

PERIODIC THERMAL INSTABILITY DURING THE DIFFERENTIAL THERMAL ANALYSIS OF PYRITE

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The cause of oscillations in high resolution DTA curves was investigated using simultaneous TG supported by microscopic and XRD examination of quenched samples. The latter techniques showed the instability resulted from the sequential ignition of individual or small groups of particles. This behaviour was different to that observed in our earlier 'isothermal' tests where the oscillations were caused by periodic cracking of the oxide film.

The oxidation of sulphide minerals liberates heat which raises the temperature of the reacting particles above the ambient thus leading to thermal instability in controlled temperature experiments. In an earlier article [1] the authors reported periodic thermal instability which was encountered during the 'isothermal' oxidation of pyrite (FeS_2) at temperatures in the vicinity of 450° . The earlier study found this resulted from the periodic cracking of the protective oxide film which was caused by the volume mismatch between the oxide and the underlying pyrite. Periodic thermal instability has also been encountered during DTA studies of sulphide minerals. McLaughlin [2] ascribed this to the periodic ingress of oxygen into the crucible while Bollin [3] attributed it to sequential ignition of grains or groups of grains. Little, however, in the way of experimental evidence was provided to support either conclusion. The present study was undertaken to see whether our explanation of the instability during 'isothermal' experiments also applied to the DTA experiments. In the conduct of this investigation the DTA technique was supported by simultaneous TG, microscopic and XRD examination of quenched samples.

Experimental

The pyrite used in this work was the 53-74 μm screen size fraction of pyrite flotation concentrate obtained from the Mount Morgan mine in Queensland and was the same material used in our earlier study. The chemical analysis of this material, description of the equipment and the liquid nitrogen quenching techniques used to obtain material for phase identification and microscopic examination have been described elsewhere [4].

The experimental details quoted by McLaughlin are meagre, consequently it was not possible to repeat his experiments. In the case of Bollin's measurements the thermal effects were small and only became apparent when high resolution DTA techniques were used. Thus in the present study high sensitivity was ensured by using shallow (4.5 mm I. D. by 2.5 mm deep) light-weight platinum crucibles of low heat capacity ($6.2 \times 10^{-3} \text{ J K}^{-1}$) and good thermal conductivity (thermal conductivity of platinum $72 \text{ W m}^{-1} \text{ K}^{-1}$). Small sample weights (approx. 2 mg) gave about 50% coverage of the bottom of the crucible and ensured ready access of oxygen.

Results

A typical high resolution record of thermal analysis is shown in Fig. 1. The DTA curve showed a major exothermic peak at 547° which was preceded by 4 minor peaks the first of which occurred at 439° . The time period between the first two peaks was 2 minutes but this decreased to 1.4 minutes between the fourth and fifth peak. The number of minor peaks and the period between them depended upon the sample but they were generally as shown in Fig. 1. The exothermic activity was accompanied by a step (wt. loss) in the TG curve. However the latter was not sensitive enough to register any marked distinguishing features corresponding to the minor DTA peaks.

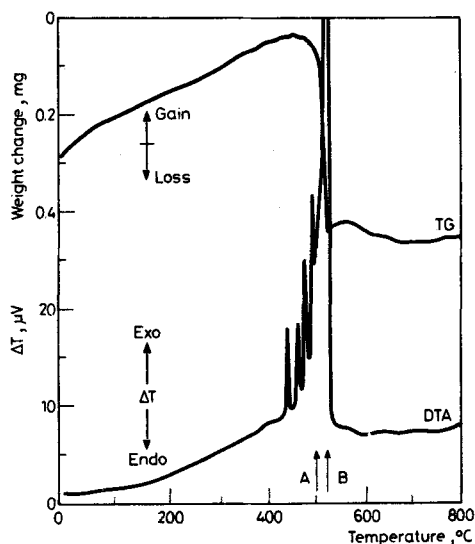


Fig. 1 High resolution records of thermal analysis. (Sample wt. 2.45 mg, particle size $53\text{--}74 \mu\text{m}$, heating rate $10^\circ/\text{min}$, air flowrate $120 \text{ cm}^3 \text{ min}^{-1}$, light platinum crucible.) See text for significance of letters

