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PROCESSES IN THE Cu_2S–$CuO.CuSO_4$ SYSTEM

ANALIZA PROCESÓW W UKŁADZIE Cu_2S–$CuO.CuSO_4$

The paper presents research on the course of the reaction in the system of Cu_2S–$CuO.CuSO_4$. It has been found out that reactions are running through the creation of copper sulphure (I) Cu_2SO_4. The final composition of products depends on the molar ratio of substrates. The processes run with the presence of liquid phase at a specific stage.

W pracy przedstawiono badania przebiegu reakcji w układzie Cu_2S–$CuO.CuSO_4$. Stwierdzono, że reakcje przebiegają poprzez tworzenie się siarczanu miedzi (I) Cu_2SO_4. Końcowy skład produktów reakcji zależy od stosunku molowego substratów. Reakcje zachodzą z wytworzeniem na pewnym etapie fazy ciekłej.

1. Introduction

In the research on the mechanism of metal sulphide deoxidisation, an important role is attributed to the processes between metal sulphides and sulphates. In many cases, the result is indirect products, most often in the form of base sulphates. Occurrence of such products was found out in the systems of ZnS–$ZnSO_4$, [1, 2], PbS–$PbSO_4$ [3, 4] or in mixed systems like ZnS–$PbSO_4$ [2, 5–8], PbS–$ZnSO_4$ [4], etc. Base sulphates may react with substrates, making it difficult to selectively differentiate between the successive process stages. This is the case where the temperature range for the original reaction overlaps the temperature range for secondary reactions.

An attempt of interpretation of processes in the system of Cu_2S–$CuSO_4$, given in [9], indicates that the reaction between copper sulphide (I) and copper sulphate (II)

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is occurring with indirect products. One of these may be base copper sulphate (II), resulting from the decomposition of $CuSO_4$ sulphate, as well as a result of sulphide deoxidisation with oxygen from sulphate decomposition. Base copper sulphate may in turn react with copper sulphide resulting in copper oxide I) or copper sulphate (I). The thermodynamic analysis of the possible course of reaction in this system, given in figure 1, indicates that reactions between Cu_2S and $CuO.CuSO_4$ may run even at lower temperatures than reactions between Cu_2S and $CuSO_4$. As a result, processes may overlap, and their identification is made more difficult.
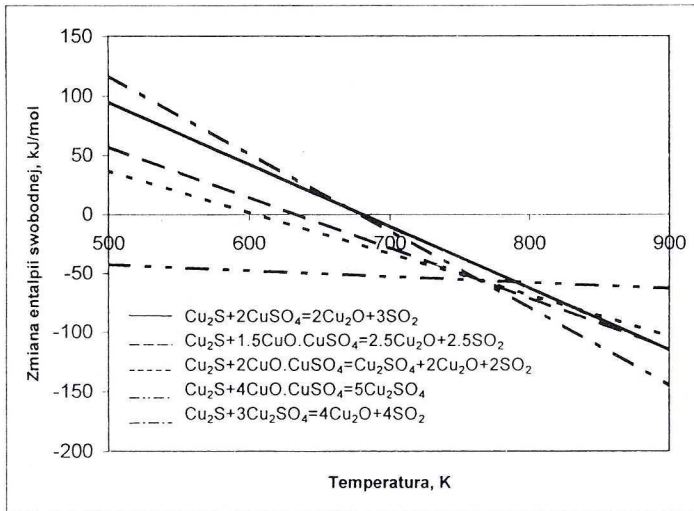

Fig. 1. Change in the reaction free enthalpy in the function of temperature

Literature does not provide much information on the processes in the system of $Cu_2S–CuO.CuSO_4$. In [10], the results of research over the reactions

$$2\,Cu_2S + 3\,CuO.CuSO_4 = 5\,Cu_2O + 5\,SO_4$$

are given for the molar ratio corresponding with stoichiometry of the above reaction, in the temperatures of 723, 803 and 873 K. It has been found out that during the reaction, a liquid phase originals in each of the tested temperatures. The final product of the process is Cu_2O. Finding of copper sulphate (I) Cu_2SO_4 during the reaction seems controversial, whose presence in this system is excluded by R o s e n - q v i s t [11]. It has to be noticed here that thermodynamic calculations indicate the possibility of this product origination in the indirect stage. Moreover, it has been noticed that the process speed is comparable with the speed of reactions in the system of $Cu_2S–CuSO_4$.

