Thermochimica Acta, 82 (1984) 191—200
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THE USE OF A MICROBALANCE TECHNIQUE TO STUDY HIGH-TEMPERATURE OXIDATION/SPALLATION OF A STAINLESS STEEL

R.C. LOBB

Central Electricity Generating Board, Berkeley Nuclear Laboratories,
Berkeley, Gloucestershire, U.K.

ABSTRACT

A facility is described which incorporates the use of electronic microbalances to follow gravimetric changes due to the formation or spallation of surface oxides on metals or alloys during high temperature oxidation. The outputs from the balances are fed into a data acquisition system which allows easy collection and analysis of the data from more than one microbalance.

The sensitivity of the technique is illustrated by reference to the measurements of oxidation and spallation on a 20Cr/25Ni/Nb stabilised stainless steel oxidised in flowing CO_2 based gas at 1 atmosphere pressure and 850°C.

INTRODUCTION

Over many years, microbalances have been used to study solid/gas interactions. In particular, the high temperature oxidation of metals and alloys has received considerable attention using either periodic weighing techniques or continuous gravimetric readings from thermobalances. In this latter instance, analysis of the data was usually effected by interpretation of chart recorder traces.

This paper describes a facility which uses electronic microbalances to follow, precisely, changes in weight due to the formation or spallation of surface oxides on samples during high temperature exposure in an oxidising environment. The outputs from the microbalances are linked to a data acquisition system which enables easy collection and analysis of the data from more than one microbalance.

DESCRIPTION OF FACILITY

The facility consisted of eight microbalances, each with its own independently controlled reaction vessel and gas supply (oxidant). A general view showing the arrangement of two of these microbalances and ancilliary equipment is illustrated in Figure 1.

Microbalance

The microbalances were C.I. Electronics Robals with a maximum capacity of 5g.

