Thermochimica Acta, 55 (1982) 287–291
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

A NEW SIMPLE INSTRUMENT FOR THERMOMAGNETOMETRY. APPLICATIONS TO SIMULTANEOUS THERMOMECHANICAL MEASUREMENTS

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(Received 4 November 1981; revised 5 January 1982)

ABSTRACT

A new instrument has been set up to study magnetic materials. Curie points measured by means of this simple apparatus are in perfect agreement with those given by a conventional magnetic balance. The apparatus may be used alone, but also combined with an electronic thermodilatometer. Curie points are emphasized simultaneously by the thermodilatometric and impedance curves. It appears that the sensitivity and reliability of the apparatus demonstrate magnetic phenomena of very low intensity such as the order point of α-Fe_2O_3.

INTRODUCTION

Curie point determination is usually done by measuring the force exerted on the sample in a magnetic field, the strength of which vanishes as soon as the Curie temperature is reached. Conventional magnetic balances used for this purpose are rather sophisticated and expensive and are not easy to combine with other thermal analysis techniques. The apparatus set up in our laboratory is very simple and easy to use alone or combined [1].

EXPERIMENTAL

The sample lies in the center part of a platinum coil wound around the sample holder. This coil provides a good thermal conductivity to the jacket (Fig. 1). The refractory cement used must present almost no variation of magnetic permeability with temperature. Powder samples are placed in a thin alumina or silica tube while compacted or massive ones may be in direct contact with the measurement thermocouple without any sample holder.

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This thermocouple, if NiCr–Ni, gives an internal temperature reference. The platinum coil is connected to an electric generator providing a high frequency current. The Curie point detection is easily done by means of an oscillating circuit or by an impedance measurement.

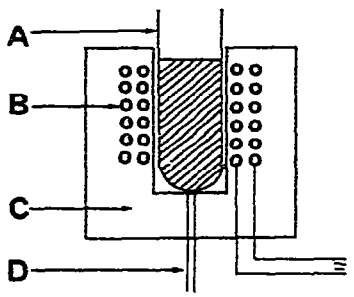

Fig. 1. Cross-section of the apparatus. A, Sample holder; B, platinum coil; C, cement jacket; D, thermocouple.

EXPERIMENTAL RESULTS

Apparatus used alone

Curie point determination of a cobalt ferrite sample $CoFe_2O_4$ is done with a magnetic balance and the described apparatus. Experimental curves are shown in Fig. 2. Each series of curves exhibits an important evolution with the first three cycles of heating; this evolution is evidenced by an increase of the magnetic force, $K\chi$, developed in the balance and by an increase of the impedance fall, Y, at the Curie point. This evolution may be attributed to a morphologic development of the sample (size of crystallites) [2].

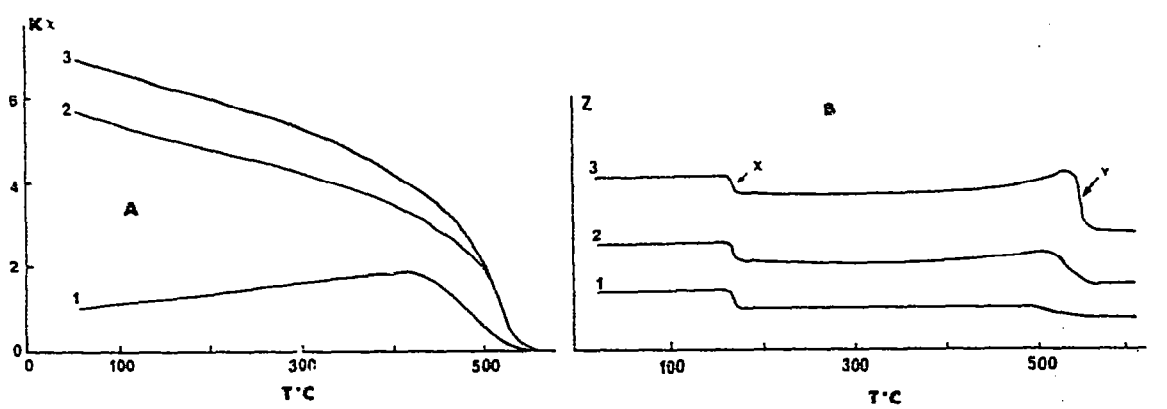

Fig. 2. Experimental curves for the Curie point determination of a cobalt ferrite sample, after 1, 2 cycles of heating and after annealing at 1000°C. A, By means of a magnetic balance; B, by means of the described apparatus. X and Y represent, respectively the Curie point of the thermocouple and the Curie point of the sample.

