

QUANTITATIVE ANALYSIS OF PHASES FORMED DURING THE OXIDATION OF COVELLITE (CuS)

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Abstract

A sample of covellite of particle size 45–90 μm was heated in air at $20^\circ\text{C min}^{-1}$ in a simultaneous TG-DTA apparatus. The phase compositions of the products at various temperatures were determined quantitatively by XRD and FTIR. By 500°C , 5.8% of Cu_2O had formed, and this increased to a maximum of 44.8% at 585°C after which it decreased to zero by 750°C . 10% of CuO had formed by 680°C , and then steadily increased to 83.6% at 1000°C . 5.9% of $\text{CuO}\cdot\text{CuSO}_4$ was found at 610°C , and increased to a maximum value of 79% after which it decomposed completely by 820°C .

Keywords: covellite, FTIR, oxidation, quantitative analysis, TG-DTA, XRD

Introduction

In a previous publication [1], building on the reports of other authors [2–8], we have described a thermal analysis study of the oxidation of covellite, CuS . Part of the research method involved the isolation of samples taken at various key temperatures, as indicated by thermal events in the TG-DTA record, followed by qualitative determination of the phases present. This enabled a reaction scheme to be written. This paper describes the quantitative determination of three of the main phases formed as a function of temperature. Cu_2O and CuO were determined by XRD methods, and $\text{CuO}\cdot\text{CuSO}_4$ was determined by an FTIR method.

Experimental

The quantitative XRD experiments were performed using a Siemens D500 Bragg–Brentano Diffractometer consisting of a copper X-ray tube, rotating specimen stage, and a sodium iodide detector. Pure samples of Cu_2O and CuO were obtained and used as internal standards. Each of the oxides was mixed with low-quartz ($\alpha\text{-SiO}_2$) in the ratio 85:15% mass/mass respectively. Approximately 20 mg of each of the mixtures was gently pressed onto a low background quartz sample holder using a glass slide.

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The samples were then analysed for Cu_2O and CuO using the reference intensity ratio (RIR, or more simply R) method [9]. Several lines from each phase were used to calculate the mass percentage, from which a mean value was obtained.

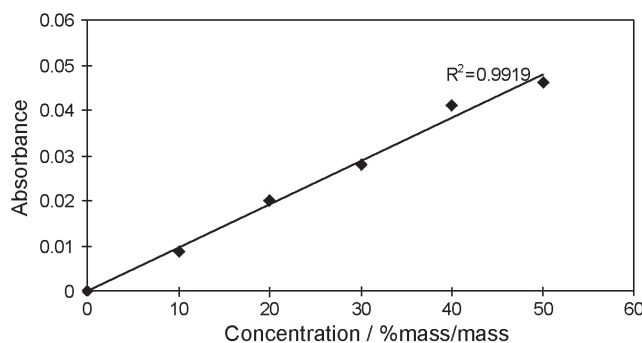


Fig. 1 Calibration curve for $\text{CuO}\cdot\text{CuSO}_4$ in a KBr matrix from peak height measurements of the line at 439 cm^{-1} in the FTIR spectrum

FTIR experiments were carried out on a Perkin Elmer 1720 FT-IR Spectrometer fitted with a deuterated triglycine sulfate (DTGS) detector. The quantitative analysis for $\text{CuO}\cdot\text{CuSO}_4$ involved accurately weighing about 7 mg of the partially oxidised sample and mixing it thoroughly with 1393 mg of KBr by grinding in a mortar and pestle. Approximately 200 mg of the sample/KBr mixture was further ground for 10 min to ensure complete homogeneity and reduce particle size. For each temperature in question, two discs were prepared as described above and analysed. A peak at 439 cm^{-1} in the $\text{CuO}\cdot\text{CuSO}_4$ spectrum was chosen as it was not interfered with by any of the other phases likely to be found in the matrix [10]. A calibration curve was constructed by plotting the measured peak height vs. concentration of known amounts of $\text{CuO}\cdot\text{CuSO}_4$ in a KBr matrix. The plot followed the Lambert–Beer law over the range of concentration of $\text{CuO}\cdot\text{CuSO}_4$ used (Fig. 1). Other matrices made from copper oxides and copper sulfate did not have any effect on the response of the peak height measured at 439 cm^{-1} .

Results and discussion

Covellite samples were thermally oxidised in dry air using a simultaneous TG-DTA apparatus. A typical TG-DTA record is shown in Fig. 2. In general, mass increases were associated with the formation of sulfates, and mass losses with oxidation reactions with the liberation of sulfur dioxide. The oxidation was stopped by programming the furnace to turn off at various temperatures, substituting air with nitrogen, and cooling the sample rapidly back to ambient temperature. The partially oxidised samples were analysed quantitatively by XRD and FTIR spectroscopy.

