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THE EFFECT OF EXPERIMENTAL VARIABLES ON THE MULTIPLE PEAKING PHENOMENON OBSERVED DURING THE OXIDATION OF PYRITE

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ABSTRACT

TG-DTA and heat-flux DSC traces were obtained on samples of a pyrite heated under oxidising conditions. Particular attention was given to the sharp exothermic peaks that occurred prior to the major exothermic peak. Experimental variables such as particle size, heating rate, oxygen concentration and sample mass were all found to influence the number and intensity of these peaks.

INTRODUCTION

One of the characteristic features observed in the DTA/DSC record during the oxidation of sulphides is a number of sharp exotherms which precede the major exotherm. They have been attributed to a number of causes, which include periodic oxygen starvation (1); preferential oxidation of some particles (2,3); and periodic cracking of protective oxide coatings which expose fresh sulphide for reaction (4,5).

We have investigated this effect as part of a general study of the oxidation of pyrite under a variety of experimental conditions. Another explanation is given for the presence of the peaks

EXPERIMENTAL

The pyrite was a natural mineral from the Dominican Republic. Electron Probe Microanalysis (EPMA) and chemical analysis determined the major elements to be Fe (46.1%) and S (52.8%). The remaining 1.1% consisted of Ti, Si, Al, Ca, K, and Cl. The structure was confirmed by X-ray diffraction.

Air and oxygen were of industrial grade and obtained from Commonwealth Industrial Gases Ltd.

A quantity of the pyrite was hand ground in an agate mortar and pestle, in a glove box under nitrogen. The product was then sieved using brass Endecott Laboratory Test Sieves to isolate fractions of particle size <45 and 90-120µm. A further sample was crushed to <45µm, and fractionated using 30, 20, and 10µm screens on a sonic sifter.

Measurements were made using a Stanton Redcroft STA-781 simultaneous TG-DTA instrument interfaced to an IBM compatible microcomputer. Heat flux DSC data was acquired with a Du Pont 1090 Thermal Analyser equipped with a standard DSC cell and microprocessor unit.

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The platinum sample crucibles were 5.2mm in internal diameter and 4.00mm in height. A gas flow of 30ml min^{-1} was used.

RESULTS and DISCUSSION

Particle size effects

Samples of the pyrite were screened into fractions of size <10, 10-20, 20-30, and 30-45μm. The individual fractions were microscopically examined to ensure that only particles in the expected size range were present. Some fractions were discarded because of incorrect size distributions, and others because significant quantities of fines were adhering to the larger particles. The selected fractions were oxidised in the simultaneous TG-DTA equipment at a heating rate of 2.5°C min^{-1} in an air or oxygen atmosphere. The thermal records obtained are reproduced in Figure 1.

The sharp exothermic peaks are evident at temperatures between 380-410°C. As the particle size increases, two effects are apparent. Firstly, although the number of peaks remains relatively constant at 8 or 9 for each of the smaller size fractions, the peaks disappear above a particle size of 30μm (see Fig. 1d). Although Fig. 1d was obtained at a ten times more sensitive setting than the others, there was still no evidence of the sharp peaks. Other fractions tested of 45-75, 75-90 and 90-125μm under identical experimental conditions also showed no evidence of the sharp exotherms. Secondly the intensity of the peaks diminishes as the particle size increases. These results indicate that the sharp exothermic peaks are particle size dependent.

Effect of heating rate

Samples of the <45μm fraction of pyrite were oxidised in an air atmosphere at heating rates between 2.5-40°C min^{-1}. The TG-DTA records are presented in Figure 2. The number of sharp exothermic peaks decreases as the heating rate increases. This trend was noted in other experiments using sample holders made from other materials, and in oxygen atmospheres (see Fig.3).

This effect may be due to the loss of instrument resolution. As the heating rate increases, a broad, weak exotherm replaces the sharp peaks.

Effect of oxygen concentration

Samples of pyrite of particle size <45μm were oxidised at various heating rates in oxygen in both TG-DTA and heat-flux DSC equipment, and the latter results are presented in Figure 3.

An increase in the partial pressure of oxygen causes an increase in the number of sharp exotherms observed. Comparing, for instance, the results obtained at a heating rate of 2.5°C min^{-1}, the number of peaks present in air is 6 (Fig. 2a), and in oxygen it is 13 (Fig. 3a).