0040-6031/84/$03.00

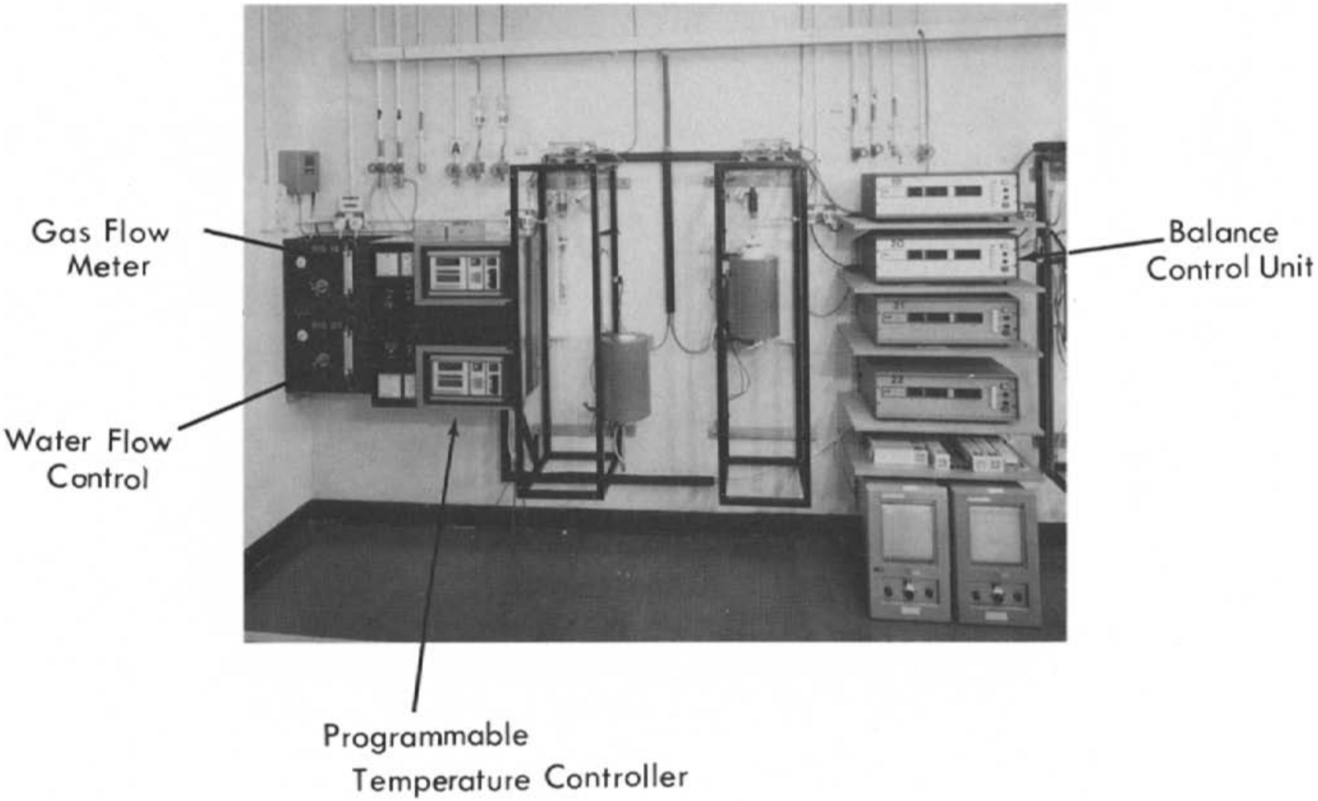

Fig. 1. General view of microbalances and ancillary equipment.

