Thermochimica Acta, 156 (1989) 107–115
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

INVESTIGATION OF THE OXIDATION OF SKUTTERUDITE BY THERMAL ANALYSIS

L.J. WILSON and S.A. MIKHAIL

Mineral Sciences Laboratories, CANMET, Department of Energy, Mines and Resources, Ottawa, Ont. K1A 0G1 (Canada)

(Received 18 April 1989)

ABSTRACT

The interaction of the mineral skutterudite (Co, Fe, Ni)As_{3-x} with oxygen was studied using differential thermal analysis. Thermogravimetry and X-ray diffraction were used as supplementary techniques. The oxidation was found to be a complex process which included the simultaneous dissociation of the mineral to lower arsenides and arsenic, and the oxidation of the products to arsenates and arsenic oxide vapour. The resulting mixture was composed of two arsenates ($2CoO \cdot As_2O_5$ and $3CoO \cdot As_2O_5$). The relative amounts of each arsenate were dependent on the partial pressure of oxygen. There was no evidence of the formation of any cobalt oxide species.

The thermal dissociation behaviour of skutterudite in an inert atmosphere was also examined by thermal analysis. There was a two-step release of arsenic vapour accompanied by the formation of the di- and monoarsenides. Synthetic $CoAs_3$ was also examined and the results were compared with those of the mineral.

INTRODUCTION

Cobalt arsenide minerals are minor constituents in some Canadian base metal sulphide ores, particularly in the silver veins of Cobalt, Ontario and in the copper–nickel minerals of Sudbury, Ontario, and Lynn Lake and Thompson, Manitoba [1]. The most important minerals involved are the higher arsenides skutterudite, (Co, Fe, Ni)As_{3-x} and safflorite, (Co, Fe, Ni)As_2 and sulpho-arsenides such as cobaltite, CoAsS. As indicated by the chemical formulae, extensive substitution of the transition metals occurs in the naturally occurring arsenides.

During pyrometallurgical processing of arsenic-bearing concentrates, arsenic volatilizes and may be emitted with the flue gases creating a potential environmental hazard. A better understanding of the oxidation of cobalt arsenides would be of value in developing control strategies which can reduce arsenic emissions.

Two previous publications have examined the oxidation of the mineral skutterudite using differential thermal analysis (DTA) in air. Asensio and Sabatier [2] produced characteristic diagrams for skutterudite ($Co_{0.8}Fe_{0.2}$-

$As_{2.5}$) and reported that the oxidation of the mineral occurred in one step between 500 and 650 °C. In a similar work, Maurel [3] observed a single peak between 500 and 700 °C during the oxidation of the skutterudite mineral $(Co_{0.6}Ni_{0.3}Fe_{0.1})As_3$. The oxidation products were reported to be a complex arsenate (or a mixture of arsenates) and As_2O_3. An aggregate formula for the arsenate was determined by chemical analysis to be 5(CoO, NiO, FeO) · $2As_2O_5$.

In the present work, the oxidation of skutterudite was studied in order to determine its oxidation route and to identify the final products. The thermal dissociation of skutterudite in an inert atmosphere and the effects of skutterudite particle size and of oxygen partial pressure on the oxidation process were examined. The present work utilizes thermogravimetry (TG) as well as DTA to follow the reaction process. X-ray diffraction (XRD), spectrochemical and electron microprobe analyses were used in the identification of the starting materials and the reaction products.

EXPERIMENTAL

Two specimens were used in this study: a crystalline skutterudite mineral sample from Bou-Azzer, Morocco and a synthetic $CoAs_3$ sample. The skutterudite mineral was crushed and sized into fractions of 74–105 μm (−150 + 200 mesh), 45–53 μm (−270 + 325 mesh) and < 38 μm (−400 mesh). The identity of the mineral was confirmed by XRD to be skutterudite, $(Co, Ni, Fe)As_{3-x}$. Spectrochemical and electron microprobe analyses indicated that the impurity content is less than 2% and that the composition can be represented by the following chemical formula: $(Co_{0.73}Ni_{0.17}Fe_{0.10})$-$(As_{2.91}S_{0.06})$. The identity of the synthetic material (< 2 μm particle size) was confirmed by XRD and microprobe analysis to be stoichiometric $CoAs_3$. No impurities were detected.

