00					
3	V <sub>2</sub> O <sub>5</sub>	33.34	40.00	40.0	20.0	V <sub>2</sub> O <sub>5</sub> CuSb <sub>2</sub> O <sub>6</sub> $\alpha$ -CuV <sub>2</sub> O <sub>6</sub>	620±5°C
	CuSb <sub>2</sub> O <sub>6</sub>	33.33					
	$\alpha$ -CuV <sub>2</sub> O <sub>6</sub>	33.33					
4	$\alpha$ -CuV <sub>2</sub> O <sub>6</sub>	29.55	58.84	28.82	12.94	$\beta$ -CuV <sub>2</sub> O <sub>6</sub> CuSb <sub>2</sub> O <sub>6</sub> $\alpha$ -Cu <sub>2</sub> V <sub>2</sub> O <sub>7</sub>	640±5°C
	CuSb <sub>2</sub> O <sub>6</sub>	30.99					
	$\alpha$ -Cu <sub>2</sub> V <sub>2</sub> O <sub>7</sub>	39.46					
5	$\alpha$ -Cu <sub>2</sub> V <sub>2</sub> O <sub>7</sub>	34.29	65.50	21.0	14.0	$\beta$ -Cu <sub>2</sub> V <sub>2</sub> O <sub>7</sub> CuSb <sub>2</sub> O <sub>6</sub> Cu <sub>3</sub> V <sub>2</sub> O <sub>8</sub>	760±5°C
	CuSb <sub>2</sub> O <sub>6</sub>	40.00					
	Cu <sub>3</sub> V <sub>2</sub> O <sub>8</sub>	25.71					
6	Cu <sub>3</sub> V <sub>2</sub> O <sub>8</sub>	75.00	75.00	22.5	2.5	Cu <sub>3</sub> V <sub>2</sub> O <sub>8</sub> CuSb <sub>2</sub> O <sub>6</sub> Cu <sub>11</sub> V <sub>6</sub> O <sub>26</sub>	760±5°C
	CuSb <sub>2</sub> O <sub>6</sub>	12.50					
	Cu <sub>11</sub> V <sub>6</sub> O <sub>26</sub>	12.50					
7	Cu <sub>11</sub> V <sub>6</sub> O <sub>26</sub>	2.38	78.00	17.0	5.0	Cu <sub>11</sub> V <sub>6</sub> O <sub>26</sub> CuSb <sub>2</sub> O <sub>6</sub> Cu <sub>5</sub> V <sub>2</sub> O <sub>10</sub>	745±5°C
	CuSb <sub>2</sub> O <sub>6</sub>	23.81					
	Cu <sub>5</sub> V <sub>2</sub> O <sub>10</sub>	73.81					
8	Cu <sub>5</sub> V <sub>2</sub> O <sub>10</sub>	10.52	82.62	8.69	8.69	Cu <sub>5</sub> V <sub>2</sub> O <sub>10</sub> CuSb <sub>2</sub> O <sub>6</sub> CuO	795±5°C
	CuSb <sub>2</sub> O <sub>6</sub>	10.52					
	CuO	78.96					

temperatures of the remaining phases coexisting at equilibrium in a given partial system were determined on the basis of the DTA tests conducted on the samples whose compositions were presented in Table 2.



**Fig. 2** DTA curves of selected samples at equilibrium: sample a – no. 1, binary system  $\text{CuSb}_2\text{O}_6\text{-V}_2\text{O}_5$ , b – no. 4, binary system  $\text{CuSb}_2\text{O}_6\text{-Cu}_3\text{V}_2\text{O}_8$ , c – no. 5, binary system  $\text{CuSb}_2\text{O}_6\text{-Cu}_{11}\text{V}_6\text{O}_{26}$ , d – no. 6, binary system  $\text{CuSb}_2\text{O}_6\text{-Cu}_5\text{V}_2\text{O}_{10}$ , e – no. 11, binary system  $\text{CuSb}_2\text{O}_6\text{-SbVO}_5$ , f – no. 15, binary system  $\text{CuSb}_2\text{O}_6\text{-Cu}_2\text{V}_2\text{O}_7$ , g – no. 7, subsidiary subsystem  $\text{Cu}_5\text{V}_2\text{O}_{10}\text{-CuSb}_2\text{O}_6\text{-CuO}$ , h – no. 13, subsidiary subsystem  $\text{V}_2\text{O}_5\text{-CuSb}_2\text{O}_6\text{-CuV}_2\text{O}_6$ , i – no. 14, subsidiary subsystem  $\text{CuV}_2\text{O}_6\text{-CuSb}_2\text{O}_6\text{-Cu}_2\text{V}_2\text{O}_7$

