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STUDY OF THE DECOMPOSITION KINETICS OF Cu_2SO_2 UNDER NON-ISOTHERMAL CONDITIONS

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ABSTRACT

The decomposition of Cu_2SO_2 is an example of a reaction proceeding in a solid–liquid–gas system owing to the fact that liquid Cu_2SO_2 decomposes into a solid product (Cu_2S and Cu_2O) and gaseous SO_2. The decomposition of the liquid phase has been studied in a solid matrix composed of inert Al_2O_3 particles. TG, DTA and isothermal gravimetric methods were used to examine the samples which had a varied liquid content in the starting sample and a solid inert particle diameter. The liquid content as well as the particle size and the extent of reaction have been found to strongly influence the decomposition rate, and this is discussed.

INTRODUCTION

We previously reported [1,2] that the reaction

$$2CuSO_4 + 2Cu_2S = 3Cu_2SO_2 + SO_2 \tag{1}$$

results in a Cu_2SO_2 phase which melts congruently at 650 K, and is stable as a liquid at least up to 680 K. In the solid state, Cu_2SO_2 undergoes two reversible phase changes at 372 and 411 K, respectively [3]. Decomposition of liquid Cu_2SO_2 studied in SO_2 at ~ 101 kPa takes place at a considerable rate above 750 K in agreement with the equation

$$3Cu_2SO_{2(l)} = 2Cu_2O_{(s)} + Cu_2S_{(s)} + 2SO_{2(g)} \tag{2}$$

On studying $CuSO_4$–Cu_2S mixtures, with initial compositions determined by a molar ratio corresponding to $2:10 \leqslant n_{CuSO_4}/n_{Cu_2S} \leqslant 2:2$, it has been found that the $Cu_2SO_{2(l)}$ decomposition kinetics are intricately related to the solid Cu_2S content of the reacting mixture at the beginning of Cu_2SO_2 decomposition [4].

The purpose of this work is to indicate the primary parameters affecting Cu_2SO_2 decomposition and to estimate the dependence of the decomposition kinetics on these parameters. Elucidation of the problem is also of importance in understanding the mechanism and kinetics of the Cu_2S/$CuSO_4$ reaction and the kinetics of decomposition of the liquid into two solids and a gas. DTA, TGA and isothermal gravimetry appear to be the most reliable methods of answering these questions.

EXPERIMENTAL

Cu_2SO_2 obtained by the method described in ref. 3 and an inert substance, Al_2O_3 (POCh, Gliwice) were used in the experiments. Elemental analysis and X-ray powder diffraction showed that the purity of Cu_2SO_2 exceeded 95%. Chemically pure alumina was calcined at 1300 K and separated into three fractions of particles with $d = 225$, 98 and < 60 μm, respectively. Specimens of ground Cu_2SO_2 without Al_2O_3 and those with the Al_2O_3 fraction of $d = 98$ μm were studied. The compositions (by weight) were termed by mass ratios $w = m_{Cu_2SO_2} : m_{Al_2O_3} = 8:1, 6:1, 5:1, 4:1, 3:1, 2:1, 1:1$ and $1:2$, respectively, each of the mixtures containing the same amount of Cu_2SO_2, i.e., $m_{Cu_2SO_2} = 300$ mg. Mixtures with a composition corresponding to $w = 3:1$ and containing the Al_2O_3 fractions with $d < 60$ μm or $d = 225$ μ were also investigated. Mixtures composed of $CuSO_4$ and Cu_2S were also studied. The mixture compositions expressed by the molar ratio corresponding to $n_{CuSO_4} : n_{Cu_2S} = 2:2$ are in agreement with eqn. (1) and those with ratios of $2:4$ and $2:10$, i.e., with a Cu_2S excess with respect to eqn. (1).

The thermogravimetric (TG) and differential thermal analysis (DTA) measurements were carried out in SO_2 at $p_{SO_2} \approx 101$ kPa under non-isothermal conditions at temperatures ranging from ambient to 900 K and at a heating rate of $4\,^\circ C\ min^{-1}$.

Isothermal gravimetric measurements were made on all the above compositions in SO_2 at 759 ± 1 K with thermogravimeters such as those described in ref. 4.

RESULTS AND DISCUSSION

The results of non-isothermal experiments are given in Table 1 and some of the results from isothermal experiments are shown in Figs. 1 and 2. They were derived from experimental records of mass change versus time. The fractional decomposition, α, was calculated as a ratio of mass loss at a given instant to the theoretical maximum value of the loss developed from eqn. (2). The decomposition rate, $d\alpha/d\tau$ was assessed graphically from the plots of mass loss versus time.