The purpose of this paper is to attempt an analysis of processes in the system of $Cu_2S–CuO.CuSO_4$ for different molar ratios of their reagents. The phase analysis of

products after a specific reaction stage in reference to the thermogravimetric analysis should allow for suggesting the description of the order of the chemical processes.

2. Experimental results and their description

Preparations for research in the processes in the system of Cu_2S-$CuO.CuSO_4$ have been made of the mixture of copper sulphide (I) and base copper sulphate (II) obtained from decomposition of sulphate in the temperature of 900 K. The X-ray phase analysis of the decomposition product suggested existence of the $CuO.CuSO_4$ phase alone. The material was mixed with Cu_2S obtained according to the procedure referred to in paper [1], in molar ratios of $1:1$, $2:1$ and $4:1$. The mixtures were first subjected to chemical analysis, the results of which allowed for accurate determination of the molar ratio of sulphide to base sulphate. It was:

- $Cu_2S + 1.007\ CuO.CuSO_4$
- $Cu_2S + 2.041\ CuO.CuSO_4$
- $Cu_2S + 3.932\ CuO.CuSO_4$

Then, the preparations were subjected to thermogravimetric analysis in the atmosphere of argon, at linearly increasing temperature with the rate of 10 degree per minute. The temperatures obtained are reported in figures 2–4. The analysis of the course of lines TG and DTA indicates that reactions begin in the temperature of ca. 700 K, irrespective of the molar ratio of sulphide to base sulphate. For the preparation of $Cu_2S + CuO.CuSO_4$, in the TG line, two ranges of mass loss are noticed, whereas for other molar ratios three ranges are found out. Moreover, for the

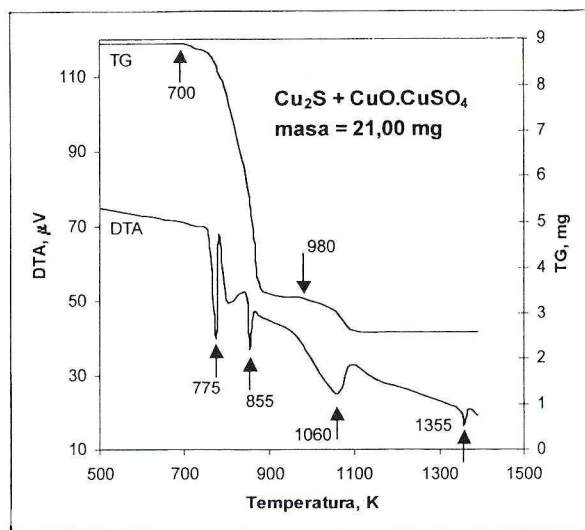Fig. 2. The thermogramme for the preparation of $Cu_2S + CuO.CuSO_4$

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preparations of $Cu_2S + CuO.CuSO_4$ and $Cu_2S + 2\,CuO.CuSO_4$, in the first stage of the process, two endothermic effects are noticed in the DTA line, with three effects for the $Cu_2S + 4\,CuO.CuSO_4$ preparation. The shape of DTA peaks is to be taken into account, which appear in the temperature range of ca. 780 K and 850 K. These peaks are very sharp, yet featuring low thermal effects (especially in the preparations
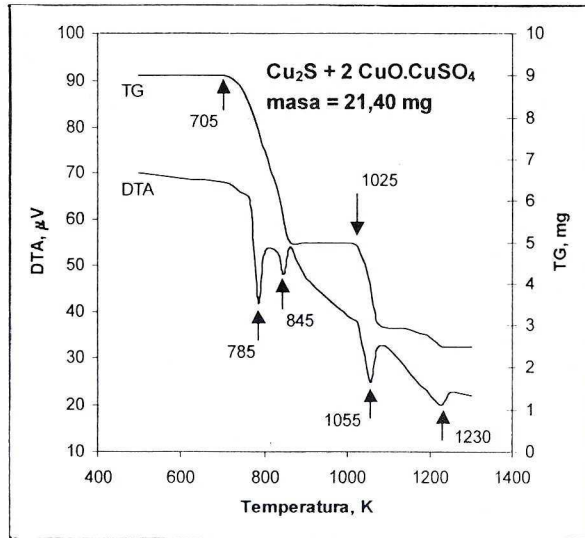