Effect of sample mass

Samples of particle size <45μm were oxidised in air at heating

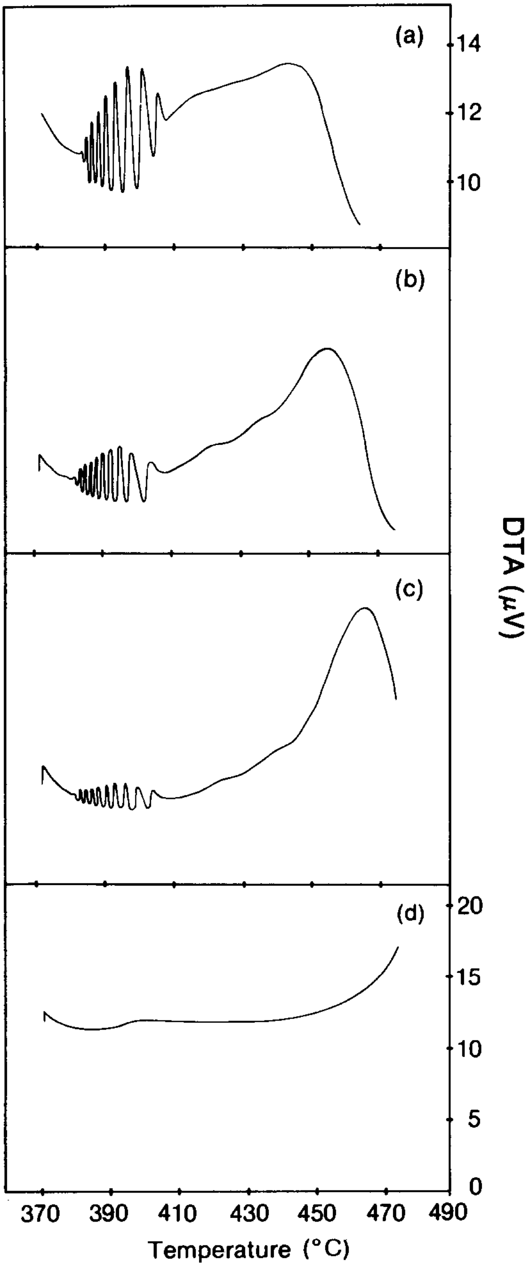

Figure 1. DTA traces of various fractions of pyrite heated at 2.5°C min^{-1}
(a) <10μm, 1.0mg, air; (b) 10-20μm, 1.7mg, air;
(c) 20-30μm, 1.7mg, air (d) 30-45μm, 1.8mg, oxygen.

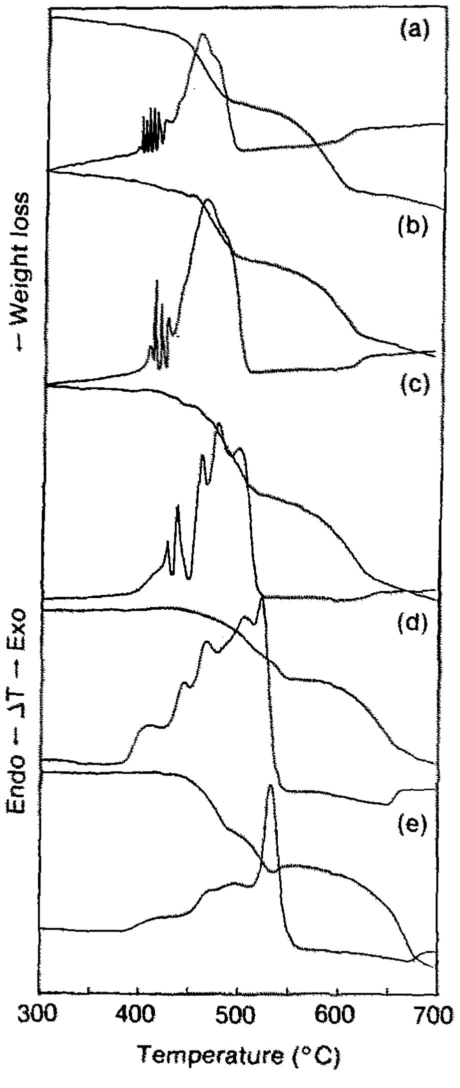

Figure 2. TG-DTA traces for ≈1.8mg pyrite (<45μm) heated in air.