Non-isothermal experiments have shown the position of the maximum melting effect to be independent of the Al_2O_3 content of a specimen (column 2, Table 1). Hence, the presence of the inert solid does not cause significant changes in the thermal properties of the specimens. Nevertheless, a marked influence of the inert substance on the position of the effects

TABLE 1

Results of non-isothermal measurements of mixtures of Cu_2SO_2 and Al_2O_3. $p_{SO_2} \approx 101$ kPa, heating rate 4°C min^{-1}, $Cu_2SO_2 = 300$ mg, $d_{Al_2O_3} = 98$ μm

Composition $w = m_{Cu_2SO_2}/m_{Al_2O_3}$	DTA			TG		α at maximal rate
	Temp. of melting maximum (K)	Temp. of beginning of decomposition (K)	Temp. of decomposition maximum (K)	Temp. of 0.01 decomposition fraction (K)	Temp. of Maximal rate (K)	
1:2	641	746	778	734	788	0.47
1:1	641	748	793	729	791	0.44
2:1	643	746	798	731	801	0.60
3:1 [a]	640	741	798	719	801	0.62
3:1	646	747	811	739	814	0.66
3:1 [b]	648	775	827	759	838	0.70
4:1	640	765	812	749	829	0.74
5:1	638	777	835	764	841	0.77
6:1	647	783	836	772	849	0.82
8:1	641	781	838	761	840	0.80
Pure Cu_2SO_2	641	780	828	773	849	0.84

[a] $d_{Al_2O_3} < 60$ μm.
[b] $d_{Al_2O_3} = 225$ μm.

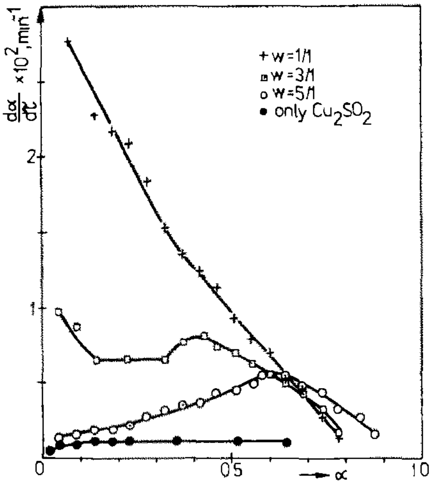

Fig. 1. Cu_2SO_2 decomposition rate dependence on the liquid Cu_2SO_2 content, w, and the progress of the reaction at 759 K and $d_{Al_2O_3} = 98$ μm.

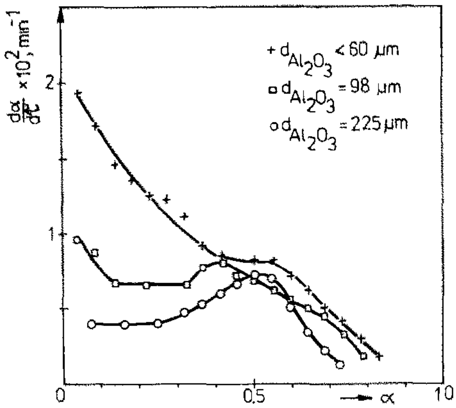

Fig. 2. Cu_2SO_2 decomposition rate dependence on the diameter of inert solid particles and the progress of the reaction at the original composition $w = 3:1$ and 759 K.

involved at other temperatures can be inferred from the shapes of the DTA and TG curves. Since the decomposition starts at temperatures much higher than that at which Cu_2SO_2 melts and because Al_2O_3 is a solid at the temperature range under study, the decomposition kinetics will depend on the amount of liquid in a specimen. In general, a decrease in liquid content leads to a decrease of the decomposition temperature and to an increase in the rate of the process (Table 1). But the dependence is not directly proportional and the effect of the liquid content manifests itself in the range $2:1 \leqslant w \leqslant 5:1$.

Hence, one can assume that the initial decomposition temperature is not lower than 720–730 K. A decrease in the Al_2O_3 particle dimensions at $w = 3:1$ seems to affect the process in a similar way (Table 1).

Isothermal experiments show that the decrease in liquid content of a specimen accounts for a high increase in the decomposition rate and for a significant change in the effect of the fractional decomposition, α, on the Cu_2SO_2 decomposition rate. At $4:1 \leqslant w \leqslant 8:1$, the decomposition rate increases with the progress of the process under study to achieve a maximum at $\alpha = 0.45$–0.55. On the other hand, at the liquid content corresponding to $w \leqslant 2:1$, the exclusive effect of the progression of the process is the decrease in the process rate. At $w = 3:1$, the shape of the curve $\mathrm{d}\alpha/\mathrm{d}\tau = \phi(\alpha)$ is complex (Fig. 1).