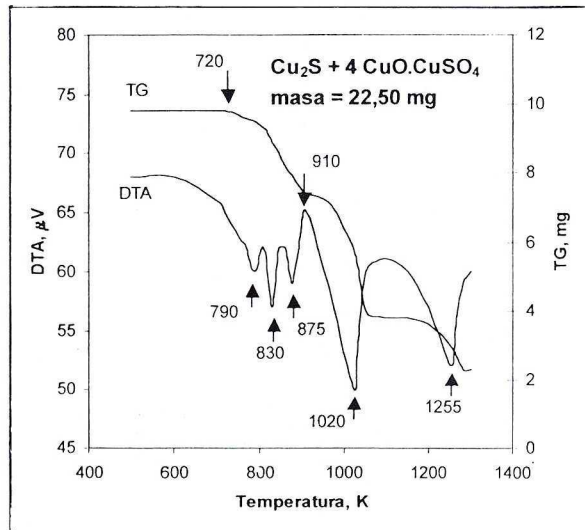Fig. 3. The thermogramme for the preparation of $Cu_2S + 2\ CuO.CuSO_4$

Fig. 4. The thermogramme for the preparation of $Cu_2S + 4\ CuO.CuSO_4$

of $Cu_2S + CuO.CuSO_4$ and $Cu_2S + 2\ CuO.CuSO_4$). Such peaks are characteristic of physical transformations rather than chemical reactions. Moreover, they appear in the beginning an in the end of the I stage of mass loss, thus not corresponding with mass loss. The analysis of the DTA line indicates that the combined endothermic effect increases with the increasing molar ratio of base sulphate to sulphide. This may be different in the partial thermal reactions, corresponding to the I stage of the process.
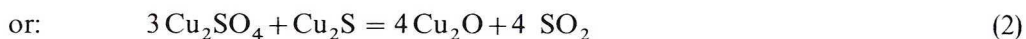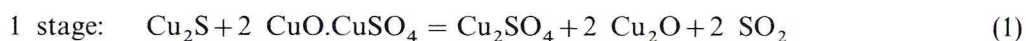
In order to determine the type of products originating during the processes, samples of the preparations, after a specific reaction stage, were subjected to the X-ray phase analysis. Its results are given in table 1. The phase analysis suggests the possibility of origination of copper sulphate (I) Cu_2SO_4 in the process. Cu_2O is the final product of the process. For preparations with the molar ratio of sulphate to sulphide of $2:1$ and $4:1$, the CuO phase is also appearing.
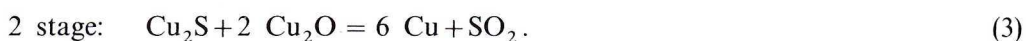
TABLE 1

Comparison of preparation mass changes: calculated against obtained from TG

Preparation	Stage of reaction	Relative preparation mass change in %	
		TG	from theoretical calculations
$Cu_2S + CuO.CuSO_4$	1	26.68	26.52
	2	4.76	5.22
	Σ	**31.44**	**31.74**
$Cu_2S + 2\ CuO.CuSO_4$	1	18.33	19.77
	2	10.14	10.33
	3	3.18	2.66
	Σ	**32.15**	**32.76**
$Cu_2S + 4\ CuO.CuSO_4$	1	12.44	11.66
	2	15.87	17.07
	3	7.47	7.07
	Σ	**35.78**	**35.80**

When the results of product phase analysis were taken into account after a specific stage of the reaction and the results were included for thermodynamic calculations (figure 1), the following scheme of the reaction course was assumed:

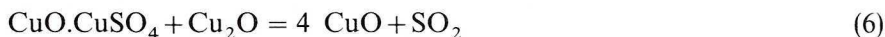1 stage: $\qquad Cu_2S + 2\ CuO.CuSO_4 = Cu_2SO_4 + 2\ Cu_2O + 2\ SO_2$ \hfill (1)

or: $\qquad 3\ Cu_2SO_4 + Cu_2S = 4\ Cu_2O + 4\ SO_2$ \hfill (2)

and with larger surplus of Cu_2O:

2 stage: $\qquad Cu_2S + 2\ Cu_2O = 6\ Cu + SO_2.$ \hfill (3)

With stoichiometry as for the (1) reaction:

2 stage: $Cu_2SO_4 = 2\ CuO + SO_2$ (4)

3 stage: $2\ CuO = Cu_2O + \frac{1}{2}\ O_2$ (5)

With surplus $CuO.CuSO_4$ in the second stage, apart from the reaction (4) there is a reaction:

$$CuO.CuSO_4 + Cu_2O = 4\ CuO + SO_2$$ (6)

and reaction (5) in the third stage.

