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THERMAL STUDIES IN CuO–Cu_2O–SnO_2 SYSTEM AT TWO OXYGEN PRESSURES, AS OBSERVED BY DTA/TG EXPERIMENTS

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Abstract

This study reports experimental investigations by DTA/TG analysis of $(1-x)SnO_2-x$CuO compositions, up to 1773 K and at two oxygen partial pressures (i.e. air and argon). In air, DTA/TG results showed thermal effects due exclusively to CuO presence in the initial mixture. No binary compounds were formed. The reduction process of CuO to Cu_2O over 1273 K as well as the formation over 1373 K of the liquid phase, have been evidenced. In argon atmosphere, CuO to Cu_2O reduction reaction is shifted toward 1205 K, while the liquid phase appears in the studied mixtures over 1473 K. The formation of an eutectic composition between SnO_2–Cu_2O, melting at 1491 K, coordinates: $0.932Cu_2O+0.068SnO_2$, has been experimentally established in argon.

Keywords: DTA studies, phase equilibria, sensor's materials, tin dioxide

Introduction

The phase diagram of SnO_2–CuO binary system may be very helpful in determining the optimum conditions for preparation and characterization of SnO_2-based sensor materials, especially if the sensor temperature reaches values higher than 1273 K [1]. However, probably due to the fact that the stability of the end members (i.e. SnO_2 and CuO) is strongly influenced by the oxygen content of the reaction atmosphere, phase diagram data on SnO_2–CuO_x systems are not available in literature [2–5]. For a complete description of the non-condensed systems (as it is the system Cu–O) it is therefore necessary to specify not only the composition and temperature of the condensed phases (i.e. solid and liquid), which are present in the system, but also the corresponding equilibrium pressure of oxygen in the gas phase [2]. That is why the experimental work on SnO_2–CuO_x system is very difficult to carry into practice, due to the influence of the oxygen partial pressure on the stability of copper oxides, and moreover to the high corrosive effect of the formed liquid phase, rich in copper oxides [3, 4].

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This study is an extention of the research activities on modelling and calculation of the Sn–Cu–O phase diagram [6, 7], devoted to DTA/TG experimental investigations on $(1–x)SnO_2–xCuO$ initial compositions in air and argon, up to 1773 K.

Experimental

Reagent grade SnO_2 and CuO (Merck Co.) were used to prepare the mixtures of $(1–x)SnO_2–xCuO$ general formula, with x=0, 0.10, 0.15, ... 0.85, 0.90, 1. The oxide components were sieved, grounded to a particle size below 45 μm, and wet homogenised with CH_3OH in an agate mortar, during 30 min interval. The stability of the obtained mixtures was studied from room temperature up to 1773 K by DTA measurements using a Perkin Elmer Instrument – Pyris 7 Differential Thermal Analyser. For this purpose, platinum reference pan was loaded with an amount of α alumina powder equal to the mass of the powder in the sample pan. All DTA tests were performed with heating rates of 7 K min^{-1} and natural cooling rates, in air (p_{O_2} = 0.21 atm) and in argon ($p_{O_2}=2.78\cdot10^{-4}$ atm). Mass losses associated with the various transformations were observed using a Perkin Elmer Instrument – Pyris 7 Thermogravimetric Analyser. Supplementary, a Carl Zeiss MHO-2 high temperature microscope, working up to 1773 K, was used to visualise in air the solid–liquid transitions of the samples. For phase determination, a Scintag Automated Diffractometer fitted with a solid state counter, working with CuK_α radiation ($\lambda_{K_{\alpha1}}$=1.54059 Å), has been used over the range 2θ=10–80°.

Results and discussion

SnO_2 and CuO initial oxides have been subjected to DTA/TG measurements under two different oxygen partial pressures (p_{O_2}=0.21 and $p_{O_2}=2.78\cdot10^{-4}$ atm) for a maximum temperature of T=1773 K. The results are given in Figs 1 and 2.

SnO_2 presents no thermal effects or a significant mass variation both in air (Fig. 1, x=0) and in argon (Fig. 2, x=0), this fact evidencing its bulk high temperature stability [8, 9].

