

## EFFECT OF HEATING RATE ON THE TG CURVE DURING THE OXIDATION OF NICKEL SULPHIDE CONCENTRATES

J.G. DUNN and S.A.A. JAYAWEERA

*School of Applied Chemistry, Western Australian Institute of Technology, Perth 6102 (Australia)*

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### ABSTRACT

Thermogravimetry has been used to study the oxidation of a floated nickel sulphide concentrate mixture at heating rates between 1 and 50°C min<sup>-1</sup>. The TG profile observed was significantly dependent on the heating rate.

### INTRODUCTION

Sample heating rate is an important parameter in thermoanalytical studies and several effects which are evident in the TG curve as a result of a change in heating rate have been documented [1–3]. The relationship between heating rate and mechanism of reaction, however, has received scant attention in standard texts. We wish to illustrate this relationship by reporting the dramatic changes which occurred in the TG curves during the oxidation of a mineral concentrate containing various nickel sulphide phases, obtained at heating rates between 1 and 50°C min<sup>-1</sup>.

### EXPERIMENTAL

#### *Sample preparation*

The material studied by thermogravimetry in this work was a mixture containing approximately 70% of a floated nickel concentrate, 12% furnace dust and 18% laterite as a fluxing agent. The composition of the mixture is the same as that of the charge used at the Western Mining Corporation's flash smelter at Kalgoorlie, Western Australia. The floated nickel concentrate contained approximately 12% nickel, present mainly as pentlandite and violarite, with nickeliferous pyrrhotite, pyrite, talc and antigorite also present [9]. The particle size of the mixture was in the range 20–100 μm.

### Procedure

Samples (15 mg) of the mixture were heated in a platinum crucible on a Stanton Redcroft TG750 thermal balance. The atmospheres used were air and oxygen at a flow rate of  $50 \text{ cm}^3 \text{ min}^{-1}$ . Heating rates were varied from 1 to  $50^\circ\text{C min}^{-1}$ . The TG curve and the furnace temperature were recorded on a Rikadenki two-channel flat bed chart recorder.

### RESULTS AND DISCUSSION

The TG curves for the sulphide mixture in oxygen and in air are shown in Figs. 1 and 2, respectively. The temperature of the maximum weight gains and the extrapolated onset temperature for the major weight loss are given in Table 1 and are presented graphically in Fig. 3. The weight gain regions can be attributed to the formation of metal sulphates and the major weight losses to the oxidative decomposition of metal sulphides and decomposition of sulphates. This behaviour has been previously reported in thermoanalytical studies on metal sulphides such as those of lead [4], zinc [5], nickel [6], iron [7] and on pentlandite [8].

In oxygen at heating rates of 1, 5 and  $10^\circ\text{C min}^{-1}$ , two distinct weight gain maxima are evident. Up to about  $500^\circ\text{C}$ , there is a steady weight gain due to the formation of metal sulphates. This is followed by a weight loss, which can be attributed to the oxidation of a sulphide phase. Further metal sulphate is then formed and the second weight maximum occurs when rapid partial oxidation of sulphide coupled with decomposition of iron(II) sulphate

TABLE 1

Temperatures of decomposition and weight gain maxima at different heating rates

Atmosphere	Heating rate ( $^\circ\text{C min}^{-1}$ )	Extrapolated onset decom- position temperature ( $^\circ\text{C}$ )	Temperature of first weight gain maximum ( $^\circ\text{C}$ )	Temperature of second weight gain maximum ( $^\circ\text{C}$ )
Oxygen	1	595	490	565
	5	630	505	605
	10	640	497	615
	15	500	495	565
	30	500	494	560
	50	470	470	555
Air	5	620	475	595
	15	645	475	625
	30	480	440	640
	50	470	415	645