Quenched samples for microscopic examination were taken at the positions marked A & B on the DTA thermal analysis curves. Sample B was taken at the DTA peak temperature (about 547°) while sample A was taken at a temperature approximately 44° lower. The polished section prepared from sample B was mainly composed of completely reacted grains, there being only a few 'unreacted' particles (i.e., apart from an initial surface oxide film) in the whole section. The completely reacted grains (Fig. 2) showed a thin outer layer of initial oxide 3–5 μm thick surrounding a core

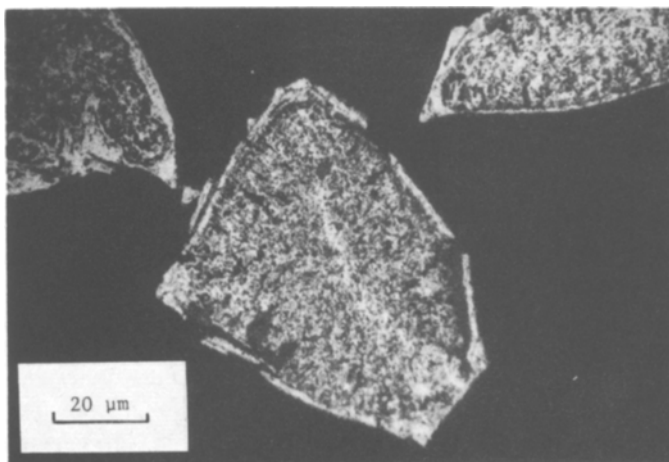


Fig. 2 Optical micrograph of completely reacted pyrite grain

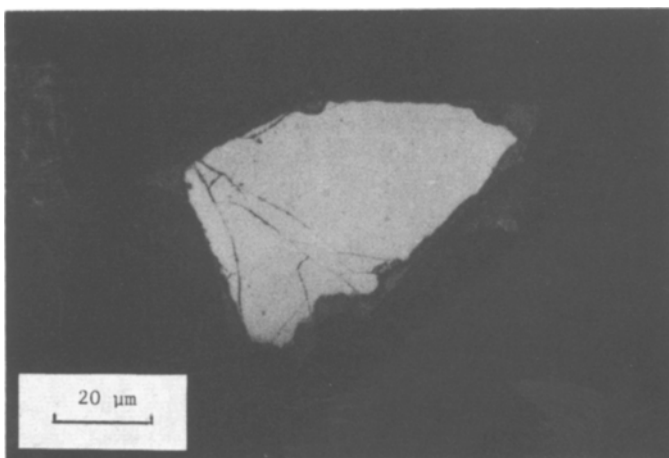


Fig. 3 Optical micrograph of 'unreacted' grain

of porous oxide. Both oxides were hematite (Fe_2O_3). The occasional partly reacted grain showed the outer layer of initial oxide, a thick layer of porous oxide and a core

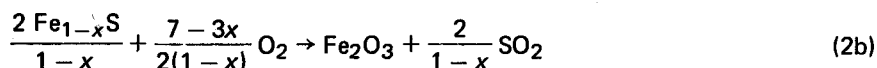
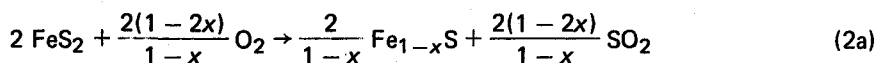
of 'unreacted' pyrite. A small amount of pyrrhotite (Fe_{1-x}S) was present at the interface between the pyrite core and porous oxide layer. The 'unreacted' grains (Fig. 3) consisted of pyrite with a thin layer of initial oxide similar to that found in Fig. 2. The polished section prepared from sample A showed mainly 'unreacted' particles. A few completely reacted grains were present showing the initial oxide layer surrounding a core of porous oxide i.e., similar to Fig. 2. Neither section showed any evidence of the layered oxide structure encountered in our earlier isothermal experiments.