DTA was performed with a laboratory-made apparatus which has been described elsewhere [4]. For the oxidation experiments, 5-mg samples were heated in platinum pans at an average rate of 7–8 °C min^{-1}. For the tests in inert atmosphere, 40-mg samples were heated in alumina crucibles at an average rate of 18–20 °C min^{-1}.

TG analysis was performed with a DuPont 9900TA–951TGA thermal analysis system. Samples of 5–40 mg, contained in quartz pans, were heated in dynamic N_2 or N_2/O_2 atmospheres at 20 °C min^{-1}.

RESULTS AND DISCUSSION

Thermal dissociation

In Fig. 1, DTA diagrams of skutterudite (< 38 μm particle size) and synthetic $CoAs_3$ in N_2 reveal two endothermic peaks indicating a two-stage

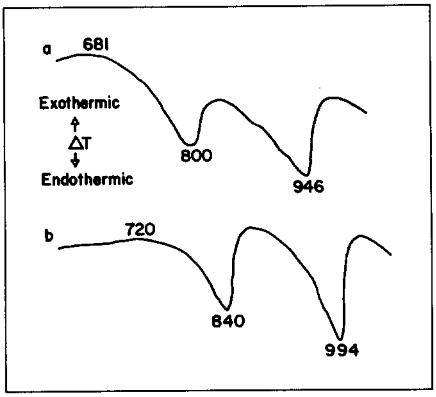

Fig. 1. DTA diagrams for (a) skutterudite (< 38 μm) and (b) synthetic $CoAs_3$ in nitrogen.

dissociation. To identify the dissociation products, some experiments were interrupted at the end of each DTA peak (T_{max}) and the samples were examined by XRD. DTA and XRD results, as presented in Table 1, indicate that the dissociation may be described on the basis of the following equations

$$CoAs_3 \rightarrow CoAs_2 + \tfrac{1}{4}As_4 \qquad (1)$$

$$CoAs_2 \rightarrow CoAs + \tfrac{1}{4}As_4 \qquad (2)$$

It is noticeable that the dissociation of skutterudite mineral is shifted downwards in temperature by 40–50 °C and the peaks are not as well defined as those for the synthetic material. This is probably because of the presence of iron and nickel in the mineral.

The dissociation of skutterudite and $CoAs_3$ in N_2 were also examined by TG. The results, as illustrated in Fig. 2, show that the synthetic material displays a clear two-step process. The weight losses at the plateaus (26.0 and 52.5%) coincide closely with the theoretical cumulative weight losses of 26.4 and 52.8% for reactions (1) and (2), respectively. It is also noticeable that the

TABLE 1

DTA of thermal dissociation of skutterudite

Onset (°C)	Peak 1 (°C)	Peak 2 (°C)	T_{max} (°C)	Weight loss (%)	Identification of T_{max} product by XRD
–	–	–	708	6.6	major: (Co, Ni, Fe)As_3 minor: (Co, Ni, Fe)As_2
680	799	–	836	30.4	major: (Co, Ni, Fe)As_2 minor: (Co, Ni, Fe)As_x
681	800	946	1019	49.8	major: (Co, Ni, Fe)As
720 [a]	840	994	1059	53.0	major: CoAs

[a] Synthetic $CoAs_3$.