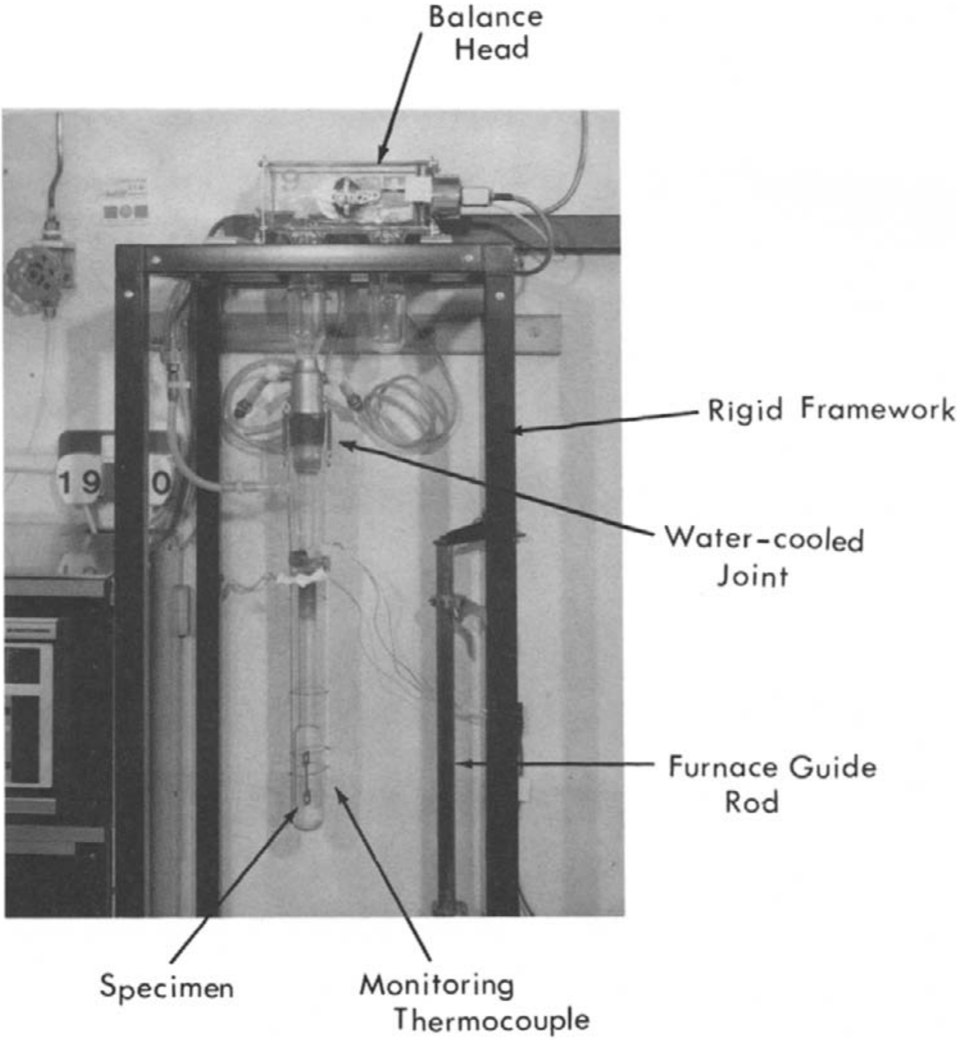

Fig. 2. Detailed view of balance head and silica reaction vessel.

These were based upon the principle of an electronic bridge circuit maintained in continuous equilibrium by a servo system which electromagnetically balanced the torque produced by the specimen weight. When the equilibrium was disturbed by the specimen either gaining or losing weight, a small current flowed in the appropriate arm of the bridge circuit, which was measured and calibrated to a given weight change of the sample by the balance control unit.

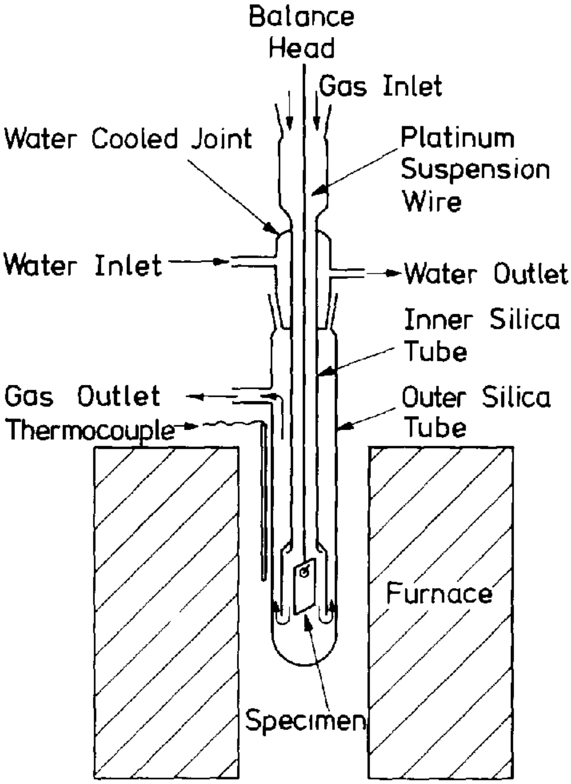

Fig. 3. Schematic diagram showing silica reaction vessel, gas flow and specimen suspension arrangement.

The balance head was attached to a rigid framework on a load bearing wall. The reaction vessel was a vertical silica tube and the arrangement of this is shown in more detail in Figure 2. The specimen was suspended in the hot zone of the reaction vessel from the balance head by means of platinum wire (diameter ∿ 0.125 mm). The oxidising gas flowed downwards over the specimen from the balance head* as shown diagrammatically in Figure 3. The gas flow rate was maintained constant over the period of testing to minimise any changes in downthrust due to the gas flow. In addition, buoyancy effects arose from the difference in density of the oxidant at test temperature compared with that at

---

*In this particular instance the oxidant flowed through the balance head, but in the case of more corrosive gases it may be necessary to have inert gas flowing through the head and the oxidant through the reaction vessel only.

ambient temperature. The magnitude of this effect depended upon the size and shape of the specimen as well as on the oxidant used, but in general, this was found to be small (< 0.02 mg/cm^2 of specimen area) in comparison with the weight changes observed during testing.

