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Note

A precautionary note on thermogravimetry with magnetic materials

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In our recent study of the rate of oxidation of magnetite, Fe_3O_4, we observed an anomaly in the thermogravimetric (TG) curve in the vicinity of its magnetic transition[1]. Since a possible irregularity in the rate at the Curie temperature, T_c, was the subject of our investigation, this was initially very misleading. Isothermal studies, using a different apparatus, revealed a genuine and striking anomaly in the rate of oxidation in the vicinity of T_c and it was disconcerting to be unable to correlate the observed TG change with the isothermal results.

It was finally concluded that the peculiarity in the TG curve must arise from spurious sources, for example, extraneous magnetic fields. In an effort to establish this conclusion a similar TG experiment was performed using a different material having a similar T_c. An Fe–Ni alloy (Perkalloy) was found which has a T_c of 596 °C, compared with about 590 °C for Fe_3O_4.

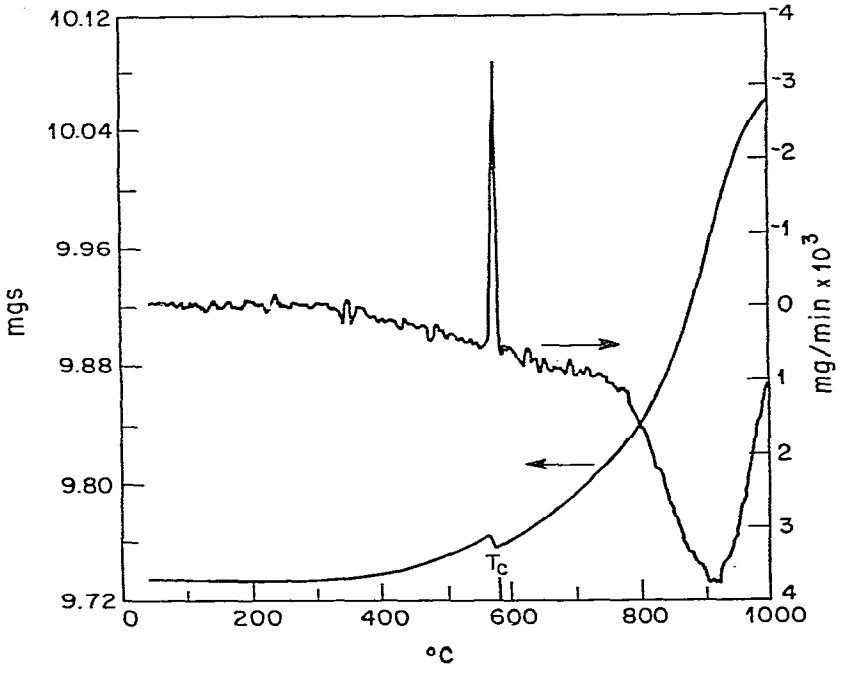

Fig. 1. TG and DTG curves of Fe_3O_4 heated in air at 2.5 °C min^{-1}.

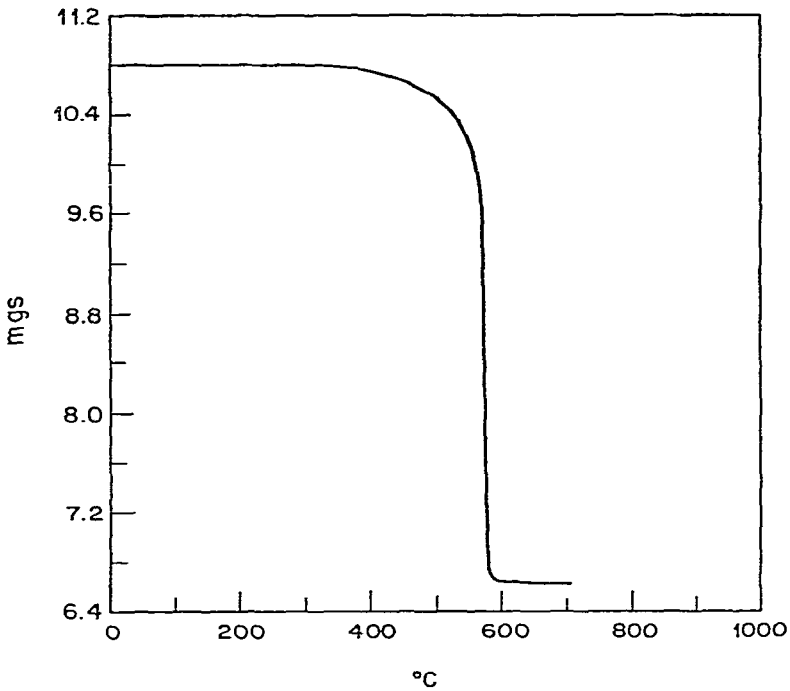

Fig. 2. TG curve of Fe_3O_4 heated in Ar at 2.5 °C min^{-1} in a magnetic field.