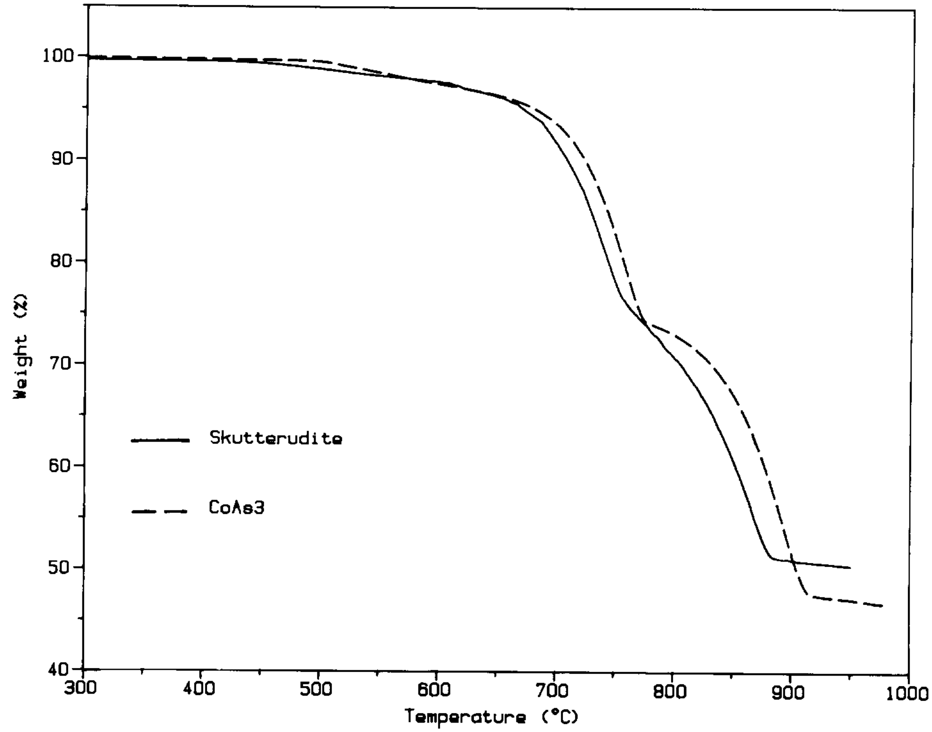

Fig. 2. TG diagrams for skutterudite (< 38 μm) and synthetic $CoAs_3$ in nitrogen.

mineral exhibits a more gradual weight-loss curve with inflections at weight losses which are less than the theoretical values for $CoAs_3$. As expected, the weight loss due to the release of arsenic started at a lower temperature for the mineral (~ 430 ° C) than for the synthetic material (~ 495 ° C). The shift towards lower temperatures of the TG weight-loss steps relative to the DTA peaks is probably as a result of instrumental factors.

The results of this series of experiments in inert atmosphere showed that the dissociation of the mineral may represent an integral part of the total oxidation process.

Oxidation

There is agreement between earlier investigators that the oxidation of skutterudite occurs in one step. This was confirmed in the present study and is illustrated in the DTA curves of Figs. 3 and 4 and the TG curves of Fig. 5. It must be noted that the oxidation reaction is highly exothermic and care had to be taken to select the sample size and heating rate so that thermal runaway did not occur.

It is obvious from the DTA diagrams in Fig. 3 that the major exothermic peak shifts to a lower temperature with a decrease in skutterudite particle