The potential accuracy of measurement on these microbalances was 10 µg. However, as encountered previously in microbalances (ref.1), thermal convection in the hot zone of the reaction vessel produced fluctuations (noise) in the balance readings. This effect may be minimised by either 'damping' the output signal by use of a large capacitance or by suitable design of the silica reaction vessel. This latter approach was used in the present facility, where it was found that incorporating an inner concentric silica tube around the platinum suspension wire (see Figure 3) considerably reduced the noise level in the balance readings. The accuracy of measurement at temperature was within the range 30 to 50 µg.

Ancillary Equipment

The furnace surrounding the reaction vessel was capable of 1200°C and was mounted on a guide bar which enabled it to be raised or lowered for rapid heating or cooling of the specimen. Temperatures in the reaction vessel were controlled from Pt/13%Rh-Pt thermocouples near the furnace windings by means of a Eurotherm Type 212 programmable controller. This allowed thermal cycling tests to be performed in addition to isothermal tests. Thermocouples were also attached to the silica reaction vessel to provide continuous monitoring. The temperature difference between these thermocouples and the specimen were known from measurements made during calibration runs on the furnace.

The pressure and flow rate of individual gas supplies and water (for water-cooled joints) to each rig were controlled by pressure reducing and fine needle valves. The gas pressure and flow rates were typically 1 atmosphere and $\sim$ 250 mm^3.s^{-1}.

Data Acquisition System

The data acquisition system was based upon a Hewlett-Packard 9835A computer. A general view of this system is shown in Figure 4. Analogue signals from each of the eight balance control units and monitoring thermocouples were fed into the scanner. This was a simple multiplexer capable of switching a maximum of 60 channels to a single channel, via the digital voltmeter, to give sequential readings that were subsequently fed into the computer. The computer stored the data on a permanent memory store (floppy disc) for eventual analysis of data by individual programmes. The sampling time for data could be varied from 0.5s upwards, depending upon the kinetics of the oxidation process.

