Journal of Thermal Analysis, Vol. 32 (1987) 35–41

THE Cu_2SO_2 PHASE

Its preparation and some properties

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(Received April 3, 1985; in revised form March 11, 1986)

The conditions of synthesis of the Cu_2SO_2 phase, its thermal characteristics and its reactivity with respect to some other phases occurring in the Cu–S–O system below 710 K, at P_{SO_2} = 101 kPa, have been given. It has been established that the phase undergoes two reversible solid-state transitions, melts without decomposition at 610 K, and in the liquid state is stable up to 680 K. It is pointed out that Cu_2SO_2 is a phase thermally more stable than Cu_2SO_4.

We recently reported the existence of the previously unknown Cu_2SO_2 phase in the Cu–S–O system, and gave its X-ray pattern [1]. We found that Cu_2SO_2 is an intermediate product of the reaction of copper(II) sulphate with copper(I) sulphide at 710–780 K and $P_{SO_2} \cong 101$ kPa, according to the equation:

$$CuSO_{4(s)} + Cu_2S_{(s)} = 1.5\ Cu_2SO_{2(l)} + 0.5\ SO_{2(g)} \qquad (1)$$

The non-stoichiometric copper(I) sulphide first undergoes conversion to Cu_2S:

$$Cu_{1.96}S + 0.03\ CuSO_4 = 0.98\ Cu_2S + 0.0375\ SO_2 + x\ X \qquad (2)$$

where X is an unidentified product. Under these conditions, the Cu_2SO_2 phase appears to be a liquid [1–3].

The existence of the liquid below 850 K has already been ascertained by a number of investigators; however, their opinions as to its composition are controversial [4–7]. The authors of a recent publication [8] suggested that this liquid is Cu_2SO_4. They established that the melting temperature of Cu_2SO_4 is 696 K. They also found that, when heated from ambient temperature upward, Cu_2SO_4 decomposes completely at a temperature far below its melting point. Therefore, it seemed reasonable to try to synthetize Cu_2SO_2 and to investigate its properties, especially its behaviour at temperatures up to 700 K, and its reactivity towards other compounds in the Cu–S–O system.

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Experimental

The starting materials were anhydrous copper(II) sulphate p.a. and copper(I) sulphide containing exclusively the phase $Cu_{1.96}S$. They had a granulation of below 60 μm. Cu_2SO_4 used for the experiments was obtained by a method reported earlier [9]; its purity was 93.54 ± 2.04 wt%. The chemical compositions of the reactants were checked by methods described previously [3]. The phase composition of the products was studied by X-ray analysis with Cu–$K\alpha$ radiation (DRON 3). Some of the samples were also studied by means of scanning electron microscopy (SEM) combined with X-ray microanalysis (Stereoscan, Cambridge). The thermal (DTA) and thermogravimetric (TG) measurements were made both non-isothermally and isothermally in SO_2, with a thermobalance. The apparatus was constructed in the Institute of Industrial Automatics at the Technical University of Szczecin. The isothermal and non-isothermal measurements were carried out at temperatures between 298 and 900 K in SO_2 at a pressure of ~ 101 kPa.

Preparation of the Cu_2SO_2 phase

6 g of an equimolar mixture of copper(II) sulphate and copper(I) sulphide was annealed for ca 2 h at 723–733 K in SO_2, using a tubular furnace. The heating was stopped at the stage where the mass loss corresponded to the fractional conversion $\alpha = 0.35$–0.37, calculated according to the balance equation for the overall process:

$$2\ CuSO_4 + Cu_2S = 2\ Cu_2O + 3\ SO_2 \qquad (3)$$

The fractional conversion $\alpha = 0.35$–0.37 was related with the complete reaction of the substances, in accord with Eqs 1 and 2. Under the given conditions, the heating was stopped after 2 h. All the portions of the product were ground and mixed. Afterwards, the whole of the product was annealed in SO_2 at 673 K, when the product was completely liquified. After 1 h, the temperature was decreased to 573 K and the liquid which solidified was homogenized for 10 h. The fractional conversion of the final product was $\alpha = 0.356$.