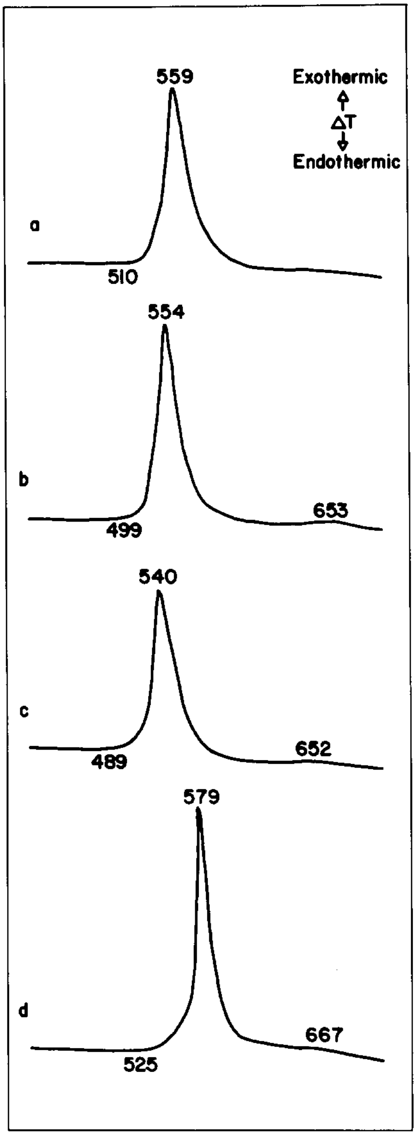

Fig. 3. DTA diagrams for different particle sizes of skutterudite: (a) 74–105 μm; (b) 45–53 μm; (c) < 38 μm; and for synthetic $CoAs_3$ (d) in pure oxygen.

size. This is to be expected as the surface area exposed to oxidation is larger with smaller particle sizes. The samples were weighed before and after the DTA experiments and the recorded weight losses associated with the DTA peaks are given in Table 2. These weight losses did not correspond to the formation of any single oxidation species, but rather to a mixture of $2CoO \cdot As_2O_5$ (2 : 1) and $3CoO \cdot As_2O_5$ (3 : 1) arsenates, according to the XRD analysis. XRD did not indicate the presence of any oxides. The

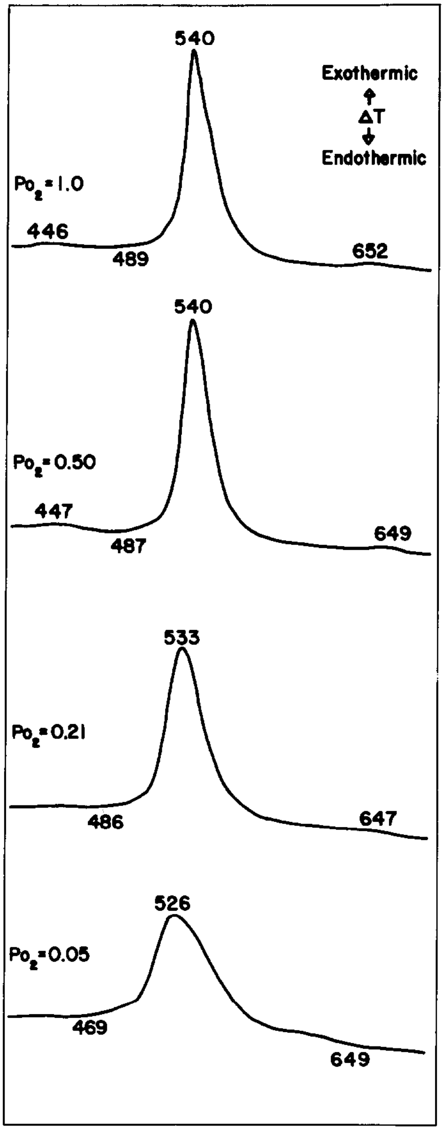

Fig. 4. DTA diagrams for skutterudite (< 38 μm) in different oxygen partial pressures.

oxidation may actually be a combination of two reactions

$$12CoAs_3 + 39O_2 \rightarrow 6(2CoO \cdot As_2O_5) + 6As_4O_6 \tag{3}$$

$$12CoAs_3 + 37O_2 \rightarrow 4(3CoO \cdot As_2O_5) + 7As_4O_6 \tag{4}$$

The theoretical weight losses associated with reactions (3) and (4) are 33.1 and 46.6%, respectively, and a mixture of (2 : 1) and (3 : 1) arsenates would result in weight losses similar to those obtained experimentally. It should be noted that the weight loss increased with an increase in the sample particle

