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A THERMOGRAVIMETRIC ANALYSER FOR CORROSIVE ATMOSPHERES AND ITS APPLICATION TO THE CHLORINATION OF ZrO_2–C MIXTURES

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ABSTRACT

We report on a thermogravimetric analyser, built on the basis of a Cahn 2000 electrobalance, suitable for using with corrosive atmospheres. We discuss the corrections for buoyancy and gas flow effects, which strongly modify thermogravimetric curves.

As an application, we studied the kinetics of a reaction between Cl_2 and a mixture of ZrO_2 and C. We were able to measure the uptake of Cl_2 by C and the reaction rate within the first 50 s. We present evidence of a transition to quite a different reaction rate at longer times.

INTRODUCTION

Thermogravimetry (TG) has been extensively used for the study of the kinetics of gas–solid reactions, e.g. for determining reaction mechanisms, and kinetic parameters relevant in technological applications.

Many interesting reactions in extractive metallurgy involve corrosive gases. This fact limits the use of some commercial high-resolution thermogravimetric analysers (TGA). Therefore, we have developed our own TGA, suitable for corrosive atmospheres, on the basis of a Cahn 2000 electrobalance.

The measurement of weight changes in the range of micrograms is hampered by several effects [1–5] such as buoyancy [3,5], gas flow effects [6], thermomolecular flow effects (TME) [2,4,7], free gas convection [4,8], electrostatic effects [6], zero drift [4,9], etc.

An appropriate design of the hang-down tube reduces some of these disturbing effects, such as free gas convection and electrostatic effects [1,3,9]. Buoyancy, TME and gas flow effects can be compensated for in

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symmetrical TGA [1,9,10]. However, under corrosive atmospheres it is not advisable to use a symmetrical TGA because the corrosive gas might circulate between the hang-down tubes and damage the weighing unit of the electrobalance.

Therefore, most of high accuracy TGAs for corrosive atmospheres reported in the literature are asymmetrical [11–13]. However, the use of an asymmetrical TGA requires a calibration TG curve (using an inert sample of the same volume as the actual sample) for each set of experimental conditions, e.g. gas flow, heating rate, sample size, gas composition, etc.

The purpose of the present paper is to demonstrate the performance of our asymmetrical TGA by measuring the chlorination kinetics of ZrO_2 in the presence of C, using non-isothermal and isothermal techniques. The reaction, which takes place [14] at temperatures above 400 ° C, may be represented by

$$ZrO_2(s) + 2Cl_2(g) + 2C(s) \rightarrow ZrCl_4(g) + 2CO(g) \qquad (1)$$

Different mechanisms for this reaction have been suggested [15,16]. However, a comprehensive model of this reaction does not exist [17]. In this work we present preliminary results on the reaction rate which were obtained through a careful evaluation of the systematic errors involved in TG techniques.

EXPERIMENTAL SYSTEM

Figure 1 shows a block diagram of the TGA system constructed on the basis of a Cahn 2000 electrobalance. This electrobalance has a sensitivity of 0.1 μg and mechanical and electrical tares of 1 g and 100 mg respectively. The sample is contained in a quartz crucible which hangs from one of the arms of the balance by a quartz wire. The mechanical counterweight hangs on the other arm. A quartz hang-down tube, which is similar to one previously described [9], carries the gases to the sample. This design [9] reduces the effects of aerodynamic forces acting on the crucible, and also increases the linear velocity of the gas mixture in the zone of the furnace, where there is a higher temperature gradient. This reduces the undesirable thermal segregation effects [18]. The outer surface of the hang-down tube is painted with Pt paint over a length of 10 cm and is electrically grounded to eliminate electrostatic forces. The temperature of the sample is measured using a Pt–Pt(10% Rh) thermocouple encapsulated in quartz, which is placed 2 mm below the crucible.