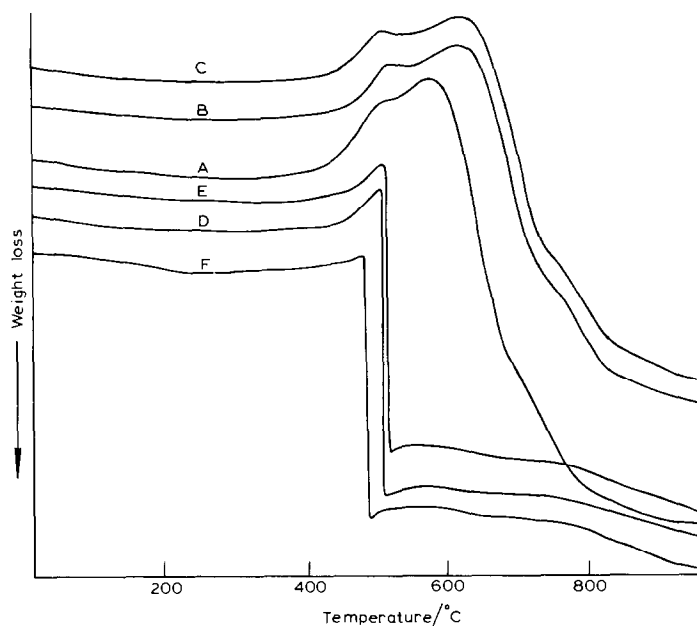


Fig. 1. TG curves of nickel sulphide concentrate mixture in oxygen. Heating rate ( $^{\circ}\text{C min}^{-1}$ ): A, 1; B, 5; C, 10; D, 15; E, 30; F, 50.

take place [7]. The oxidation of  $\text{Ni}_3\text{S}_2$  is reported to occur at about  $800^{\circ}\text{C}$  and above  $800^{\circ}\text{C}$ ,  $\text{NiSO}_4$  decomposes [8]. The reaction profiles are typical of stepwise reaction sequences, as commonly found at moderate heating rates.

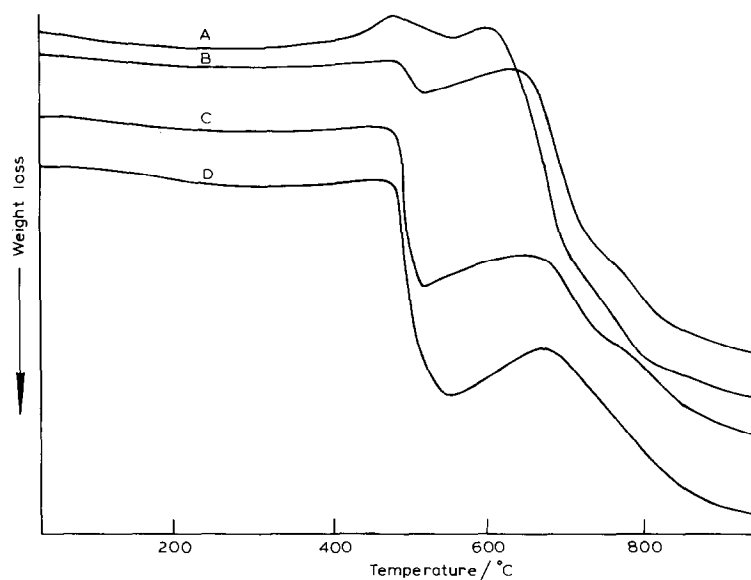


Fig. 2. TG curves of nickel sulphide concentrate mixture in air. Heating rate ( $^{\circ}\text{C min}^{-1}$ ): A, 5; B, 15; C, 30; D, 50.