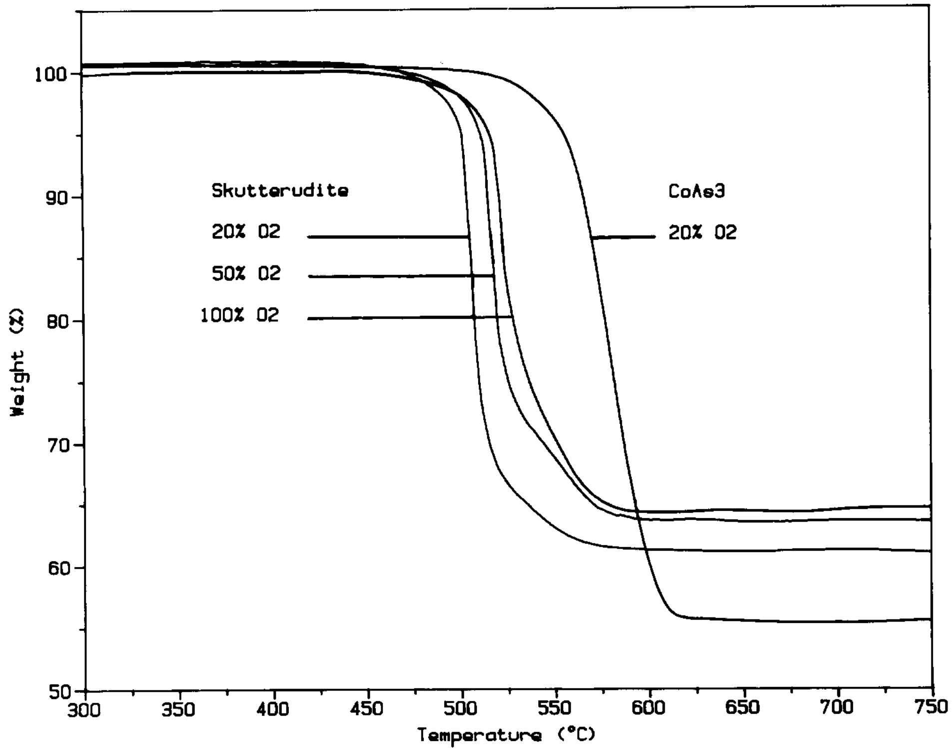

Fig. 5. TG diagrams for skutterudite (< 38 μm) and synthetic $CoAs_3$ in different oxygen partial pressures.

size. It is reasonable to conclude that with larger particle size material, more (3 : 1) and less (2 : 1) arsenates are produced on oxidation.

If thermal dissociation (reaction (1)) precedes the oxidation process, it is possible that reactions (3) and (4) occur via a complex process consisting of

TABLE 2

DTA of oxidation of skutterudite

Particle size (μm)	P_{O_2} (atm)	Onset (°C)	Peak (°C)	Weight loss (%)
74–105	1.0	510	559	40.4
45–53	1.0	499	554	35.2
< 38	1.0	489	540	34.3
< 38	0.5	487	540	36.6
< 38	0.21	486	533	37.4
< 38	0.05	469	526	38.3
< 2 [a]	1.0	525	579	40.2

[a] Synthetic $CoAs_3$.

an endothermic dissociation of skutterudite and highly exothermic oxidation reactions involving O_2, As_4 and $CoAs_2$ to form As_4O_6 vapour and arsenates.

Closer examination of the DTA curves for smaller particle sizes (Fig. 3) reveals a small exothermic peak at ~ 650 ° C. It is suggested that a rapid oxidation reaction may result in the formation of an impervious arsenate product layer at the surface of the reacting particles before all of the skutterudite has been oxidized. As the sample continues to be heated, the thermal dissociation of unreacted skutterudite (reaction 1)) and hence, the release of arsenic, causes the rupture of the surface layer and exposes the unreacted cores to oxygen.