An electrical furnace controlled by a PID regulator controls the temperature of the sample, which we can vary from room temperature up to 1200 ° C. The maximum noise of the TGA system is 5 μg peak-to-peak at 1100 ° C at a flow rate of 9 l h^{-1} (NTP). The weighing unit is protected from

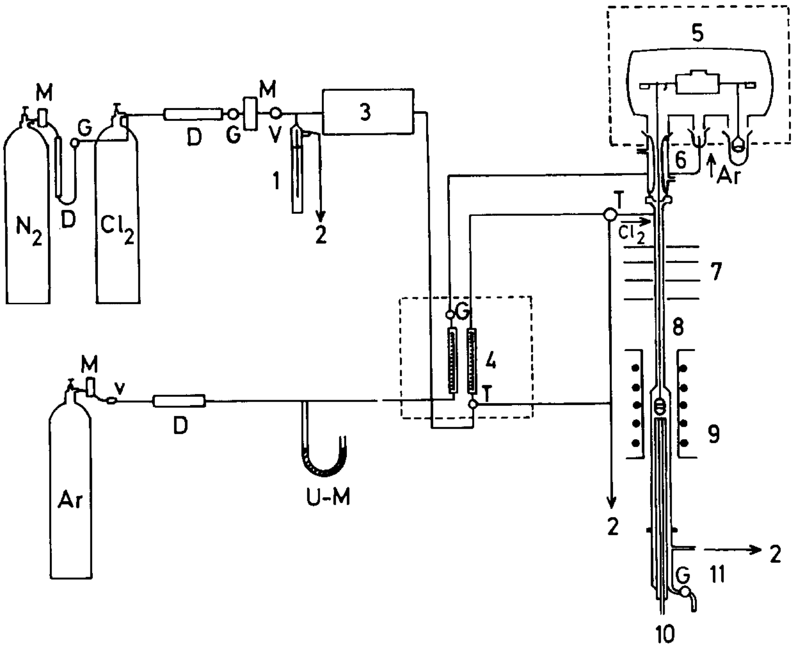

Fig. 1. Schematic diagram of the TGA: M, manometer; V, needle valve; D, drying column; U-M, U-tube manometer; G, on-off valve; T, three-way valve; 1, bottle with H_2SO_4, used as an automatic pressure relief valve; 2, exit of gases to hood; 3, drying tube; 4, flowmeters; 5, electrobalance; 6, jacket for condensation of eventual vapours; 7, radiation shields; 8, hang-down tube; 9, furnace; 10, closed-end quartz sheath for thermocouple; 11, collector for eventual liquid products.

the corrosive action of Cl_2 by a stream of Ar (see Fig. 1). At the exit of the weighing unit, this Ar stream mixes with Cl_2 generating the reactive mixture which circulates in the hang-down tube downstream, as is illustrated in Fig. 1. The reaction products that condense at room temperature are collected in the bottom of the hang-down tube. The gas flow rate and composition are controlled by means of a Matheson multiple flow controller.

The data acquisition is performed by means of an IBM PC/XT computer using a Data Translation DT 2805 interface. This interface also allows programming of the furnace temperature.

EXPERIMENTAL

In our experiments we used the smallest possible specimens which were compatible with accurate measurements, as is usually recommended in TG experiments [19,20]. The high sensitivity of our TGA system allowed us to perform the kinetic studies using samples of 2–10 mg. As we explain later, samples of 10 mg were large enough to observe the uptake of Cl_2 by C. The samples were prepared by mechanical mixing of ZrO_2 powder and C powder. The starting materials were ZrO_2, 99.9% purity (Koch-Light Labs.) with a BET surface area of 4.5 m^2 g^{-1}, and C with a BET surface area of 17.5 m^2 g^{-1}. Carbon was obtained by thermal decomposition of sucrose (Mallinckrodt Chemical Works).

To eliminate any spurious volatile substances, the samples were first heated at 950 °C in a circulating Ar atmosphere. Then the temperature and flow rate were adjusted to the values corresponding to the beginning of the experiment and the reactive gas was subsequently introduced. The gases used were Ar, 99.99% purity (AGA, Argentina), and Cl_2, 99.9% purity (Indupa, Argentina).

All operational control, data acquisition and manipulation was through the computer. The data were acquired every 0.1 s. This rate is compatible with the period of the Cahn 2000 electrobalance.