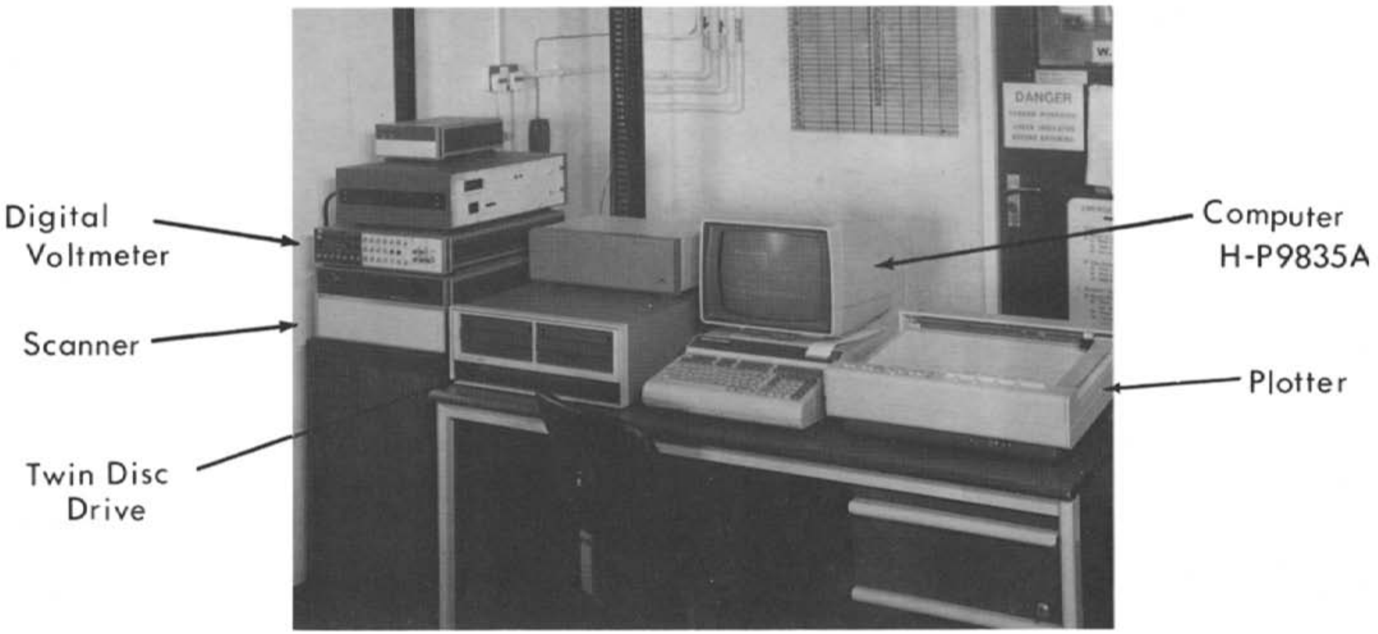

Fig. 4. General view of data acquisition system.

EXPERIMENTAL

The sensitivity of the microbalances described in the previous section may be best illustrated by reference to the isothermal oxidation of a stainless steel and subsequent initiation of a temperature trip. In this particular experiment, a 20%Cr/25%Ni/Nb-stabilised stainless steel was oxidised at 1 atmosphere pressure in flowing CO_2 gas containing 2%CO, with 300 vpm CH_4 and 300 vpm H_2.

The isothermal oxidation period extended to $\gtrsim$ 750h at 850°C and under these conditions it was known that a protective, chromia-type film (containing various quantities of iron and manganese) formed rapidly on the specimen surface. Once the temperature trip was initiated differential contraction strains of the oxide and metal produced stresses at the oxide/metal interface. When the stresses were sufficient to produce decohesion spallation resulted. Although some specimens experienced a number of thermal cycles, the spallation results presented here were obtained from the first temperature cycle to 100°C at a linear rate of 86°C.h^{-1}.

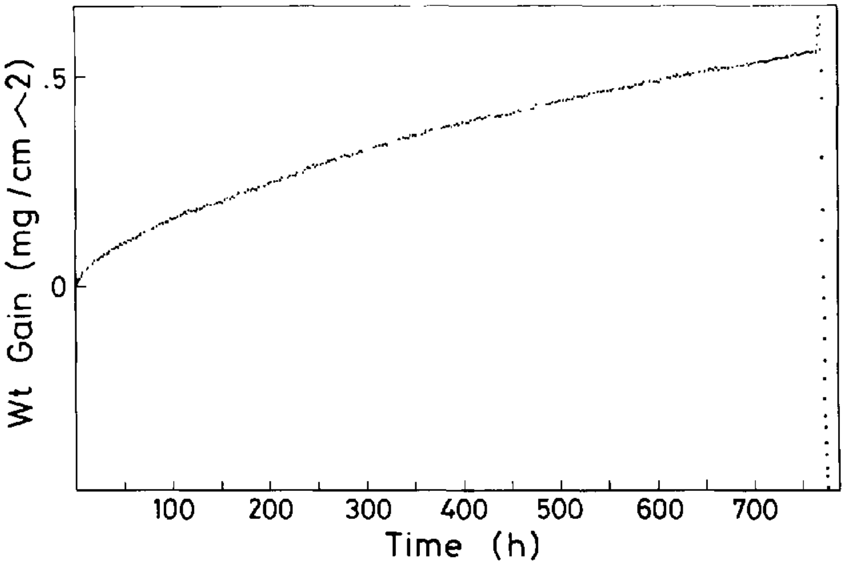

Fig. 5. Computer graphics print-out of weight change/time profile for 20%Cr/25%Ni/Nb steel oxidised for ∿ 764h in CO_2/2%CO at 850°C, followed by 1 cycle to 100°C.