The assumed reaction course for preparations with varied molar ratios of reagents was used for calculation of mass changes in the successive process stages. The summary of calculated values with the ones received according to the TG mass change line are given in table 2. When performing the calculations, it was assumed that every stage of the process is running to the very end. For each of the analysed preparations, good conformity was found between experimental values and those from theoretical calculations, especially for the total mass loss. Slight differences of the relative mass change in specific stages may result from the difficulty in the accurate delineation of particular process stages.

TABLE 2

Results of phase analysis of samples after a specific reaction stage

Preparation	Relative sample mass loss in %	Phases found
$Cu_2S + CuO.CuSO_4$	20	Cu_2O, Cu_2S, $CuO.CuSO_4$, Cu_2SO_4 — very little
	30	Cu, Cu_2O
$Cu_2S + 2\ CuO.CuSO_4$	15	Cu_2O, Cu_2SO_4, Cu_2S, $CuO.CuSO_4$
	28	Cu_2O, CuO
	32	Cu_2O
$Cu_2S + 4\ CuO.CuSO_4$	10	$CuO.CuSO_4$, Cu_2O, Cu_2SO_4, Cu_2S — little
	28	CuO, Cu_2O — little
	35	Cu_2O

The results of the base analysis and calculations performed based on the assumed course of the processes indicate that reactions in the system of Cu_2S–$CuO.CuSO_4$ run with the indirect product of copper sulphate (I) Cu_2SO_4. The final composition of the reaction products depends on the initial molar ratio of base sulphate to sulphide. For the molar ratio equal to or higher than 2, Cu_2O is the final product. With the value lower than 2, mixture of Cu and Cu_2O is the final product. One could believe that with high surplus of sulphide, Cu with unprocessed Cu_2S will be the final product.

3. Conclusions

The process reaction research in the system of Cu_2S–$CuO.CuSO_4$ indicate a multi-stage course of the processes, dependent on the molar ratio of reagents. On the basis of phase analysis of samples after a certain stage of reaction, it has been found out that in the I stage of the process, copper sulphate (I) Cu_2SO_4 originates, and the final composition of products depends on the molar ratio of substrates. The analyses executed allowed for suggesting the following process course:

- For the molar ration of $CuO.CuSO_4 : Cu_2S$ equal 2:

  I stage $\quad Cu_2S + 2\ CuO.CuSO_4 = Cu_2SO_4 + 2\ Cu_2O + 2\ SO_2$

  II stage $\quad Cu_2SO_4 = 2\ CuO + SO_2$

  III stage $\quad 2\ CuO = Cu_2O + \frac{1}{2}O_2$

- For the molar ration of $CuO.CuSO_4 : Cu_2S$ lower than 2:

  I stage $\quad Cu_2S + 2\ CuO.CuSO_4 = Cu_2SO_4 + 2\ Cu_2O + 2\ SO_2$

  $\qquad\qquad 3\ Cu_2SO_4 + Cu_2S = 4\ Cu_2O + 4\ SO_2$

  II stage $\quad Cu_2S + 2\ Cu_2O = 6\ Cu + SO_2$

- For the molar ration of $CuO.CuSO_4 : Cu_2S$ larger than 2:

  I stage $\quad Cu_2S + 2\ CuO.CuSO_4 = Cu_2SO_4 + 2\ Cu_2O + 2\ SO_2$

  II stage $\quad Cu_2SO_4 = 2\ CuO + SO_2$

  $\qquad\qquad CuO.CuSO_4 + Cu_2O = 4\ CuO + SO_2$

  III stage $\quad 2\ CuO = Cu_2O + \frac{1}{2}O_2$

On the basis of sample appearance, after a specific process stage, it has been found out that processes run at a specific stage with the presence of liquid phase.

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