Heating rate (°C min^{-1}); (a) 2.5 (b) 5 (c) 10 (d) 20 (e) 40

DTA sensitivity (μV); (a) 50 (b) 100 (c) 100 (d) 200 (e) 200

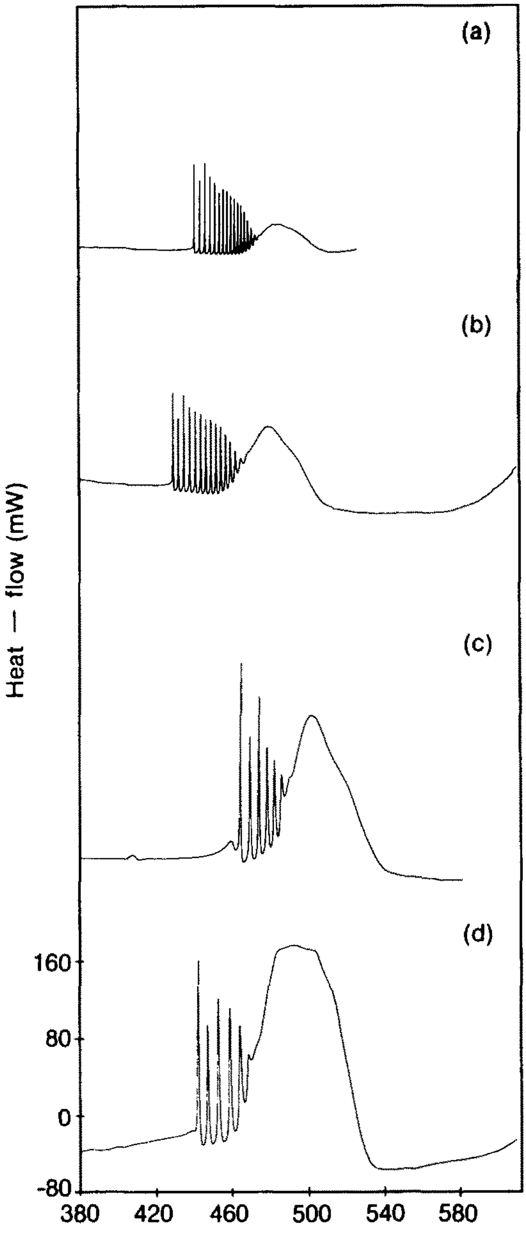

Figure 3. Heat flux DSC traces for ≈1.8mg pyrite heated in oxygen. Heating rate (°C min^{-1}); (a) 1 (b) 2.5 (c) 5 (d) 10.

rates between 2.5-40°C min^{-1} at sample masses of approximately 1.8, 3.6 and 7.2mg. Only at the lowest heating rate were any peaks evident for the two heavier samples, and these were of weak intensity and poorly resolved. Hence increasing the sample mass decreased the number of sharp exotherms found.

Product characterisation

Samples of pyrite of particle size <45μm were heated at 2.5°C min^{-1} in air in the TG-DTA or DSC equipment to just above the temperature at which the sharp exotherms appeared. The partially oxidised sample was quenched rapidly, and examined by quantitative XRD and SEM. Fe_2O_3 was not detected by XRD. This is not surprising, since the TG results showed a minor weight loss of 72μg in the same temperature range as the sharp exotherms. This corresponds to the formation of 45μg of Fe_2O_3, which is below the detection limit of the XRD equipment.

Examination by SEM showed that many of the smaller particles, i.e., less than 10 μm in size, had completely reacted. Quantitative determinations of the iron/sulphur ratio gave values of typically 1:0.1. Other particles of the same size had not reacted at all. Larger particles, i.e. 30-40 μm, showed either an oxide rim around an unreacted core, or no evidence of reaction. The latter were very similar in appearance to particles of unreacted pyrite particles.

CONCLUSIONS

This paper reports the results of the first systemic study of the effect of experimental variables on the multiple peaking effect. Hence results given and the conclusions drawn have not been previously published.

The results indicate that the peaks are due to the oxidation of the fines fraction of the pyrite. The number of the sharp exotherms increased with:

(a) decrease in the heating rate
(b) increase in the partial pressure of oxygen
(c) decrease in the sample mass

Under the best conditions to enhance the appearance of the sharp exotherms, of particles <30μm in size, a heating rate of 1° min^{-1}, an oxygen atmosphere and 2mg sample, up to 19 of these peaks were observed.

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