In contrast, for pure CuO two distinct temperature peaks may be observed on the DTA curves. Besides that, the endothermic thermal effects in air are accompanied by a loss and a gain in mass – TG curve from Fig. 1 (x=1), while in argon there is only a mass decrease occurring in association with the first observed endothermic effect (Fig. 2, x=1). The negative mass variation is both in air and in argon, due to the dissociation process of CuO taking place according to the following reaction

$$2CuO \rightarrow Cu_2O+0.5O_2 \quad (1)$$

The data presented in Table 1 show a very good agreement between the calculated and experimental mass variation confirming, in accordance with previous reported results [3, 10, 11], that the reduction process described by reaction (1) proceeds completely until the whole initial amount of CuO is transformed into Cu_2O. In this connection, it is obvious that reaction (1) is displaced to lower temperatures when moving from air (1345 K) to argon atmosphere (1205 K).

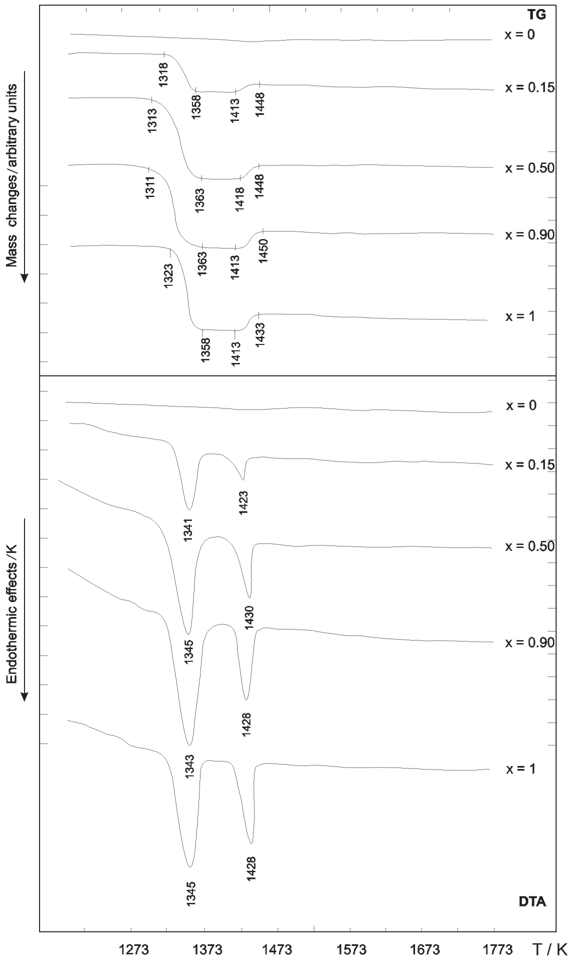

Fig. 1 DTA/TG results for (1–x)SnO_2–xCuO initial compositions; air, 7 K min^{-1}

Additionally, as regards the behaviour in air at higher temperatures (T>1373 K), using a high temperature microscope, a sudden melting of the sample consisting initially from pure stoichiometric CuO (x=1) was visualised at 1423 K. That is why at 1428 K the second endothermic thermal effect (Fig. 1, x=1) might be assigned to the formation in air of a liquid phase due to the melting of Cu_2O previously formed by reaction (1). Moreover, the broad shape and the pronounced asymmetry of the latter suggest the fact that more than one chemical processes take place at the same time. To assign this latter peak, the molar fraction of oxygen was supplementary calculated for T=1433 K (i.e. immediately after the gain in mass observed in Fig. 1 for x=1). The obtained results are presented and compared with the literature data in Table 2. Considering these data, the 1428 K second peak (Fig. 1, x=1), was initially assigned to the incomplete oxidation reaction of Cu_2O to CuO, to form the composition corresponding to the eutectic between Cu_2O and CuO (i.e. moles of Cu_2O:CuO=0.58:0.42 – in the ratio reported by [4]), and to the melting of the latter binary eutectic. The mentioned processes may be summarised as follows

Table 1 DTA/TG results for (1–x)SnO_2–xCuO initial compositions; air, 7 K min^{-1}

