

THERMOMAGNETOMETRY AND THERMOGRAVIMETRIC ANALYSIS OF CARBONYL IRON POWDER

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ABSTRACT

Carbonyl iron powder (CIP) is a purified iron powder prepared from iron pentacarbonyl in a thermal decomposition process, and can contain up to 0.9% of nitrogen and 0.8% of carbon. Whether carbon and nitrogen are present in elemental form or in carbide and nitride phases is still unreported in the literature. The roles of carbon and nitrogen in the crystalline (or “onion-skin”) microstructure of CIP are also not fully understood. The presence of carbide and nitride phases has been reported in the literature as a result of X-ray diffraction studies of CIP samples annealed above 300 °C. This laboratory has found high temperature DTA to be insufficiently sensitive to detect carbide and nitride Curie transitions in CIP. The combination of a thermogravimetric (TG) analyzer with a calibration magnet reproducibly attached to the furnace during programmed heating/cooling (thermomagnetometry, TM) was found to be the most sensitive technique for detecting all Curie transitions in CIP. This is the first time the presence of carbide and nitride phases in CIP below 300 °C (i.e. the typical manufacturing process temperature of CIP) has been observed. In the present work, CIP samples were compared to pure iron, iron carbide and iron nitride using conventional TG and TM techniques to characterize the CIP in detail.

INTRODUCTION

Carbonyl iron powder (CIP) is used largely for the production of magnetic cores of transformer and inductance coils because of its favorable magnetic properties, especially at high frequencies. Its advantages over other iron powders include high purity, high hardness, small particle size (3–7 μm) and solid spherical particles. CIP is made by thermal decomposition of iron pentacarbonyl vapor at atmospheric pressure and temperatures above 250 °C. The cyclical sequence of formation of iron crystals upon nucleation in the thermal decomposition process produces a characteristic morphology consisting of concentric spherical shells, which has been described as an “onion-skin” structure upon electron microscopic investigation [1].

From elemental analysis, CIP is known to contain up to 0.9% of nitrogen and 0.8% of carbon. Whether carbon and nitrogen are present in their elemental forms or as carbide and nitride phases is still unresolved in the

literature [2–4]. The presence of carbide and nitride phases has been observed as a result of X-ray diffraction (XRD) studies of CIP samples annealed above 300 °C [2]. In the present study, CIP was compared to pure iron, iron carbide and iron nitride using thermomagnetometry (TM) as well as conventional TG and DTA techniques to characterize the various major and minor Curie transitions.

EXPERIMENTAL

Materials

The samples used in this study were CIP (E Grade) from the GAF Chemicals Corporation; pure iron powder from Johnson Matthey Chemicals Ltd. (Grade 1, Batch S92704B); and iron nitride ($\text{Fe}_3\text{N} + \text{Fe}_4\text{N}$, Lot 022186) and iron carbide (Fe_3C , Lot 102185), both from Alpha Products.

Thermogravimetric analysis

A Perkin–Elmer Model TGA-7 thermogravimetric analyzer was used to measure percent weight change as a function of temperature up to 900 °C. The heating rate was 20 °C min^{-1} up to 400 °C and 10 °C min^{-1} above 400 °C. The temperature axis of the TGA was calibrated in a helium environment using the Curie transition temperatures of standard iron and nickel. All tests were performed using helium as a purge gas at a flow rate of 100 ml min^{-1} . The sample size was about 30 mg.

Thermomagnetometry

TM was carried out using a Perkin–Elmer TGA-7 by applying a fixed magnetic field to the samples. The arrangement is similar to the Guoy balance used to measure magnetic susceptibility. The position and height of the calibration magnet were fixed in the first heating cycle and kept constant throughout the study. A reproducible apparent weight gain resulting from the applied magnetic field can be achieved in this manner. The apparent weight change W in TG is a measure of the magnetic susceptibility k of the sample, according to the equation [5]

$$W = kvH \frac{\partial H}{\partial n}$$

where W is the apparent weight gain owing to the external magnetic field, k is the susceptibility per unit volume, v is the volume of the sample, H is the magnetic field strength, and $\partial H/\partial n$ is the magnetic strength gradient in the vertical direction.

For a TM experiment only W and k are variables in the above equation, since a fixed magnetic field H is applied to the sample. The temperature calibration, helium purge rate, heating rate and sample size were exactly the same as in the regular TG experiment. The second heating was performed at $20^\circ\text{C min}^{-1}$ after cooling to 40°C at $20^\circ\text{C min}^{-1}$.

Differential thermal analysis

High temperature DTA was performed up to 1500°C by Harrop Industries, Columbus, OH, with argon as a purge gas at a flow rate of 1400 ml min^{-1} . The heating and cooling rates were $10^\circ\text{C min}^{-1}$. The sample cups were alumina, and the sample size was 400 mg . A Harrop Model TA-700 DTA was used, with a type S thermocouple (platinum/platinum-10% rhodium).

Carbon and nitrogen analysis

Carbon and nitrogen contents were determined using the CHN-S/O elemental analyzer, model 1106, made by Carlo Erba Instruments. The combustion and reduction furnace temperatures were 1050 and 650°C , respectively. Combustion time was 8 min , and the sample size was about 5 mg .