The last DTA curve in Fig. 3 is for synthetic $CoAs_3$. It is a sharper peak than that for the mineral, probably because of its purity. XRD analysis identified the product as a mixture of (2 : 1) and (3 : 1) arsenates. The peak is shifted to a higher temperature by 40 ° C relative to the mineral of smallest particle size, as it was for the thermal dissociation in N_2.

The DTA curves obtained by heating the mineral sample at different partial pressures of oxygen (P_{O_2}) are shown in Fig. 4. Upon closer examination of the curves for $P_{O_2} = 1.0$ and 0.50, a very small exothermic effect can be seen at ~ 446 ° C. This exothermic activity was more apparent when larger samples were used. It is postulated that some initial oxidation takes place with the formation of an impervious product layer at the surface of the particles which prevents further rapid reaction. Disruption of this product layer at higher temperatures would lead to the exposure of new surfaces to further oxidation as revealed by the major exothermic peak on the diagrams. There was no change between XRD patterns before and after the minor peak indicating that the surface layer was very thin. At lower oxygen partial pressures, no product layer seems to have formed (the low temperature exothermic peak was absent) and the major oxidation reaction occurred earlier. Moreover, it is noticeable that the rate of the oxidation reaction decreased with the decrease in oxygen partial pressure as indicated by the shape of the peak. This suggests that the oxidation reaction may be controlled by the diffusion of oxygen through the gas boundary layer. It is also evident (Table 2) that with lower oxygen partial pressure the weight loss increases, which implies an increase in the (3 : 1) arsenate formation.

Figure 5 depicts the TG curves of skutterudite and synthetic $CoAs_3$ in different partial pressures of oxygen. In concurrence with the DTA results, the weight-loss step shifts down in temperature and the total weight loss increases as the partial pressure of oxygen decreases. In addition, the slight weight change at temperatures greater than 600 ° C coincides with the previously observed exothermic activity. The weight loss for synthetic $CoAs_3$ in air is 44.5%, which indicates that the product is almost entirely (3 : 1) arsenate as was confirmed by XRD.

CONCLUSIONS

The oxidation of the skutterudite mineral was found to be a complex process which includes the simultaneous dissociation of the mineral to lower arsenates and arsenic, and the oxidation of the products to arsenates and arsenic oxide vapour. The composition of the resulting arsenate mixture is dependent on the partial pressure of oxygen.

The above results indicate that a complete removal of arsenic from skutterudite-bearing ores in a roasting operation is not readily achievable under either oxidizing or inert conditions. Under oxidizing conditions, skutterudite undergoes incomplete oxidation to form a mixture of arsenates and thus retains arsenic in the solid product. Under inert conditions, skutterudite dissociates sequentially to the di- and monoarsenides, but further removal of arsenic occurs with difficulty.

ACKNOWLEDGEMENTS

The authors wish to thank K. Besso and P. Carrière for XRD analysis, R. Horton and J. Hole for spectrochemical analysis, G. Laflamme for electron microprobe analysis and A.M. Turcotte for the preparation of the synthetic $CoAs_3$. Thanks are also extended to A.H. Webster for his valuable discussion. Copyright of this paper belongs to the Minister of Supply and Services Canada, 1989.

REFERENCES

1 R.S. Young (Ed.), Cobalt—Its Chemistry, Metallurgy, and Uses, Am. Chem. Soc. Mono. Ser., No. 149, Reinhold, New York, 1960, pp. 16–23.
2 I. Asensio and G. Sabatier, Bull. Soc. Fr. Mineral. Cristallogr., 81 (1958) 12.
3 C. Maurel, Bull. Soc. Fr. Mineral. Cristallogr., 87 (1964) 377.
4 L.J. Wilson and S.A. Mikhail, Thermochim. Acta, 112 (1987) 197.