In XRD analysis, the ratio of line intensity for a given phase and an internal standard are related by the following equation.

$$\frac{I_{ij}}{I_q} = \frac{k_{ij}}{k_q} \left(\frac{X_{ij}}{X_q} \right) \quad (1)$$

where, I_{ij} =intensity of line i for phase j , I_q =intensity of a given quartz line, k =constant, X =mass fraction. k_{ij}/k_q is called the reference intensity ratio (RIR) or simply R . If the mass fractions of a given phase and internal standard are known, then R can be calculated and substituted in the equation to calculate the mass fraction of a phase in an unknown sample. A partial set of data for two Cu_2O lines in a $\text{Cu}_2\text{O}/\alpha\text{-SiO}_2$ is shown in Table 1.

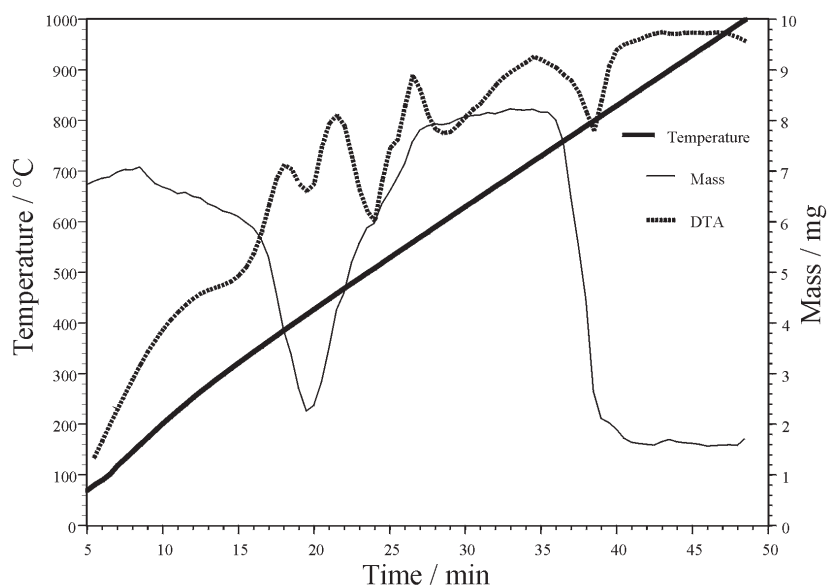


Fig. 2 TG-DTA record for oxidised covellite, particle size 45–90 μm , from ambient to 820°C in dry air at a heating rate of 20°C min^{-1}

Table 1 R data calculated for two Cu_2O lines from the XRD pattern of a $\text{Cu}_2\text{O}/\alpha\text{-SiO}_2$ mixture

Cu_2O		2θ	I	2θ	I
		29.303	39	36.171	1000
$\alpha\text{-SiO}_2$		R		R	
2θ	I				
26.364	95	0.07		1.86	
43.063	29	0.24		6.13	
50.207	11	0.62		16.04	
67.539	17	0.40		10.38	
67.947	20	34		8.82	

For example, from the XRD pattern Cu_2O has a line at $2\theta=36.17$, of $I=1000$, and $\alpha\text{-SiO}_2$ has a line at $2\theta=26.364^\circ$, of $I=95$. The mass ratio of Cu_2O and $\alpha\text{-SiO}_2$ in the mixture was 0.85:0.15, respectively. Substituting these values into the equation gives $1000/95=R(0.85/0.15)$, from which $R=1.86$. This method was used to calculate R values for the five strongest peaks for $\text{Cu}_2\text{O}/\alpha\text{-SiO}_2$ mixtures, as well as for mixtures of CuO and $\alpha\text{-SiO}_2$.

Table 2 Cu_2O and CuO content in the partially oxidised CuS samples

Temperature/ $^\circ\text{C}$	Cu_2O present/mass%	Mean	Standard deviation
500	3.5, 7.6, 8.5, 9.3, 2.2, 4.6, 5.2, 5.6	5.82	2.46
550	20.9, 28.4, 35.9, 19.9	26.3	7.45
585	44.8, 53.5, 48.6, 36.2, 49.1, 47.6, 30.6, 36.8, 51.6, 49.0	44.8	7.60
610	17.2, 32, 22.8, 29.6, 18.8, 24.4	24.1	5.83
630	29.8, 24.6, 31.5, 25.1, 21.8, 26.5, 21.9, 19.1, 23.2	24.8	3.96
653	18.1, 11.3, 11.8, 12.7, 13.3, 17.0	14.0	2.83
680	12.3, 10.9, 16.4, 10.9, 9.6, 14.5	12.4	2.56
Temperature/ $^\circ\text{C}$	CuO present/mass%	Mean	Standard deviation
680	11.5, 10.2, 9.9, 8.7, 10.3, 9.1	9.95	0.99
750	27.4, 37.2, 23.9, 32.4, 22.7, 21.7	27.6	6.13
821	62.8, 52.7, 54.2, 62.3, 54.8, 54.2, 73.5, 59.7, 56.3	58.9	6.58
1000	84.5, 85.0, 85.2, 85.1, 86.9, 75.1	83.6	4.26