Figure 3 shows the reaction of $CuSO_4$ with Cu_2S at the decomposition stage of the resultant Cu_2SO_2 for a variety of original compositions relevant to different amounts of unprocessed Cu_2S at the start of decomposition of Cu_2SO_2. It also implies that the effect of the solid Cu_2S content of the reacting mixture on the Cu_2SO_2 decomposition kinetics can be compared with that of Al_2O_3.

The shapes of the curves $\mathrm{d}\alpha/\mathrm{d}\tau - \alpha$, especially for $w = 3:1$ and $1:1$, indicate the impossibility of controlling the reaction rate through the nucleation process alone. Equation (2) implies that the decomposition rate is dependent on the rate of transport of the gaseous product (SO_2) from the reaction zone to the outside. Scanning electron microscopy [2,5] has proved that reaction (2) occurs at the liquid–gas interface and that the solid reaction products are porous. Samples with excess Cu_2S are also porous and the Cu_2S particles are covered with a Cu_2SO_2 layer. Accordingly, the rate of the reaction of interest should be proportional to the area of the liquid–gas interface and to the transport rate of SO_2 being transferred through the sample to the outside after SO_2 formation at the interface. In the SO_2 atmosphere, the transport of SO_2 takes place due to a pressure gradient between the sample's interior and exterior. Hence, the transport rate should, at constant temperature, be inversely proportional to the flow resistance, which increases with increasing mean length of the transport path and with the decreasing diameter of the pores through which SO_2 flows.

When the liquid content is small at the outset of decomposition, the

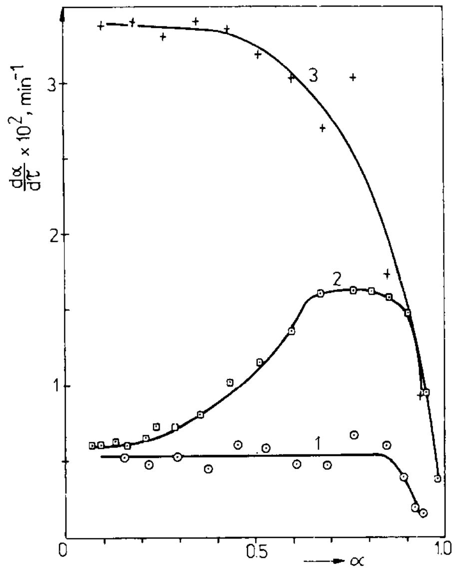

Fig. 3. Dependence of the rate of the reaction of $CuSO_4$ with Cu_2S at decomposition of Cu_2SO_2 on the progress of reaction at 772 K: (1) $n_{CuSO_4} : n_{Cu_2S} = 2:2$; (2) $n_{CuSO_4} : n_{Cu_2S} = 2:4$; (3) $n_{CuSO_4} : n_{Cu_2S} = 2:10$.

specimens can be characterized as shown in Fig. 4a. The Al_2O_3 particles are covered with a relatively thin layer of the liquid causing interparticle spaces which make the pores completely open. As the liquid layer is thin, one can suggest that the gas–liquid interface is equivalent to a planar surface. For this reason its area is independent of the decomposition process.

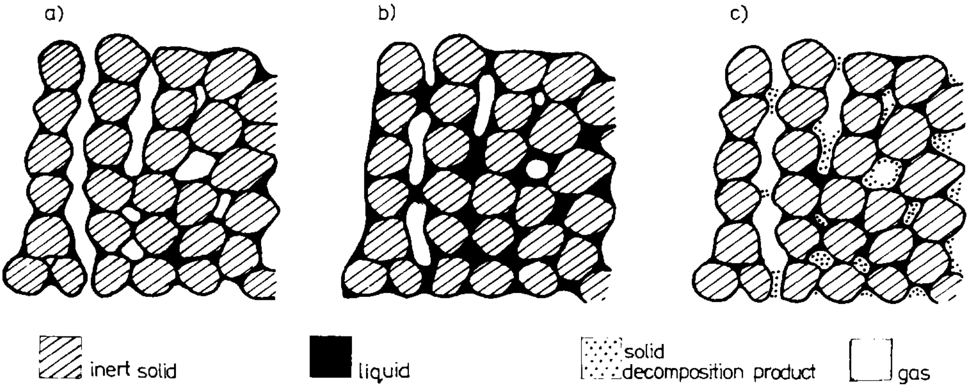

Fig. 4. Simplified model of the dependence of the sample macrostructure on the liquid content of starting samples and the progress of reaction. (a) Low liquid content, (b) high liquid content at the beginning of decomposition, (c) high liquid content at a certain extent of decomposition.