Results and discussion

Chemical analysis revealed that the composition of the preparation obtained is relevant to Cu_2SO_2 at the significance level of 95%. Phase X-ray analyses were made of the product in the initial stage of the synthesis of the final product

(α = 0.356), and of the Cu_2SO_4 synthetized separately. The fragments with suitable X-ray patterns are shown in Fig. 1. It was established by X-ray analysis that the Cu_2SO_2 phase contained 3 mol % of $CuSO_4$ and 6 mol % of Cu_2S at most, and no Cu_2SO_4. The X-ray pattern of Cu_2SO_2 showed all the qualities required of a well-crystalline solid phase. This was concluded from the lack of any marked broadening of appropriate diffraction lines and from the stable position of the base line (Fig. 1).

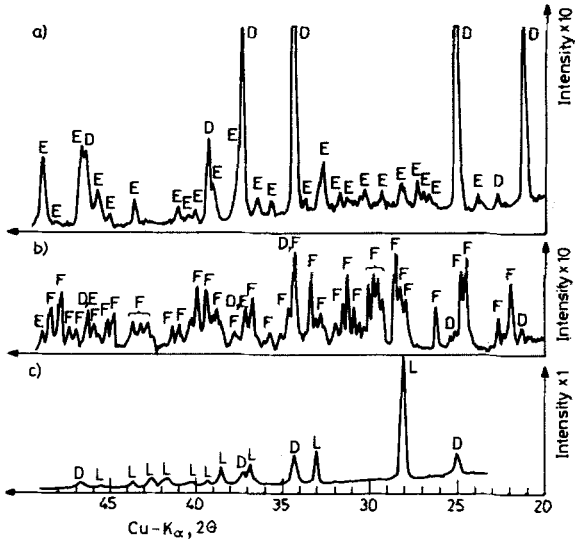

Fig. 1 The X-ray diffraction patterns with Cu-Kα radiation: D = $CuSO_4$, E = Cu_2S, F = Cu_2SO_2 and L = Cu_2SO_4. (a) Product of the preparation of Cu_2SO_2 at α = 0.035. (b) The final product of the preparation of Cu_2SO_2 at α = 0.356. (c) Cu_2SO_4 prepared by heating Cu_2O and $(CH_3)_2SO_4$

Phase X-ray analysis was performed on the products from the reaction of Cu_2S with $CuSO_4$ for the initial compositions $n_{CuSO_4}/n_{Cu_2S} > 1$, and at values of α higher than those related with the complete reaction of the substrates to Cu_2SO_2. In such cases, the presence of Cu_2SO_4 was easy to detect. On the other hand, attempts to ascertain the presence of Cu_2SO_4 in the reaction products failed whenever the initial composition of the mixture corresponded to $n_{CuSO_4}/n_{Cu_2S} \leqslant 1$. Therefore, one can certainly exclude the presence of Cu_2SO_4 in the preparation. Further, the intensities of the Cu_2S lines indicate that its content in the product is below 6 mol %. Accordingly, the possibility of Cu_2SO_2 being an equimolar eutectic mixture of Cu_2S with Cu_2SO_4 [5–7] can be neglected.

Cu_2SO_2 is not a saturated solid solution. This follows from the rigid positions of the diffractionlines ascribed to this phase; the positions are independent of the product composition. This fact was found on the evidence of the X-ray patterns of

the reaction products at $0<\alpha<1$ and $0.2 \leqslant n_{CuSO_4}/n_{Cu_2S} \leqslant 10$. Scanning electron microscopy confirmed the results of the X-ray analysis. It was found that only at $n_{CuSO_4}/n_{Cu_2S} = 1$ and $\alpha = 0.347$ did the product consist of one phase and not contain noticeable amounts of either substrates or Cu_2O. The results of the Cu_2SO_2 phase study indicate that the phase is a chemical compound stable enough to be isolated.