CORRECTIONS

Buoyancy

To determine the absolute mass of the sample, it is first necessary to determine the buoyancy effects [21]. Figure 2 shows the correction curve due to buoyancy determined with an empty crucible in a static Ar atmosphere under a pressure of 700 Torr. The mass gain is ~ 170 μg at 950 °C. This value is three orders of magnitude higher than the sensitivity of the electrobalance and represents about 10% of the smallest sample mass used in our

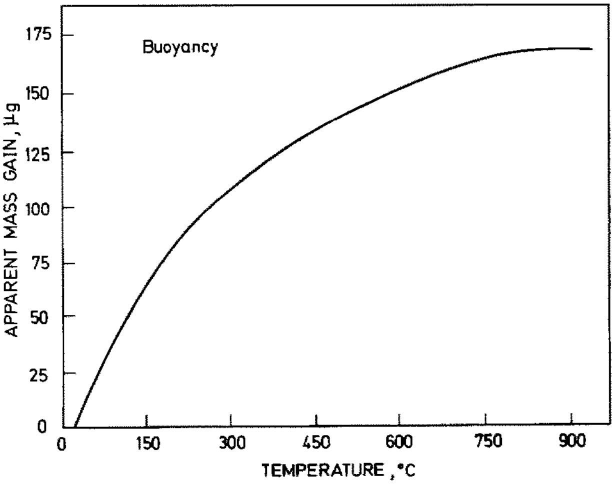

Fig. 2. Apparent mass gain due to buoyancy for an empty crucible in a static Ar atmosphere as a function of temperature.

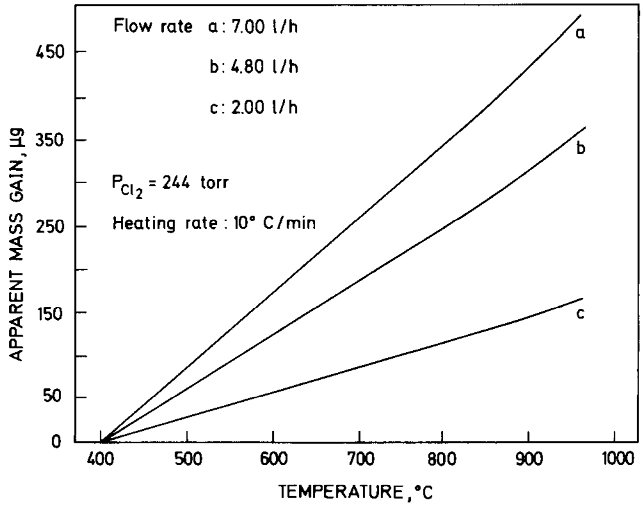

Fig. 3. Apparent mass gain for an empty crucible in a flowing mixture Ar–Cl_2 (PCl_2 = 244 Torr) as a function of total flow rate, using a heating rate of 10 °C min^{-1}.

experiments. In view of the small size of our samples their contribution to the total buoyancy effects was neglected.

Flow effects

Non-isothermal kinetics is based on determining the mass change of the sample under a fixed heating rate in a given atmosphere. Typical corrections are shown in Fig. 3, where we plot the apparent mass change as a function of temperature under a Cl_2 partial pressure (PCl_2) of 244 Torr and a heating rate of 10 °C min^{-1}, for three different flow rates: a, b and c.

It is evident that the apparent mass gain due to flow effects is higher than that owing to buoyancy, see Fig. 2.

Apparent mass change due to a simultaneous change in composition and flow rate of the gaseous atmosphere at constant temperature

In heterogeneous kinetics, it is often useful to determine the initial reaction rate, which may give valuable information about the reaction mechanism. In this case the kinetic study is performed under isothermal conditions. The sample is kept at constant temperature in an inert gas atmosphere and then the reactive gas is introduced into the reactor. This produces a change in gas composition and gas flow rate which disturbs the measurements. In Fig. 4 we show the apparent mass change of an empty crucible at 950 °C when a flowing Ar atmosphere of 1.32 l h^{-1} is disturbed by the injection of two different flow rates of Cl_2. This apparent mass

