

APPARATUS FOR COMBINED TG + DTA IN A CHLORINE OR OTHER CORROSIVE ATMOSPHERE

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ABSTRACT

Apparatus for combined TG+DTA in a chlorine or other corrosive atmosphere is described and demonstrated. The DTA thermocouples are protected from corrosion by close-fitting silica sheaths on which the crucibles sit. Although built primarily to study reactions between minerals and corrosive gases, the apparatus may prove useful in materials science.

INTRODUCTION

High-temperature reactions of sulphide or oxide minerals with Cl_2 are of importance in the extraction of metals [1]. Such reactions are used in the commercial production of Ti, Zr and Hf, and some Mg [2], and have been investigated for extracting most other metals, particularly Al. Useful information on reactions between Cl_2 and several minerals has been obtained by TG [3,4] and by DTA [5,6], and the logical extension of that work is to combine these techniques.

Two problems with combined TG + DTA in a Cl_2 atmosphere are: (a) the isolation of the microbalance from the Cl_2 ; (b) the protection of the DTA thermocouples from high-temperature corrosion. In the all-silica apparatus described here, a counter-flow of N_2 prevents Cl_2 from entering the microbalance chamber, and each DTA crucible sits on a finger-shaped projection which contains and protects the thermocouple. To demonstrate the apparatus, results are given for the reaction of Cl_2 with galena (PbS).

APPARATUS

Microbalance protection

Chlorine enters the bottom of the main tube as shown in Fig. 1, flows as far as the funnel and exits through the side arm. Nitrogen enters the

microbalance chamber through a tube which directs the flow away from the pan containing the counterweight so as to avoid disturbing the balance. The funnel reduces to a 20 mm long, 5 mm ID tube which ensures the high linear flow velocity needed to prevent Cl_2 diffusing upstream towards the balance. This method of protecting a microbalance has been used before; for example, by Mikhail and Webster [4] in TG apparatus for studying mineral chlorination reactions.

For access to the sample crucibles, the joint between the funnel section and the main silica tube is disconnected and the balance is lifted off. The C.I. Electronics Mark 2 CT5 microbalance was coated with a film of Teflon (PTFE) to protect it against accidental contact with Cl_2 . The silica sample crucible is identical to those described below for the DTA section and sits in a cradle for attachment to the 1 mm diameter silica suspension rod. The condensation of vapours on this suspension rod and the buoyancy effect as

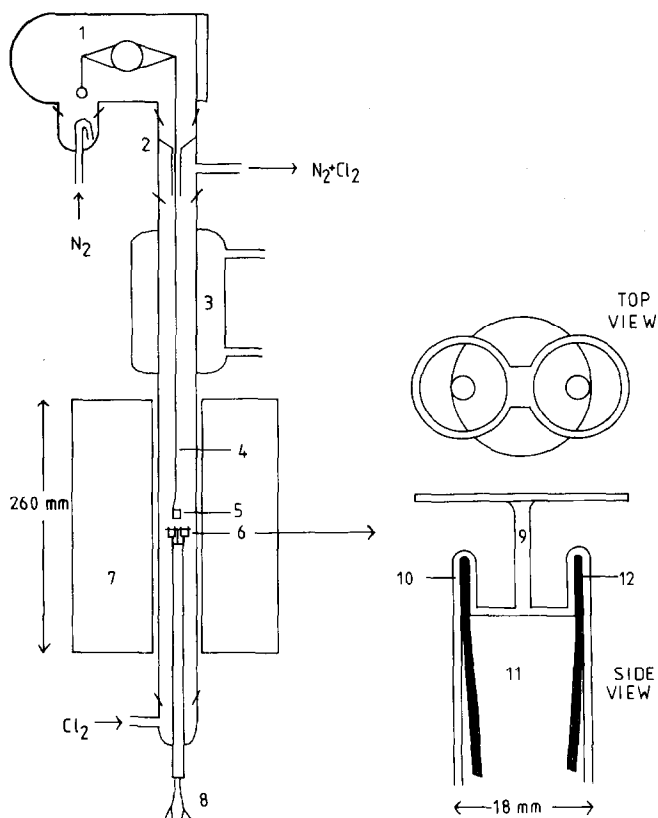


Fig. 1. TG+DTA apparatus for corrosive atmospheres. (1) microbalance; (2) funnel; (3) condenser; (4) silica suspension rod; (5) crucible; (6) DTA section; (7) low-mass furnace; (8) thermocouple leads; (9) support for crucibles; (10) thermocouple sheath; (11) 18 mm OD tube; (12) 1 mm OD Inconel sheath containing a mineral-insulated chromel–alumel thermocouple.

the temperature of the atmosphere rises, are both sources of systematic error which increase the weight reading.