Simultaneous Curie point and thermodilatometric measurements

A platinum coil is set around the sample holder of an electronic dilatometer [3] as seen in Fig. 3. Curie point determinations are done by impedance measurement and corroborated by the thermodilatometric curve. Figure 4

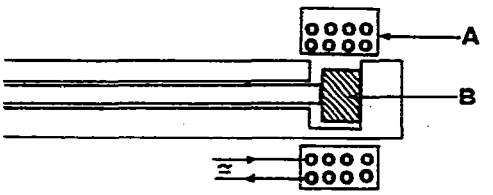

Fig. 3. Simultaneous Curie point and thermodilatometric measurements.

shows the experimental results of an iron powder pellet compacted at 1000 bars for 1 min. The impedance curve shows two jumps: the first (X) corresponds to the Curie point of Fe_3O_4 created in situ, and the second (Y) corresponds to the Curie point of iron. The latter is also evidenced by the thermodilatometric curve, as the α, γ transformation (Z).

Figure 5 shows the experimental curves of a nickel ferrite $NiFe_2O_4$ compacted in a pellet under 500 bars for 1 min. This sample was annealed at 1000°C for 1 h so as to have no evolution of the sample with the thermal cycles as for $CoFe_2O_4$.

Figure 6 shows the experimental curves for γ-Fe_2O_3. The impedance curve shows the transformation γ-Fe_2O_3 (ferrimagnetic) → α-Fe_2O_3 (antiferromagnetic). This transformation (X) is corroborated by the dilatometric curve which evidences the corresponding contraction of the crystal cell. At 675°C

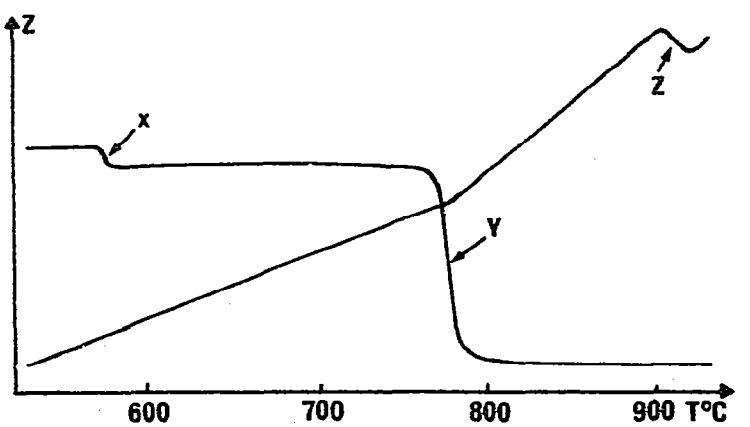

Fig. 4. Simultaneous Curie point and thermodilatometric measurements for a compacted iron powder sample.

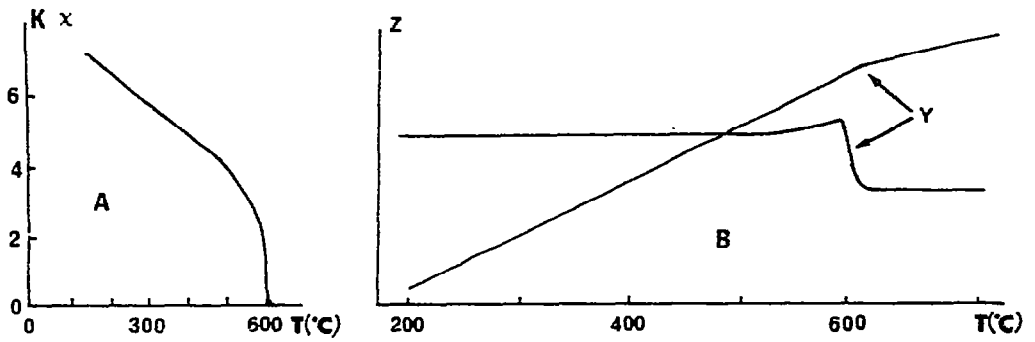

Fig. 5. Experimental curves of compacted nickel ferrite $NiFe_2O_4$ annealed at 1000°C for 1 h. A, Thermomagnetic curve; B, simultaneous Curie point and thermodilatometric measurements. Y, Curie point determination.

the impedance curve shows the order point (Y) of α-Fe_2O_3 (imperfect antiferromagnetic). This point, not shown by the thermodilatometric curve on heating (because of the important shrinkage due to the roasting), is evident on cooling and corroborated by the impedance curve. It should be noticed that on cooling both the impedance and thermodilatometric curves show no other peculiar point than (Y), which means that the former transformation is complete and not reversible.