Oxygen partial pressure	x	Thermal effects/K			Mass variation/%		Assignment
		endo		exo			
		$T_{interval}$	T_{peak}		exp.	calc.	
air (0.21 atm)	1	1323–1358	1345	–	–9.866	–10.057	reaction (1)
		1413–1433	1428	–	+2.087	+2.735	reaction (2)
				–		+2.115	reaction (3)
	0	no thermal effects					
argon ($2.78\cdot10^{-4}$ atm)	1	1098–1223	1205	–	–9.952	–10.057	reaction (1)
		1503–1538	1505	–	–	–	reaction (4)
	0	no thermal effects					

$$Cu_2O_{(solid)}+O_{2(gas)} \rightarrow \text{liquid } E_2 \qquad (2)$$

However, in such a hypothesis there is a discrepancy between the value calculated according to the mentioned assignments and the experimentally mass variation (column 7 and 6 respectively, in Table 1). Still, a very good agreement arises by comparing the experimental values obtained in this work (data from Table 2) with the oxygen molar fraction x_O which corresponds to A point in the Cu–O phase diagram (Fig. 3).

That is why, it is possible to assign the 1428 K endothermic peak (Fig. 1, x=1) to the melting in air under uptake of oxygen, of Cu_2O previously formed by reaction (1)

$$Cu_2O_{(solid)}+O_{2(gas)} \rightarrow \text{liquid A} \qquad (3)$$

the agreement between the two sets of values being excellent (Table 2).

In contrast, the 1505 K corresponding peak obtained in argon seems to be very sharp and presents a symmetrical shape, the peak temperature being in good agreement with the published data for the congruent melting point of Cu_2O: 1493 K – determined by Boudène *et al.* for $=2.70\cdot10^{-4}$ atm [10], while Santander and Kubaschewski [5] report a value of 1515 K (Fig. 3).

The corresponding process may be described by

$$Cu_2O_{(solid)} \rightarrow \text{liquid}_{(\text{congruent melting point})} \qquad (4)$$

In conclusion, data listed in Tables 1 and 2 evidence that one may argue about the congruent melting point of Cu_2O only when dealing with reaction atmospheres

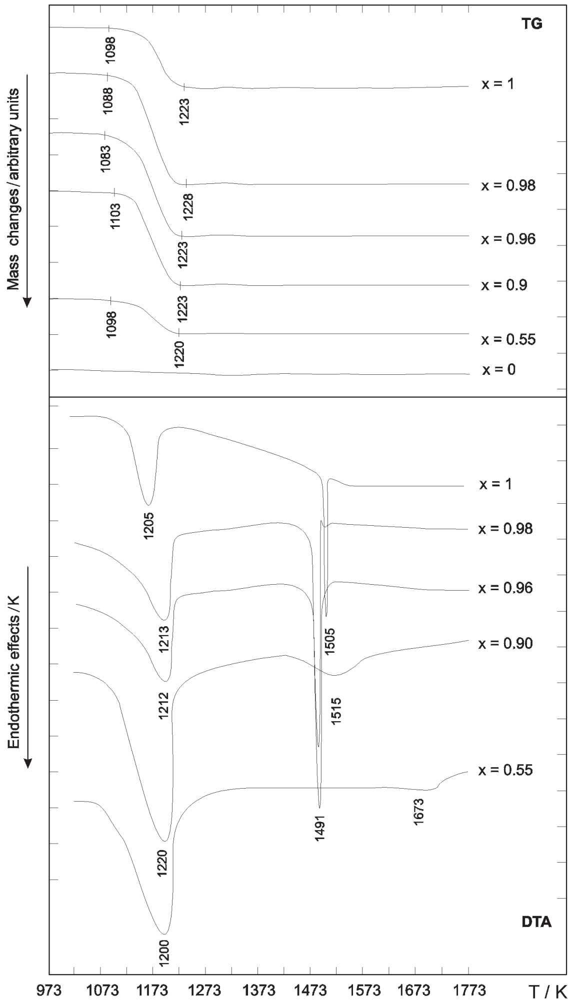

Fig. 2 DTA/TG results for (1–x)SnO$_2$–xCuO initial compositions; argon, 7 K min^{-1}

with no or very low oxygen content (i.e. inert atmospheres – as it is the case of argon atmosphere in the present work). Accordingly, as the oxygen partial pressure increases, the temperature of the CuO–Cu$_2$O transition increases as well, while the melting temperature is lowered (data listed in Table 1). Cu$_2$O already formed by the dissociation process (reaction (1)), then melts under uptake of oxygen (Fig. 1, x=1), the composition of the liquid phase (expressed by x_O, oxygen molar fraction) capable of co-existing with the solid phase being fixed at a given pressure. This situation occurs for all oxygen partial pressures lower than p_{O_2} =0.543 atm limiting pressure (corresponding to the binary eutectic), over which the CuO phase remains stable [4].