If the flow resistance through the resultant layer of solid products is significant, an inversely proportional relationship should exist between $d\alpha/d\tau$ and α. This assumption is confirmed by the shape of the $d\alpha/d\tau - \alpha$ curve for $w = 1:1$, conveying a straight-line relationship.

However, considering a rise in liquid content, one can suppose that it first results in a thickening of the liquid layer covering the Al_2O_3 particles. Hence, the diameter of the pores in the solid matrix decreases. If the liquid content increases further, however, some of the pores may be filled with liquid. Moreover, all access to other parts of the pores may be closed due to the formation of so-called "barriers" caused by an accumulation of liquid in the narrowest parts of the pores. Therefore, SO_2 transport outwards from the interior of entirely isolated spaces is blocked. Consequently, the decomposition cannot proceed at the interface inside the closed pores. Finally, a decrease in the pores' diameter fills up and isolates pores arising from an increase in the liquid content which leads to a diminution in area of the liquid–gas interface at which the reaction takes place. Additionally, all of the barriers formed make the path of SO_2 transport longer even if they do not quite close the pores. Therefore, an increase in the liquid content still causes increased SO_2 flow resistance due to the longer path of SO_2 transport and a decrease in pore diameter. The situation described above is presented in Fig. 4b. It illustrates the instant at which the progression of the process is responsible for all the effects developed from the formation of solid and porous reaction products.

As the liquid is being decomposed, it forms a thinner layer. Consequently, the pores' diameter increases. Simultaneously, previous liquid barriers form into a porous solid which is a product of the reaction. Formation of porous barriers enables transport of SO_2 from pores which were previously completely closed. Therefore, the area of the liquid–gas interface increases with the extent of decomposition due to isolated pores becoming connected with the exterior of the sample and due to an increase in the diameter of the pores. Furthermore, the increased diameter of the pores and the liquid barriers formed caused the resistance to SO_2 flow within the sample to be reduced. These processes enhance the rate of reaction (2). The situation is schematically illustrated in Fig. 4c. At a suitably high liquid content with $w \geqslant 4:1$, the agents responsible for the increase in decomposition rate during the course of the process will prevail at the beginning of the process. At a certain extent of decomposition, the possibilities of increasing the reaction surface area and of decreasing the flow resistance become negligible owing to the transformation of a large number of liquid barriers into porous product. Consequently, the reaction rate decreases because of a thickening of the solid product layer (Fig. 1).

Considering the effect of the Al_2O_3 particle size on the course of the reaction, it should be noted that for the same mass of a solid substance composed of non-porous particles, the surface area of the substance is inversely proportional to the diameter of the particles. Diminution of the particle diameter of the inert solid has a similar effect on the reaction rate as the effect of a decrease in the amount of liquid. A decreased particle diameter can be related to the decrease in pore diameter, which also facilitates blocking of the pores with the liquid. The particle size reduction has a final retarding effect on SO_2 transport and, therefore, on the reaction rate. Accordingly, the relation $d\alpha/d\tau = \phi(\alpha)$ for $w = 3:1$ and $d_{Al_2O_3} < 60$ μm will differ from the relation at $w = 1:1$ and $d = 98\mu$m (Figs. 1 and 2).

CONCLUSIONS

The decomposition temperature of the Cu_2SO_2 phase is not lower than 720–730 K. The decomposition rate of the phase mixed with an inert solid is inversely proportional to the Cu_2SO_2 content and to the particle size of the inert solid.

The decrease in Cu_2SO_2 content results in an increased reaction surface area and a decrease in the flow resistance of the gaseous product.

The decrease in particle size of the inert solid leads to an increase in both the reaction surface area and the gas flow resistance. The reaction progress enhances the SO_2 flow resistance due to the formation of a solid product layer. Simultaneously, the extent of the reaction decreases the flow resistance due to an increase in pore diameter and to a decrease in the length of the path of SO_2 transport. The increase in fractional decomposition gives rise to an enlargement of the surface area of the reaction owing to an increase in pore diameter and to the fact that closed pores are opened.

Therefore, each of the main parameters of the decomposition process, i.e., the Cu_2SO_2 content of the original mixture, the particle size of the inert solid and the progress of the reaction, strongly influence the reaction rate in a complex way.

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