Taking the DTA tests into account, the temperatures up to which the compounds belonging to appropriate real two-component systems, i.e. being the cross-sections of the examined system of oxides  $\text{CuO-V}_2\text{O}_5\text{-}\alpha\text{-Sb}_2\text{O}_4$  ( $\text{Sb}_2\text{O}_5$ ), co-exist in the solid state, were also determined. It was established that the  $\text{CuSb}_2\text{O}_6$  compound co-exists with  $\text{SbVO}_5$  up to the temperature of  $710^\circ\text{C}$ , with  $\text{V}_2\text{O}_5$  up to  $645^\circ\text{C}$ , with  $\text{CuV}_2\text{O}_6$  up to  $645^\circ\text{C}$ , with  $\text{Cu}_2\text{V}_2\text{O}_7$  up to  $760^\circ\text{C}$ , with  $\text{Cu}_3\text{V}_2\text{O}_8$  up to  $740^\circ\text{C}$ , with  $\text{Cu}_{11}\text{V}_6\text{O}_{26}$  up to  $770^\circ\text{C}$  and with  $\text{Cu}_5\text{V}_2\text{O}_{10}$  up to  $810^\circ\text{C}$ .

The DTA curves of the selected, both the tri- and di-phase, samples in the state of equilibrium, were presented in Fig. 2.

The results of all the conducted tests were demonstrated in the form of a phase scheme of the subsolidus area of the  $\text{CuO-V}_2\text{O}_5\text{-}\alpha\text{-Sb}_2\text{O}_4$  system in the whole range of components' concentrations in air (Fig. 1).

## Conclusions

The results obtained within the framework of this work allow to draw the following conclusions:

- The  $\text{CuO}$  oxide reacts with  $\text{V}_2\text{O}_5$  forming five compounds:  $\text{CuV}_2\text{O}_6$ ,  $\text{Cu}_2\text{V}_2\text{O}_7$ ,  $\text{Cu}_3\text{V}_2\text{O}_8$ ,  $\text{Cu}_{11}\text{V}_6\text{O}_{26}$  and  $\text{Cu}_5\text{V}_2\text{O}_{10}$ .
- The compound  $\text{CuV}_2\text{O}_6$  melts incongruently at the temperature of  $650^\circ\text{C}$  with a deposition of solid  $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ .
- The compound  $\text{Cu}_2\text{V}_2\text{O}_7$  melts congruently at  $760^\circ\text{C}$ .
- The compound  $\text{Cu}_{11}\text{V}_6\text{O}_{26}$  melts incongruently at the temperature of  $780^\circ\text{C}$  with a deposition of solid  $\text{Cu}_5\text{V}_2\text{O}_{10}$ .
- The reaction of  $\text{CuO}$  with  $\alpha\text{-Sb}_2\text{O}_4$  in air results in the formation of only compound, i.e.  $\text{CuSb}_2\text{O}_6$ . The oxygen contained in the air participates in the synthesis of this compound.  $\text{CuSb}_2\text{O}_6$  is solid up to the temperature of  $1200^\circ\text{C}$ , only to decompose later to  $\text{Cu}_2\text{O}$ .
- The reaction of  $\text{V}_2\text{O}_5$ ,  $\text{CuO}$  with  $\alpha\text{-Sb}_2\text{O}_4$  does not produce any compound where all the three oxides would be involved.
- The  $\text{CuO-V}_2\text{O}_5\text{-}\alpha\text{-Sb}_2\text{O}_4\text{-air (O}_2\text{)}$  system of oxides can be divided into 8 partial systems.
- On the base of the investigations on phase equilibria being established up to the solidus surface in the system  $\text{CuO-V}_2\text{O}_5\text{-}\alpha\text{-Sb}_2\text{O}_4\text{-air (O}_2\text{)}$  we have determined the components concentration ranges and temperature ranges which the compound  $\text{CuSb}_2\text{O}_6$  coexists with other phases.

The obtained experimental results already in this form could be used in projecting of components new catalysts the modern chemical processes.

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