Table 2 Oxygen molar fraction in air, at T=1433 K for Cu–O system

x	Experimental**		Theoretical***		p_{O_2}/ atm	Assignment	Ref.
	x_O*	T/K	x_O	T/K			
1	–	–	0.3887	1354	0.538	reaction (2)	[4]
	0.3768	1433	0.3770	1428	0.21	reaction (3)	[10]

*Defined as oxygen moles per total moles (oxygen moles/copper+oxygen moles);
**Calculated according to the mass variation experimentally observed in this study;
***As reported by [4, 10]

The statements mentioned above are sustained by the data presented in Table 3. In argon, the phase analysis identified only the presence of Cu_2O, which is the phase already formed during the heating at high temperatures, and remains stable after the natural cooling of DTA residue.

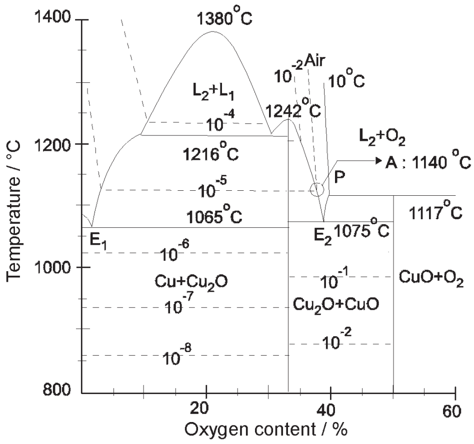

Fig. 3 Revised portion of the Cu–O phase diagram in the form published by Santander and Kubaschewski [5]

Unlike this former situation, in air the two phases identified are Cu_2O and CuO; the latter is formed as a result of reaction (1) proceeding incompletely in reverse direction. To conclude, during the natural cooling in air there is an incomplete oxidation process, leading to the presence of both CuO and Cu_2O phases (Table 3), due to the fact that the necessary amount of oxygen is limited by the presence of the liquid phase.

For $(1–x)SnO_2–xCuO$ initial mixtures, the DTA/TG experiments show two distinct behaviours.

First, in air, data presented in Fig. 1 evidence endothermic thermal effects that can be assigned only to the presence of CuO in the initial mixture, in agreement with previous reported results [11]. In this respect, the presence of SnO_2 in the initial mixture does not seem to modify the temperature characteristic values, which correspond to a certain process of copper oxide(II).

Table 3 Phase composition of the DTA residue (air and argon, 7 K min^{-1} 1773 K) of the (1–*x*)SnO_2–*x*CuO initial mixtures

x	Phase composition in air	Phase composition in argon
0.00	SnO_2	SnO_2
0.15	SnO_2+CuO	SnO_2+Cu_2O
0.50	SnO_2+CuO+Cu_2O	SnO_2+Cu_2O
0.90	SnO_2+CuO+Cu_2O	SnO_2+Cu_2O
1.00	CuO+Cu_2O	Cu_2O

Consequently, the presence of the first endothermic peak was assigned to the dissociation of CuO to Cu_2O present in the initial mixture (reaction (1)), proceeding completely over 1373 K, until a value of 0.3345±0.016 for oxygen molar fraction x_O has been reached (Table 4). The presence of the second thermal effect marked on the DTA curves from Fig. 1 (positioned at 1428±2 K) was additionally attributed to the melting with a pick up of oxygen from the gas phase of the copper oxide(I) present in the initial mixture. Data presented in Table 4 show a very good agreement concerning the experimental value obtained in this study at 1453 K for the oxygen molar fraction (average value of x_O=0.3665±0.01), and the value of x_O=0.3777 reported by Hallstedt *et al.*, Boudène *et al.* and Schmidt [4, 10, 12], calculated under the mentioned above assumptions.