Figure 7 shows the experimental curves for a sample of Fe_3O_4 compacted at 500 bars for 1 min. The impedance curve (I) recorded on heating shows three transformations (X, Y and Z) all corroborated by the dilatometric curve. The first (X) is the transformation Fe_3O_4 (ferrimagnetic) $\rightarrow$ γ-Fe_2O_3 (ferrimagnetic), then the transformation γ-Fe_2O_3 (ferrimagnetic) $\rightarrow$ α-Fe_2O_3 (antiferromagnetic) (Y), and at 675°C (Z) the order point of α-Fe_2O_3. This point (Z), as in the former example, is shown on the thermodilatometric

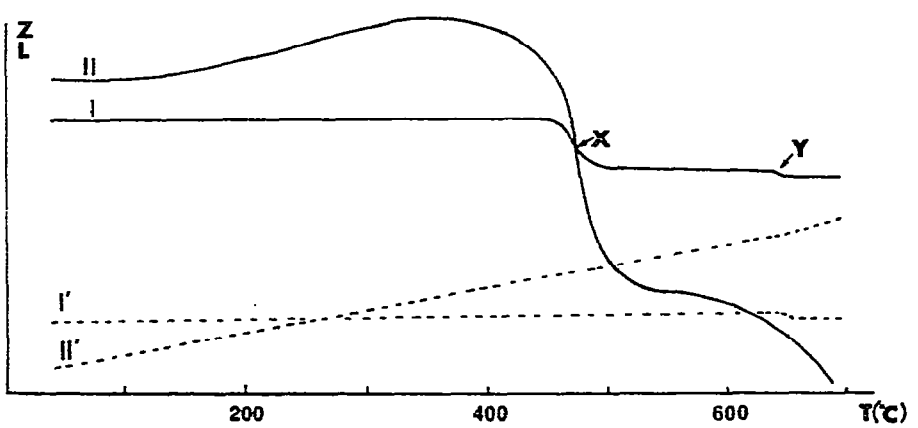

Fig. 6. Simultaneous impedance (I) and thermodilatometric (II) curves of a compacted γ-Fe_2O_3 powder sample. The dotted curves are recorded on cooling (compacting pressure 500 bars for 1 min, heating and cooling rate 7 K min^{-1}).

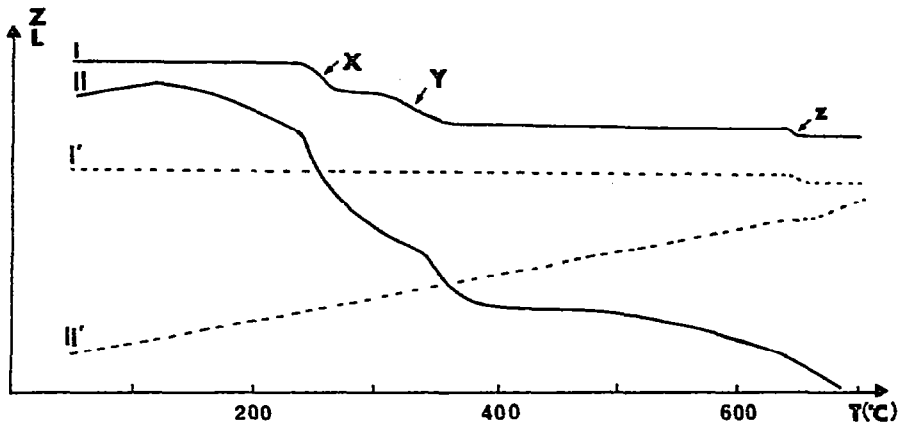

Fig. 7 Simultaneous impedance (I) and thermodilatometric (II) curves of a compacted iron oxide Fe_3O_4 powder sample. The dotted curves are recorded on cooling (compacting pressure 500 bars for 1 min, heating and cooling rate 2 K min^{-1}).

curve only on cooling because of the important shrinkage of the sample due to roasting.

CONCLUSION

These few examples show that the Curie points measured by means of this apparatus are in perfect agreement with those given by a magnetic balance. The example of cobalt ferrite shows that, as with a magnetic balance, it is possible to follow the morphologic evolution of the sample through the different heating cycles. The examples of the compacted iron and nickel ferrite powder show that the Curie point determination is perfectly corroborated by the dilatometric curves and that it is valuable to combine this apparatus with another thermal analysis technique. It appears that the sensitivity and the reliability of the apparatus allow one to demonstrate magnetic phenomena of very low intensity such as the order point of the oxide α-Fe_2O_3 and that it is possible to use this apparatus for quantitative measurements as, for instance, the determination of the iron oxide content of a hydraulic binder [4].

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