Discussion

In the present study the unstable thermal behaviour first became evident at about 440° which is similar to that shown by Bollin for pyrite. This temperature is also within the temperature range of periodic thermal instability encountered in our isothermal experiments but the micrographs shown in the earlier paper are very different to those shown here. Different oxidation mechanisms were operative in both cases. In the isothermal experiments hematite formed directly on the pyrite whereas in the DTA experiments pyrrhotite formed as an intermediate phase. Pyrrhotite formed from pyrite has a porous structure which is transmitted to the final oxide. This explains the porosity of the core oxide material shown in Fig. 2. The two reaction mechanisms may be represented by the following equations:



or



Bollin attributed his periodic thermal instability to the 'discrete initiation of reaction in individual particles or particle clusters' but did not present experimental evidence other than the DTA traces to support his claim. Our micrographs presented here clearly show that some particles had reacted more than others and are in accord with the above statement of Bollin. It is interesting to calculate (from the TG curve) that the first minor DTA peak shown in Fig. 1 corresponds to the ignition of about 10–20 average size particles. This is only a very small proportion of the 1300 or so particles in our experiments. Similarly it has also been calculated elsewhere [4] that under the conditions of our experiments reaction (2a) requires a temperature of 550° to proceed. Thus, although the first minor DTA peak only corresponds to a measured temperature difference of 0.9° , the phases present indicate that localized overtemperatures of about 100° were attained by some of the particles. Bollin explains the different reactivity of the particles in terms of different 'surfaces energy'.

Another possible explanation may be based upon heat transfer considerations involving the amount of contact of the particles with the crucible and each other. This arises from the different sizes, shapes and distribution of particles in the crucible.

The different oxidation mechanisms observed in the isothermal and the high resolution DTA tests are thought to be due to the different experimental conditions. In the high resolution DTA experiments the sample covered approximately 50% of the bottom of the crucible whereas in the isothermal tests the coverage was 4–5 layers deep. The reduced access of oxygen in the latter case restricted localized over-temperatures and prevented pyrrhotite from forming.

Conclusion

This study and an earlier one have shown two different types of periodic thermal instability. Both occur at nominally the same temperatures and if guided solely by TG and DTA experiments one would be lead to believe that the same reaction mechanism was operating in both cases. Microscopic evidence has shown however that the mechanism and the phases involved are different thus demonstrating the importance of using supporting techniques (e.g., microscopy, XRD, SEM–EDX and microprobe analysis) in studies of this type. This study supports Bollin's contention that periodic thermal instability, observed during high resolution DTA studies of pyrite is due to the sequential ignition of individual or small groups of particles.

References

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Zusammenfassung – Die Ursache von Oscillationen in hochaufgelösten DTA-Kurven wurde durch TG und gleichzeitige Ausführung von mikroskopischen und XRD-Untersuchungen von abgeschreckten Proben erforscht. Die zuletzt genannten Techniken lassen eine Instabilität erkennen, die auf eine regelmässig aufeinanderfolgende Verbrennung von individuellen oder kleinen Gruppen von Partikeln zurückzuführen ist. Dieses Verhalten unterscheidet sich von dem, das in unseren früheren "isothermen" Testversuchen beobachtet wurde, bei denen die Oscillationen durch periodisches Zerreißen des Oxidfilms verursacht wurden.

Резюме – Причина осцилляций в ДТА-кривых высокого разрешения была исследована совмещенным методом ТГ и микроскопии и рентгеновской дифракции. Последние два метода показали нестабильность, происходящую в результате последовательного воспламенения индивидуальных частиц или их небольших групп. Такое поведение отличается от установленного ранее "изотермических" испытаниях, где осцилляции были вызваны периодическим растрескиванием окисной пленки.