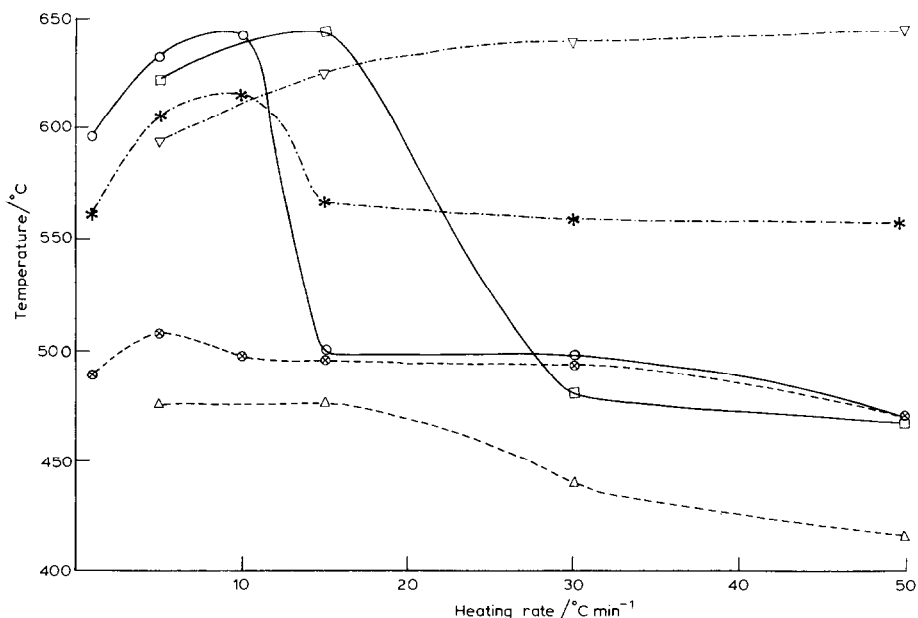


Fig. 3. Variation of temperature of decomposition and weight gain maxima at different heating rates. O, Decomposition in oxygen; □, decomposition in air; ⊗, first weight gain maximum in oxygen; Δ, first weight gain maximum in air; \*, second weight gain maximum in oxygen; ▽, second weight gain maximum in air.

The extrapolated onset temperatures for the major weight loss increase with increase in heating rate (see Fig. 3). The lower temperature weight gain maximum tended to be relatively unaffected by heating rate, but the higher temperature weight gain maximum moved to higher temperatures with increase in heating rate.

At heating rates of 15, 30 and 50°C min<sup>-1</sup>, a striking change in the reaction profile was observed. The formation of sulphate was still evident, although decreasingly so as the heating rate increased. The weight gain region was followed by a very rapid weight loss, which tended to occur at increasingly lower temperatures as the heating rate increased, and up to 170°C below the onset temperatures observed for the profiles obtained at heating rates of 10°C min<sup>-1</sup> or below. A small weight gain beyond this large weight loss indicated formation of nickel sulphate [8]. Based on the maximum amounts of oxidisable material, the extent of reaction achieved at heating rates of 15, 30 and 50°C min<sup>-1</sup> were 13.9, 13.3 and 11.7%, respectively. These reaction profiles are typical of ignition reactions where high heating rates produce a fast self-sustaining reaction which is highly exothermic. Several papers on ignition reactions in pyrotechnic systems report similar behaviour [10].

In air, the TG curves are similar in general appearance to those in oxygen, but reactions tend to occur to a lesser extent and at different temperatures. The temperature for the first weight gain maximum is always less than in

oxygen, but for the second is generally higher.

The transition from stepwise to ignition reaction was influenced also by the sample mass, larger masses requiring lower heating rates to produce the ignition reaction. Thus at a heating rate of  $10^{\circ}\text{C min}^{-1}$  in oxygen, a 25 mg sample showed an ignition reaction commencing at  $470^{\circ}\text{C}$ , whereas with a 5 mg sample, no ignition reaction was observed at a heating rate of  $20^{\circ}\text{C min}^{-1}$ . Higher masses also encouraged the formation of sulphates.

The sample container used for these experiments was made of platinum and the catalytic effect of this material on the formation of sulphates by the oxidation of sulphides is well known [5]. Hence the container may affect the extent of reactions as well as the temperatures at which they occur.

## CONCLUSION

This work emphasises the need in the thermoanalytical investigations of reactive materials to examine the effect of heating rate and sample mass on the reaction mechanism. Even small changes in either parameter could produce very different results. The effect of sample container material also should be considered.

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