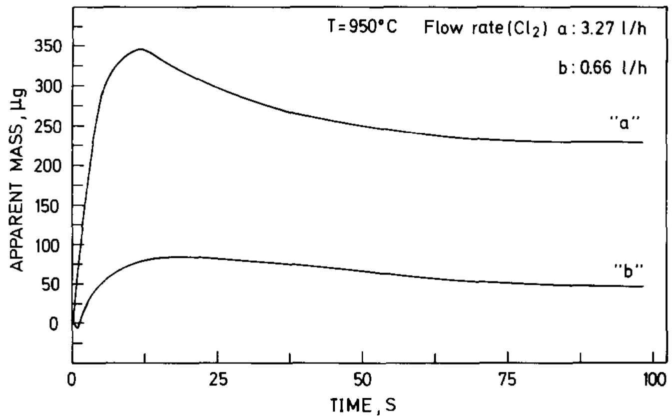

Fig. 4. Apparent mass for empty crucible at injection of Cl_2 into the reactor, as a function of Cl_2 flow rate, at 950 °C.

change must be taken into account when correcting the kinetic data obtained during the early stages of the reaction.

RESULTS AND DISCUSSION

Non-isothermal kinetics

Curve a in Fig. 5 shows the TG curve obtained using 2 mg of sample containing 20% w/w of C. This curve corresponds to a heating rate of 10 °C min^{-1} and a flow rate of 8.37 l h^{-1} with $PCl_2 = 250$ Torr. The heating was

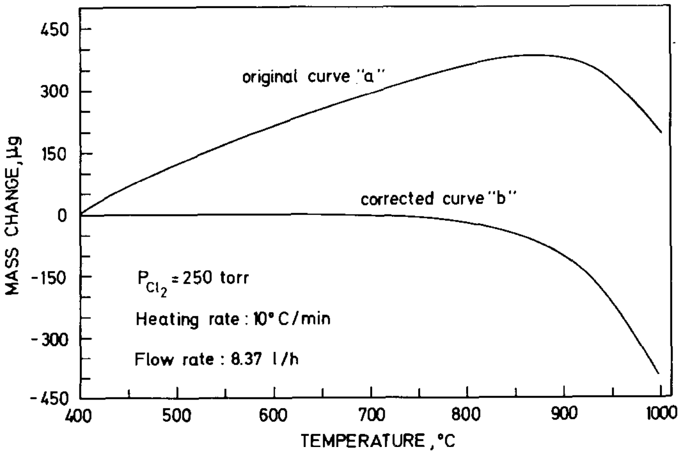

Fig. 5. Non-isothermal curves: a, empty crucible; b, 2 mg of mixture ZrO_2–C (20% w/w of C).

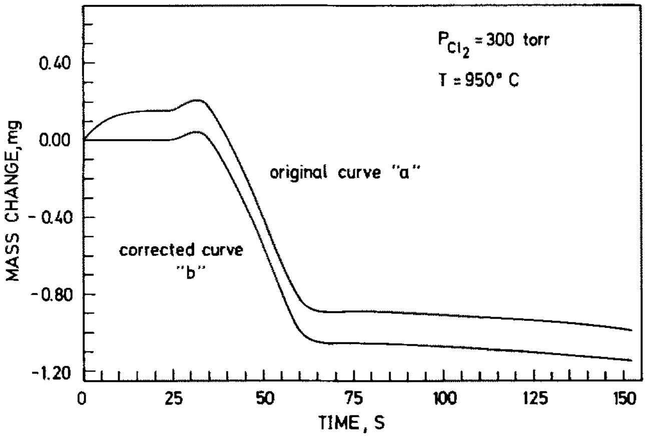

Fig. 6. Isothermal mass loss of 10 mg of mixture ZrO_2-C (70% w/w of C) at 950 °C and $PCl_2 = 300$ Torr. a, Original curve; b, curve obtained after correction for apparent mass change. Data obtained during the first 150 s.

started at 400 °C because $ZrCl_4$ is solid at lower temperatures. Curve b shows the thermogram obtained after correction for apparent mass gain.

It can be seen that the original curve is strongly modified by the apparent mass gain. No change in mass is detected below 700 °C, but at higher temperatures the reaction rate is appreciable.