The DTA and TG results on Cu_2SO_2 are shown in Fig. 2 (the measurements were performed at increasing or decreasing temperature). The DTA curves show the existence of endothermic effects with the corresponding initial temperatures 372 (382) K, 411 (412) K, and 605 (610) K. The first two effects prove that a reversible phase transition takes place in the solid state. The third effect is unquestionably associated with the melting of Cu_2SO_2. This observation was confirmed visually. Cu_2SO_2 was found to melt with no mass change, which means that Cu_2SO_2 melts without decomposition and is also stable in the liquid state.

As the DTA results show Cu_2SO_2 to be stable in a considerable temperature range (Fig. 2c), it is assumed that the phase is thermodynamically stable in the Cu–S–O system. To verify this assumption experimentally, a preliminary study of

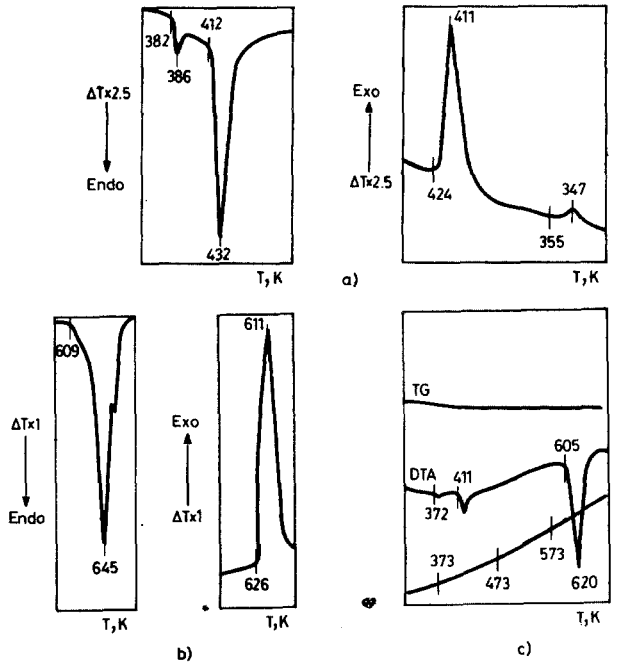

Fig. 2 Thermal analysis of Cu_2SO_2. (a) DTA of Cu_2SO_2 in solid state; heating rate 4 deg/min; cooling rate 2.5 deg/min from 425 to 395 K and 1.5 deg/min from 355 to 340 K. (b) DTA of solid-liquid change of Cu_2SO_2, heating and cooling rate 4 deg/min. (c) derivatogram of Cu_2SO_2, heating rate 5 deg/min

the following mixtures was undertaken: Cu_2SO_2–Cu_2S, Cu_2SO_2–$CuSO_4$, Cu_2SO_2–Cu_2SO_4 and Cu_2S–Cu_2SO_4. The investigation was carried out using DTA and TG in SO_2 at linearly increasing temperature. Each of the mixture components was studied separately by the same method. Measurements of selected samples were stopped at temperatures corresponding to either the initial or the final temperature of a particular effect in the DTA curves. The reaction products were quenched and their compositions were studied using X-ray analysis. The results are presented in Table 1.

Below 710 K, $CuSO_4$ shows no tendency to transformation, whereas the Cu_2SO_2–Cu_2S and Cu_2SO_2–$CuSO_4$ mixtures changes to exhibit only the phase transitions of Cu_2SO_2 and Cu_2S. Accordingly, Cu_2SO_2 is thought to be entirely inert towards Cu_2S and $CuSO_4$ below 710 K. The only compound liable to reaction is Cu_2SO_4. Below 600 K it decomposes totally to Cu and $CuSO_4$, and above 600 K Cu_2O is the final product of the reaction of Cu with $CuSO_4$. The reaction was described in detail previously [10]. Table 1 shows that the products that developed when the Cu_2SO_2–Cu_2SO_4 mixture was heated contain components whose existence can be attributed to the decomposition of Cu_2SO_4. Hence, Cu_2SO_2 and Cu_2SO_4 seem to be the other pair of compounds inert towards each other. Heating of the mixture Cu_2S–Cu_2SO_4 leads to a product comprising, in general, Cu_2SO_2 and insignificant amounts of products of Cu_2SO_4 decomposition: Cu, $CuSO_4$ and Cu_2O. Therefore, it is reasonable to expect that Cu_2SO_2 will be far more stable than Cu_2SO_4 below 710 K.