RESULTS

The raw data of continuous weight gain against time for a single specimen, produced by the computer graphics is reproduced in Figure 5. The complexity of

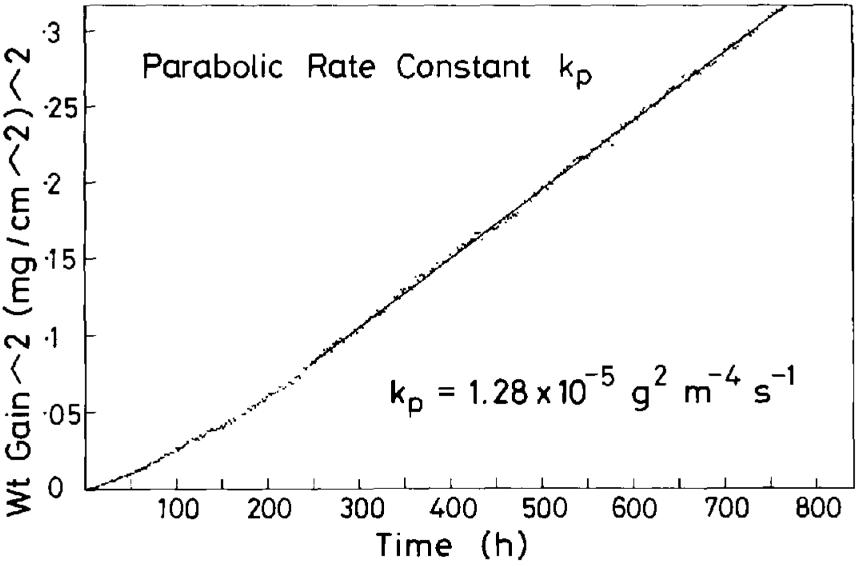

Fig. 6. (Weight gain)^2 versus time computer plot of data to first cycle shown in Figure 5.

the initial oxidation kinetics can be appreciated when the data points, up to the time of the first cycle, were analysed using (weight gain)^2/time coordinates (Figure 6). It is clear that parabolic oxidation behaviour was eventually developed after ∿ 200h oxidation but considerable deviation occurred up to this time. The final value of the parabolic rate constant was determined by the slope of the least squares line drawn on this Figure.

For the representative test shown in Figure 5, the cooling cycle was initiated after an exposure time of ∿ 764h. The first descernible effect of temperature decrease was to produce an increase in weight gain as shown in the Figure. Subsequent cooling resulted in a massive weight decrease due to loss of oxide by spallation, such as indicated in a scanning electron micrograph of the steel surface after cycling (Fig. 7). The relevant portion of Figure 5 could be enlarged by the computer and this is shown in Figure 8(a) in association with the corresponding variation in specimen temperature (Fig. 8(b)). In this Figure, point A is defined by the first detectable increase in weight and this effect was considered to arise from cracking of the protective oxide with subsequent rapid oxidation of the chromium depleted metal substrate. The spallation of oxide was taken to occur at the maximum point B in the weight-transient curve and interrelating this with the temperature transient curve of Figure 8(b)

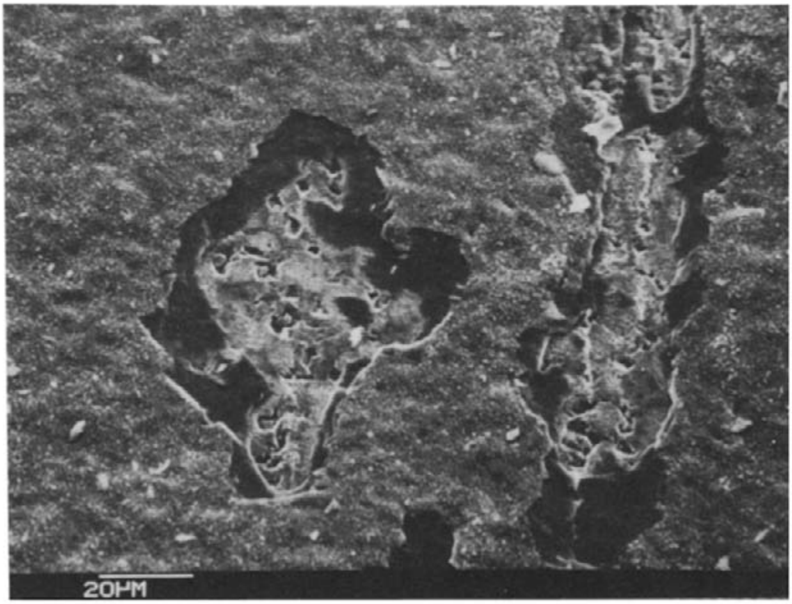

Fig. 7. Scanning electron micrograph showing areas of oxide spallation on a 20%Cr/25%Ni/Nb steel after oxidation at 850°C and 1 thermal cycle.