Thermocouple protection

Mikhail and Webster [6] have used a DTA apparatus with exposed Pt/Pt-13%Rh thermocouple wires in a Cl_2 atmosphere but made no comments on corrosion. In experiments conducted in this laboratory, this kind of thermocouple wire was repeatedly heated to and cooled from 900°C in an atmosphere of pure Cl_2 . Examination with a microscope revealed progressive corrosion: the Pt wire was pitted but not discoloured and dark-red crystals had formed on the Pt-13%Rh wire.

It was concluded that protection of the thermocouples was desirable in the long term and silica was the obvious choice of material. This approach was adopted in the DTA apparatus of Ishii et al. [5], which has chromel-alumel thermocouples in 4.5 mm OD silica sheaths dipping into 1 g masses of material. The sample and reference materials were supported on silica wool plugs in separate, vertical 10 mm ID tubes through which Cl_2 was passed. This arrangement ensured good gas-solid contact. However, the design has three unsatisfactory aspects: (a) the tip of the thermocouple sheath and the tube containing the sample must be removed and cleaned after each experiment; (b) the formation of a liquid product may interfere with the flow of Cl_2 and will complicate cleaning; (c) relatively large samples are required.

The advantage of the DTA arrangement in Fig. 1 lies in the combination of protected thermocouples and small, readily-replaced sample crucibles. The silica crucibles are 10 mm high, 10 mm OD and 8 mm ID, with indentations on their bases to ensure good contact with the tips of the thermocouple sheaths. The crucibles are held in place by silica loops. The sheaths are 8 mm long, 3 mm OD and 1 mm ID, and are joined to an 18 mm OD tube. Chromel-alumel thermocouples, mineral-insulated in their own 1 mm OD Inconel sheaths, fit closely into the silica sheaths. Such metal-sheathed thermocouples are available from several suppliers, and Inconel is the recommended metal for operation up to 1000°C in air, the gas inside the 18 mm tube.

Other aspects of the apparatus

The main tube in the apparatus (35 mm OD) is continuous with the condenser and is held centrally by Sindanyo rings in a low-mass furnace (Stanton-Redcroft model LMVS 100, max. temp. 1000°C). The furnace temperature is controlled by a Eurotherm Type 211 programmer which can apply an eight-segment profile. The T , ΔT and ΔW signals are displayed on a three-channel Linseis chart recorder.

The apparatus is operated in a fume-cupboard and there is a fail-safe

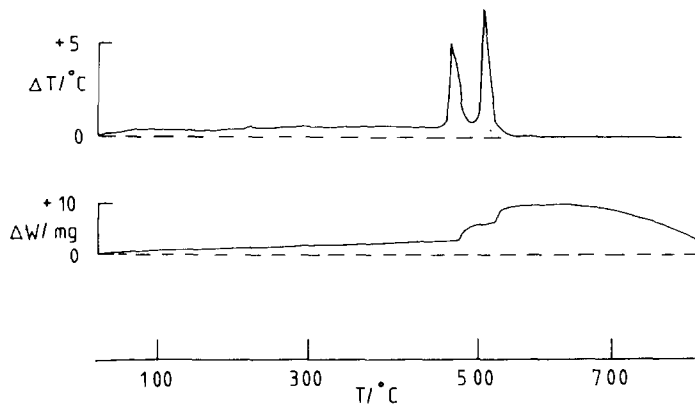


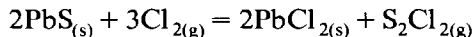
Fig. 2. Thermogram of the chlorination of galena. Details: 50 mg of 1–2-mm particles; reference crucible empty; Cl_2 atmosphere, flowrate $50 \text{ cm}^3 \text{ min}^{-1}$; heating rate $7.5^\circ\text{C min}^{-1}$.

arrangement to automatically cut the supply of Cl_2 when fume extraction stops.

RESULTS

Chlorination of galena

Natural galena was ground and a 50 mg sample of 1–2 mm particle size was used. The established reaction is



and involves a theoretical weight increase of 16.3%. The thermogram (Fig. 2) shows a small gradual increase in weight and some exothermic activity up to 450°C . This is due to the formation of a layer of solid PbCl_2 on each galena particle. At 450°C , the eutectic temperature of the $\text{PbCl}_2 + \text{PbS}$ system [7], the appearance of a liquid phase allows Cl_2 to penetrate more quickly to react with the galena. The beginning of this reaction is seen as an exothermic peak in the DTA curve and the sample weight begins to increase. As the reaction proceeds, eutectic liquid and solid PbCl_2 are produced until PbCl_2 melts at 500°C to give an all-liquid product layer. This layer allows greater penetration by Cl_2 leading to a second burst of exothermic activity and a further increase in weight. The chlorination of the galena is complete at this point but the weight increase is a little less than the theoretical value because PbCl_2 begins to vaporise significantly around 500°C .

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