No other additional thermal effects were observed on the corresponding DTA curves of (1–*x*)SnO_2–*x*CuO initial mixtures presented in Fig. 1. In the present experimental conditions (i.e. up to 1773 K), there is no interaction in air (either in solid state or with the participation of the liquid phase) between the end members of the SnO_2–CuO_x system.

Phase analysis of DTA residue determined for (1–*x*)SnO_2–*x*CuO initial compositions is presented in Table 3. Unlike the low copper compositions, a Cu_2O crystalline phase is always present along with CuO and SnO_2 for $x \geq 0.5$. This means that for the latter compositions the reverse process corresponding to reaction (1), taking place from Cu_2O to CuO, proceeds incompletely during the natural cooling in air, obviously due to the presence of the liquid phase extending from Cu–O system [3, 7].

Second, in argon the dissociation process of CuO to Cu_2O was evidenced by the presence of the endothermic peak positioned at 1202±2 K for all the studied (1–*x*)SnO_2–*x*CuO initial compositions (Fig. 2). In addition, the experimental value of x_O=0.33322±0.00028 calculated at 1243 K (Table 4) confirms the complete transition to Cu_2O (in which the O/Cu+O ratio is 1:3=0.333). Over this temperature the mass of the system and inherent, the oxygen molar fraction x_O remains constant. These statements are sustained by the phase analysis of DTA residue, which after the natural cooling in argon consists of SnO_2 and Cu_2O (Table 3).

Table 4 Oxygen molar fraction x_O in the $SnO_2–CuO_x$ system

x	p_{O_2}/atm	1243 K		1373 K		1453 K		Ref.
		x_O	x_O^*	x_O	x_O^{**}	x_O	x_O^{***}	
0.10	0.21	–	0.5	0.34463	0.3333	0.3651	0.377	[10]
	$2.78\cdot10^{-4}$	0.33301	0.3333	0.33301	0.3333	0.33301	0.3333	[4]
0.15	0.21	–	0.5	0.33321	0.3333	0.3582	0.377	[10]
	$2.78\cdot10^{-4}$	0.33321	0.3333	0.33321	0.3333	0.33321	0.3333	[4]
0.25	0.21	–	0.5	0.33331	0.3333	0.3647	0.377	[10]
	$2.78\cdot10^{-4}$	0.3335	0.3333	0.3335	0.3333	0.3335	0.3333	[4]
0.45	0.21	–	0.5	0.33242	0.3333	0.3688	0.377	[10]
	$2.78\cdot10^{-4}$	0.33326	0.3333	0.33326	0.3333	0.33326	0.3333	[4]
0.50	0.21	–	0.5	0.33395	0.3333	0.3560	0.377	[10]
	$2.78\cdot10^{-4}$	0.33304	0.3333	0.33304	0.3333	0.33304	0.3333	[4]
0.55	0.21	–	0.5	0.36101	0.3333	0.3579	0.377	[10]
	$2.78\cdot10^{-4}$	0.33294	0.3333	0.33294	0.3333	0.33294	0.3333	[4]
0.60	0.21	–	0.5	0.35253	0.3333	0.3689	0.377	[10]
	$2.78\cdot10^{-4}$	0.33310	0.3333	0.33310	0.3333	0.33310	0.3333	[4]
0.65	0.21	–	0.5	0.3494	0.3333	0.3702	0.377	[10]
	$2.78\cdot10^{-4}$	0.3335	0.3333	0.3335	0.3333	0.3335	0.3333	[4]
0.75	0.21	–	0.5	0.34551	0.3333	0.3751	0.377	[10]
	$2.78\cdot10^{-4}$	0.33328	0.3333	0.33328	0.3333	0.33328	0.3333	[4]
0.85	0.21	–	0.5	0.34504	0.3333	0.3726	0.377	[10]
	$2.78\cdot10^{-4}$	0.33330	0.3333	0.33330	0.3333	0.33330	0.3333	[4]
0.90	0.21	–	0.5	0.34814	0.3333	0.3736	0.377	[10]
	$2.78\cdot10^{-4}$	0.33329	0.3333	0.33329	0.3333	0.33329	0.3333	[4]
0.96	0.21	–	0.5	0.34003	0.3333	0.3705	0.377	[10]
	$2.78\cdot10^{-4}$	0.33327	0.3333	0.33327	0.3333	0.33327	0.3333	[4]
0.98	0.21	–	0.5	0.32920	0.3333	0.3772	0.377	[10]
	$2.78\cdot10^{-4}$	0.33325	0.3333	0.33325	0.3333	0.33325	0.3333	[4]