Isothermal kinetics

Here only the kinetic behaviour observed during the first 150 s is reported.

Curve a in Fig. 6 shows the mass evolution of a sample of 10 mg (containing 70% w/w of C) at 950 °C with $PCl_2 = 300$ Torr, obtained directly from the TGA. Curve b shows the results after correcting for apparent mass change. This correction is achieved by the software following the calibration curves previously discussed. The zero on the time scale corresponds to the injection of Cl_2 into the reactor. During the first 25 s, no change in mass is observed, corresponding to the time necessary for the Cl_2 to reach the sample. Then a small increase in mass of about 40 μg occurs, followed by a rapid mass loss of about 1 mg and then the reaction slows down appreciably.

Chlorine uptake by carbon

In view of the fact that we have corrected for apparent mass change, the increase in mass shown in Fig. 6b is real and is related to the reaction between the gas phase and the sample. As the adsorption of Cl_2 on ZrO_2 has been shown [22] to be negligible under the present experimental conditions, we only need to consider the interaction between Cl_2 and C. The Cl_2 uptake on C was determined by studying a sample of pure C under the same

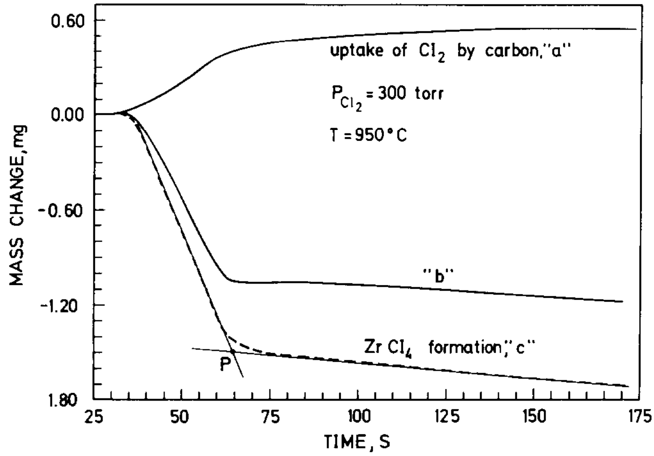

Fig. 7. Mass change due to the interaction of Cl_2: a, pure C; b, reaction with mixture ZrO_2-C (same plot as fig. 6b). Curve c shows the result of subtracting b from a.

experimental conditions. The measured mass gain for 7 mg of sample is reported in Fig. 7, curve a. The initial uptake is very fast. The final mass gain is significant and reaches a value of about 7% of the total C mass. Clearly this uptake is larger than that suggested by the mass gain observed in Fig. 6b.

Rate of $ZrCl_4$ formation

We have analysed curve b in Fig. 6 in terms of the superposition of two independent and simultaneous phenomena: a mass gain due to the uptake of Cl_2 by C, and a mass loss due to the formation of gaseous $ZrCl_4$. To consider only the mass change because of $ZrCl_4$ formation, the mass gain resulting from the uptake of Cl_2 by C is subtracted from Fig. 6 curve b. The result is represented by curve c in Fig. 7, which gives the mass loss due to formation of $ZrCl_4$ only. The same plot includes, for comparison, curve b from Fig. 6.

The slope of curve c gives the reaction rate of $ZrCl_4$ formation only. There is a transition from a high reaction rate to a low rate. Point P, obtained by a linear extrapolation of the high-rate and low-rate parts of the curve may be used to measure the extent of the reaction when the transition occurs. A mass balance based on eqn. (1) shows that, at point P, 42% of the ZrO_2 has reacted. Additional results [23] suggest that the fraction of unreacted ZrO_2 strongly depends on the reaction temperature and PCl_2.

CONCLUSIONS

We have demonstrated the performance of a high resolution TGA, suitable for using with corrosive atmospheres. The equipment allowed us to get accurate information on the initial reaction rate and Cl_2 uptake phenomena by C when studying the chlorination of a ZrO_2–C mixture. A discussion of the corrections for various types of errors has also been given. Additional results, and a discussion of the kinetics of chlorination of ZrO_2–C mixtures, will be presented in a forthcoming paper [23].

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