The results of the preliminary study and of up-to-date works [1–3, 10, 12] are the basis for the assumption that the below-mentioned phase mixtures exist in equilibrium in the system Cu–S–O below 710 K, at $p(SO_2) \cong 101$ kPa: Cu_2SO_2–Cu_2S, Cu_2SO_2–$CuSO_4$, and Cu_2S–Cu_2SO_2–$CuSO_4$. However, under these circumstances, Cu_2S cannot be in equilibrium with Cu_2SO_4. This means that the phase diagram of the Cu–S–O system at temperatures below 710 K is not complete, and calls for further study concerning the existence of Cu_2SO_2.

Conclusions

The phase Cu_2SO_2, so far not known to exist in the Cu–S–O system, is a product of the reaction of Cu_2S with $CuSO_4$ at temperatures above 710 K and at $p(SO_2) \cong 101$ kPa. This compound was synthesized and its purity was above 90 mol %. Cu_2SO_2 undergoes two reversible transitions in the solid state, at 382 K and 423 K. It melts without decomposition at 610 K and is stable up to 680 K at least. In the temperature range from ambient to 710 K, both the solid and the liquid Cu_2SO_2 are inert towards such phases of the Cu–S–O system as Cu_2S and $CuSO_4$, and, most likely, also towards Cu_2SO_4.

Table 1 X-ray diffraction analyses of the products of the interrupted thermal analyses at selected temperatures

Initial composition	Temp., K	Mass change, mg	X-ray intensity					
			Cu_2S	Cu_2SO_2	Cu_2SO_4	$CuSO_4$	Cu	Cu_2O
203.9 mg Cu_2SO_4	563	− 1.6	—	—	—	+ + +	+ + +	+
227.8 mg Cu_2SO_4	844	−27.0	—	—	—	+ + +	0	+ + +
189.7 mg Cu_2SO_2 + 251.8 mg Cu_2SO_4	569	− 7.3	—	+ + +	0	+ + +	+ + +	+
213.2 mg Cu_2SO_2 + 251.0 mg Cu_2SO_4	704	− 7.1	—	+ + +	0	+ + +	+ + +	+ +
539.7 mg Cu_2SO_4 + 404.3 mg Cu_2S	648	−18.1	+ +	+ + +	+	+ +	+	+ +
259.7 mg Cu_2SO_4 + 196.6 mg Cu_2S	698	− 7.7	+ +	+ + +	+	+ +	+	+ +
Neither Cu_2S nor $CuSO_4$ reacts with $CuSO_4$ below 710 K								

+ + + very strong, + + strong, + weak, 0 presence can not be excluded

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Zusammenfassung — Bedingungen für die Synthese von Cu_2SO_2 sowie die thermische Charakterisierung und die Reaktivität dieser Phase in Bezug auf einige andere im Cu–S–O-System unterhalb 710 K und bei $P_{SO_2} = 101$ kPa auftretende Phasen werden angegeben. Es wurde festgestellt, daß im festen Zustand zwei reversible Phasenübergänge erfolgen, die Verbindung bei 610 K ohne Zersetzung schmilzt und die Flüssigkeit bis 680 K stabil ist. Es wird darauf hingewiesen, daß Cu_2SO_2 thermisch stabiler als Cu_2SO_4 ist.

Резюме — Приведены условия синтеза соединения Cu_2SO_2 наряду с его термическими характеристиками и реакционной способностью с некоторыми другими фазами, образующимися в системе Cu–S–O при температуре ниже 710 K и давлении $P_{SO_2} = 101$ кПа. Установлено, что Cu_2SO_2 подвергается двум обратимым твердотельным превращениям, плавится без разложения при 610 K и в жидком состоянии устойчиво до температуры 680 K. Отмечено, что Cu_2SO_2 термически более устойчиво, чем Cu_2SO_4.