x_O – calculated according to the mass variation experimentally observed in this study by TG measurements performed on $(1–x)SnO_2–xCuO$ initial compositions (air+argon, 7 K min^{-1}); in calculating x_O, oxygen contributed by SnO_2 was ignored, so the ratio indicates the state of oxidation of the Cu

x_O^* and x_O^{**} – theoretical values according to reaction (1); in air the ratio corresponds to CuO (i.e. 0.5) and in argon to Cu_2O (0.3333 respectively);

x_O^{***} – theoretical values corresponding to reaction (3), as reported by [4, 10]

On the other hand, in the composition range rich in copper(II) oxide (i.e. for x=0.98 and 0.96), one may notice in Fig. 2, the presence of a supplementary endothermic thermal effect located at 1491 K. This latter peak was assigned to the melting of the eutectic composition formed between SnO_2 and Cu_2O, for which from the x=0.96 initial copper oxide(II) content a x_{Cu_2O}=0.932 molar fraction of copper oxide(I) was calculated. These data agrees quite well with the coordinates reported by Hoffman *et al.* [13] for the SnO_2–Cu_2O eutectic composition: $T_{eutectic}$=1495 K and the Cu_2O:SnO_2 molar ratio=0.989:0.011.

For the highest copper oxide content (i.e. x=0.98), there is marked on DTA curve a very small endothermic peak at 1505 K, assigned to the liquidus temperature of the compositions placed on the right side of the eutectic. Consequently, the broad endothermic effects noticed at higher temperatures (i.e. 1515 and 1673 K) for x=0.90 and x=0.55, could also be assigned to the liquidus temperatures of the compositions located on the left side of the eutectic. Moreover, for $x \leq 0.9$ it is difficult to get experimental evidences of the eutectic melting by DTA, since the amount of the formed liquid eutectic phase is too small, and therefore the corresponding heat released into the surrounding atmosphere is very small as well. On the other hand, for $x<0.50$, due to the fact that as reported by Samsonov [14] the 1958 K melting point of SnO_2 is very high, it is also difficult to notice in the present experimental conditions (i.e. up to 1773 K) the liquidus temperature.

Conclusions

DTA and TG studies were performed on the compositions of $(1–x)SnO_2–xCuO$ type, at two different oxygen partial pressures in air and in argon.

In air, DTA studies evidenced endothermic thermal effects exclusively assigned to the presence of CuO in the initial mixture, i.e. its reduction to Cu_2O, and the melting process under uptake of oxygen of the latter. No other additionally thermal effects were noticed on DTA curves obtained in air. Accordingly, the corresponding TG curves showed in association with the thermal effects mentioned above, a loss and a gain in mass.

In argon, the DTA/TG studies evidenced the reduction to Cu_2O shifted to lower temperature values both for pure CuO and for the same initial mixtures. In contrast, Cu_2O melting process, which in air proceeds under uptake of oxygen and in argon as a congruent melting process, is displaced in argon to higher temperatures.

Moreover, in argon, for the $(1–x)SnO_2–xCuO$ initial compositions, the formation of an eutectic composition between SnO_2 and Cu_2O (previously formed), was evidenced on the DTA curve with x=0.96 by the presence of a strong and well-defined endothermic peak. Consequently, the coordinates of the eutectic composition of the SnO_2–Cu_2O system are the following: $p_{O_2}=2.78\cdot10^{-4}$ atm, 0.932Cu_2O and 0.068SnO_2, melting at T=1491 K.

In conclusion, DTA/TG studies performed in this work established that the reduction process of CuO to Cu_2O transforms the SnO_2–CuO initial system into a pseudoternary of the SnO_2–CuO_x type, in which the value of x depends both on temperature T (K) and oxygen partial pressures p_{O_2} (atm) values.

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