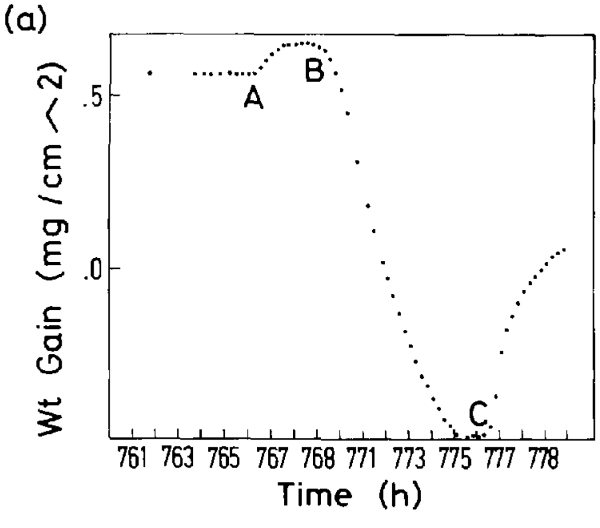

Fig. 8(a). Weight change profile during temperature cycle to 100°C for test of Fig. 5: A indicates the start of oxide cracking, B the start of oxide spallation and C the start of temperature increase.

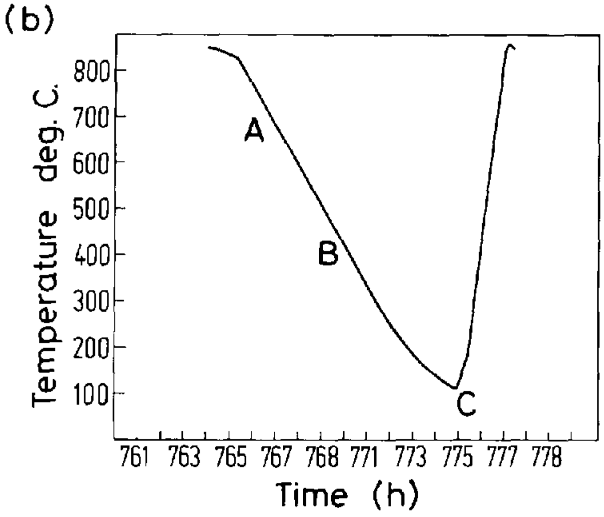

Fig. 8(b). Comparative temperature profile of cycle to 100°C showing relative positions of A, B and C.

provided an evaluation of the critical temperature change to initiate spallation from this steel. Point C is the minimum in weight change coincident with the minimum in temperature after which rapid re-oxidation took place upon the next heating cycle.

The microbalance results were used to check the concepts of initiation of spallation in terms of oxide thickness and its elastic properties. A detailed treatment of these theoretical aspects of the spallation mechanism will be published elsewhere (ref.2).

CONCLUSIONS

The microbalances in this facility have proven to be suitable for an accurate study of the high temperature oxidation of metals and alloys, with a gravimetric accuracy of within 30 to 50 μg. The data acquisition system provided easy collection and analysis of both gravimetric and temperature data for up to 60 data outputs.

ACKNOWLEDGEMENTS

This paper is published by permission of the Central Electricity Generating Board. The author gratefully acknowledges the assistance of Mr. E.J. Hoare in the design and construction of this facility and of Mr. J.P. Barnes in the computer programming.

REFERENCES

1 M.G.C. Cox, B. McEnaney and V.D. Scott, Prog. in Vacuum Microbalance Techniques, Vol. 2 (Eds. S.C. Bevan et al), 1973, p. 27.
2 H.E. Evans and R.C. Lobb, 1983, Corros. Sci., to be published.