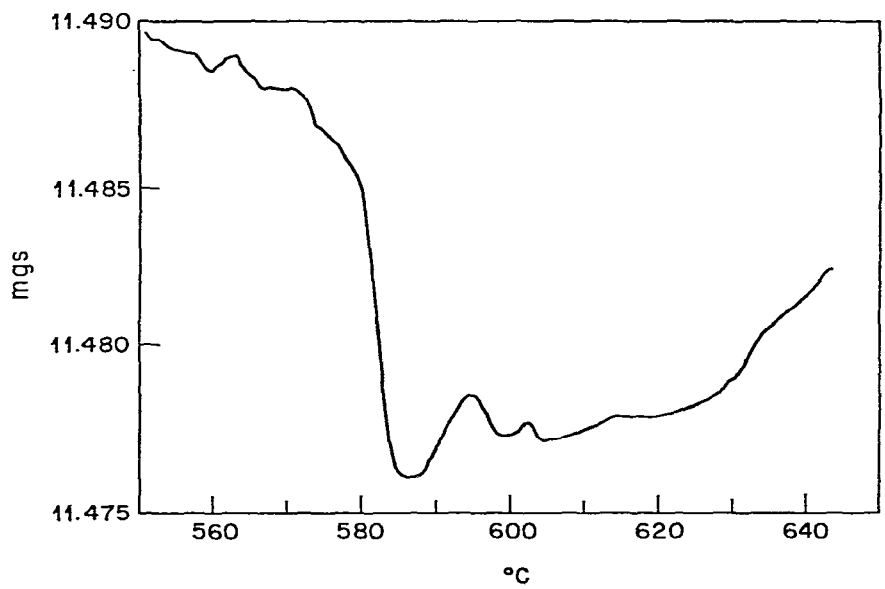

Fig. 3. TG curve of Perkalloy heated in Ar at 2.5 °C min^{-1}.

Figure 1 shows the TG and DTG curves for Fe_3O_4 (120–170 mesh fraction) heated at 2.5 °C min^{-1}. A Perkin-Elmer TGS-1 thermobalance was used which had been modified to provide a digital output[2]. A flow rate of 40 cm^3 min^{-1} of air was used. Figure 2 shows the same material heated in Ar and in the presence of the small Perkin-Elmer permanent magnet normally used in their temperature calibrating

procedure. The apparent weight loss is much more severe than in the case of no external field, Fig. 1. Figure 3 shows an expanded section of the TG curve for Perkalloy also heated in Ar. The unpurified Ar and leakage of air into the system allowed for a very slow oxidation of the metal.

In both cases, Figs. 1 and 3, there was abrupt apparent weight loss, about 0.1 %, which occurred essentially at T_c. Figure 2 verifies, in fact, the influence of even a mild magnetic field, $\sim$150 Gauss, on the apparent weight loss at T_c. This suggested that there may have been a small magnetic field gradient pulling down on the sample. A simple magnetic probe revealed this to be true. There is a DC component generated by the SCR and although the furnace is wound bifilarly[3] there is still a readily detectable magnetic gradient emphasized by the small physical dimensions of the Perkin-Elmer furnace. Similar tests using the much larger Fisher TGA system, used in the isothermal work, showed no detectable irregularities in the weight change for either material and the probe indicated that the gradient in the magnetic field was tenfold less.

Under most circumstances such slight irregularities would be unimportant or even overlooked. In this instance, it was misleading and troublesome, however, and we wish to caution and alert other investigators to this spurious effect.

REFERENCES

1 P. K. Gallagher and E. M. Gyorgy, *J. Chem. Phys.*, in press.
2 P. K. Gallagher and D. W. Johnson, Jr., *Thermochim. Acta*, 4 (1972) 283.
3 B. Cassel, Perkin-Elmer Co., personal communication.