FTIR spectroscopy was used for the determination of $\text{CuO}\cdot\text{CuSO}_4$. FTIR spectra were collected for CuS heated to 550; 585; 610; 640; 653; 680; 700; 750; 780 and 821 $^\circ\text{C}$. The peak height at 439 cm^{-1} was measured, and the quantity of $\text{CuO}\cdot\text{CuSO}_4$ determined from the calibration curve (Table 3). There is an increase in the formation of $\text{CuO}\cdot\text{CuSO}_4$ as the temperature increased above 600 $^\circ\text{C}$. At 610 $^\circ\text{C}$, 5.9% mass/mass of $\text{CuO}\cdot\text{CuSO}_4$ was formed, and increased to a maximum of 79.7% at 700 $^\circ\text{C}$, after which the concentration decreased steadily.

Partially oxidised samples of CuS taken at 500; 550; 585; 610; 630, 653; 680; 750 and 820 $^\circ\text{C}$ were mixed with $\alpha\text{-SiO}_2$ in an 85:15 mass ratio and their XRD spectra measured, using identical experimental conditions to those used for the mixtures of pure compounds. The intensities of the strongest lines with no interference for copper(I) and copper(II) oxides were determined, and the concentration of the oxides present calculated using the previously determined R values. An example of the calculation of the amount of Cu_2O present at 500 $^\circ\text{C}$ follows. Cu_2O has a line at $2\theta=61.669^\circ$ and $I=94$, and $\alpha\text{-SiO}_2$ has a line at 67.546° of $I=217$. The R value previously calculated corresponding to these lines was 1.86. Then $X_{ij}=\text{mass of unknown}$, $X_q=0.15$, $R=1.86$, $I_{ij}=94$, $I_q=217$.

Substituting into the rearranged equation gives

$$X_{ij}=(0.15/1.86)(94/217)100\%=3.5\% \quad (2)$$

This method was applied to the data collected for all the temperatures for all the possible pairs of lines. The results for Cu_2O and CuO are presented in Table 2. Cu_2O was first detected at approximately 500°C (5.82%), and this value increased with temperature to a maximum of 44.8% at 585°C . Above this temperature it was converted to either CuSO_4 or $\text{CuO}\cdot\text{CuSO}_4$, and by 750°C was no longer detected. Less than 10% by mass of the CuO was formed at 680°C . As the temperature increased, more CuO was formed by the decomposition of $\text{CuO}\cdot\text{CuSO}_4$, reaching a maximum of 83.6% at 1000°C . If CuO was the only product formed when CuS was oxidised to 1000°C , then the expected amount at this temperature would have been 100%. However, CuO decomposes to Cu_2O in the temperature range of $950\text{--}1000^\circ\text{C}$ [11].

Table 3 $\text{CuO}\cdot\text{CuSO}_4$ content in the partially oxidised CuS samples

Temperature / $^\circ\text{C}$	Peak height	Average	$\text{CuO}\cdot\text{CuSO}_4/\text{mass}\%$
610	0.0048/0.0055	0.0052	5.9
640	0.0204/0.0193	0.0198	22.5
653	0.0412/0.0423	0.0418	47.4
680	0.0603/0.0583	0.0593	67.2
700	0.0722/0.0683	0.0703	79.7
750	0.0608/0.0597	0.0602	68.3
780	0.0360/0.0388	0.0374	42.4

Conclusions

The results of quantitative phase analysis carried out on $\text{CuO}\cdot\text{CuSO}_4$, CuO and Cu_2O are presented graphically in Fig. 3.

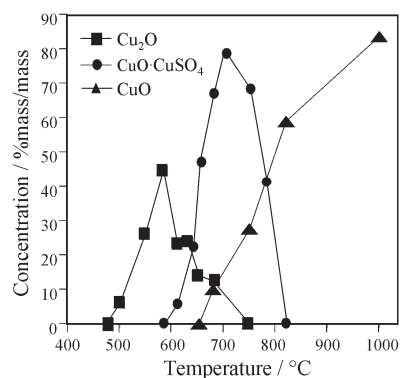


Fig. 3 Variation of $\text{CuO}\cdot\text{CuSO}_4$, Cu_2O and CuO concentrations as a function of temperature in oxidised CuS

Validation of the results was difficult, with one or two exceptions. At 750°C, with only two phases present i.e. $\text{CuO}\cdot\text{CuSO}_4$ and CuO , the results from XRD and FTIR analysis respectively summed to 96%. The mass loss beyond 653°C, due to the decomposition of the $\text{CuO}\cdot\text{CuSO}_4$, was 79% of the theoretical value if 100% of the compound was present, which compares excellently with the FTIR value of 79.7% found in a sample taken at 700°C. Hence the quantitative methods appeared to accurately reflect the phase composition of the partially oxidised samples of covellite.

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