X-ray diffraction analysis

XRD analyses were performed by Structure Probe, Inc., Metuchen, NJ. The XRD patterns were obtained for the $5\text{--}155^\circ$ range in 2θ reflection angles using a GE Model XRD-3 diffractometer.

Kjeldahl nitrogen analysis

A Buchi Model 322 distillation unit and a Buchi Model 342 titration unit were used in the Kjeldahl nitrogen analysis. The sample size was about 0.3 g .

RESULTS AND DISCUSSION

X-ray diffraction

The general characteristics of the X-ray spectra of the samples are summarized in Table 1. The CIP sample exhibited weak and broad peaks as compared to strong and narrow peaks for the pure iron. The iron nitride showed the mixed pattern of α -iron, Fe_3N and Fe_4N , while the iron carbide showed a mixed pattern of α -iron and, possibly, a mixture of Fe_3C and FeC .

TABLE 1

X-ray diffraction results

Sample	Diffraction peaks: d spacing (\AA)
Pure iron	1.28, 1.43, 2.03
Iron carbide	1.43, 2.03, 2.22, 2.38, 3.35, 3.68
Iron nitride	1.34, 1.43, 1.60, 1.90, 2.03, 2.07, 2.18, 2.41
CIP	1.43, 2.03

No nitride or carbide phase could be detected in the CIP sample by XRD at ambient temperature. It should be noted that the principal X-ray lines for α -iron and Fe_3C are reported to be 2.03 and 2.01 \AA , respectively, and appear to be not easily resolvable [6]. Borchers et al. [3] have indicated that if the cementite (Fe_3C) crystals in the powder are only 10 or 20 \AA in size, they cannot be detected by X-ray analysis. However, for CIP samples annealed above 300 $^\circ\text{C}$ both carbide and nitride phases have been detected, owing to the increase in crystallite size [2,3].

Thermogravimetric analysis

TG curves for iron nitride and iron carbide are shown in Fig. 1. For iron nitride, the actual weight loss up to 800 $^\circ\text{C}$ in TG (5.19%) is virtually the same as the nitrogen content determined by Kjeldahl analysis (5.15%) and elemental (Dumas) analysis (5.43%). This indicates that iron nitride can be

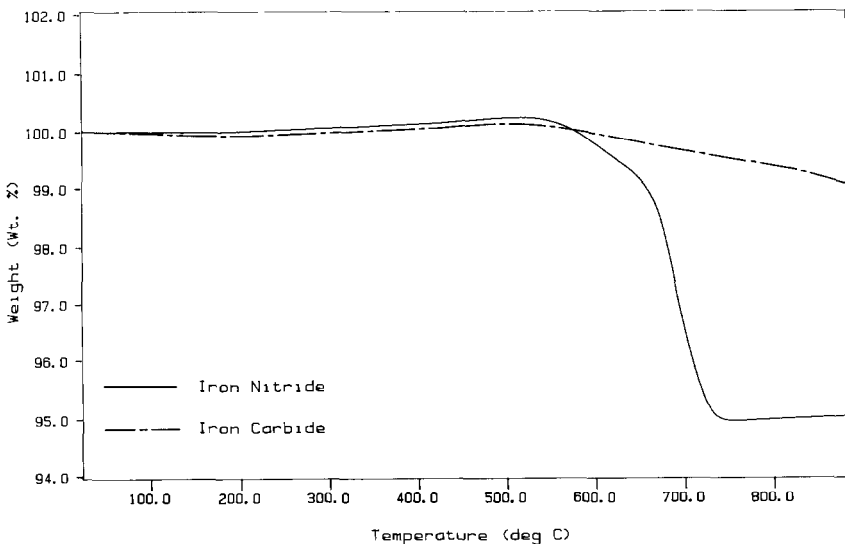


Fig. 1. TG curves for iron nitride and iron carbide.

TABLE 2
Elemental analysis of CIP, iron carbide and iron nitride

Sample	Before TG analysis		After TG analysis	
	% N	% C	% N	% C
CIP	0.95	0.95	0.01	0.03
Fe ₃ C (iron carbide)	0.00	6.28	0.00	3.73
Fe ₃ N + Fe ₄ N (iron nitride)	5.43	0.23	0.01	0.02

converted to pure iron and nitrogen by heating to 800°C in an inert environment. The results from elemental analysis (Table 2) of iron nitride before and after TG are in agreement with the TG results. The actual weight loss started at around 490°C and was completed at around 650°C.

For iron carbide, the actual weight loss started at around 500°C with a total weight loss of 0.9% up to 900°C. Figure 2 shows the weight loss of CIP during heating up to 900°C. The actual weight loss occurred from approximately 500 to 800°C, and this can be attributed to the elimination of impurities (carbon, nitrogen and oxygen), as confirmed by the elemental analysis results shown in Table 2. For pure iron, a gradual but continuous weight gain started at around 200°C, with a total weight gain of less than 1% continuing to 900°C. This was probably due to imperfect sealing of the instrument, allowing a slight oxidation (i.e. oxygen uptake) of the sample.

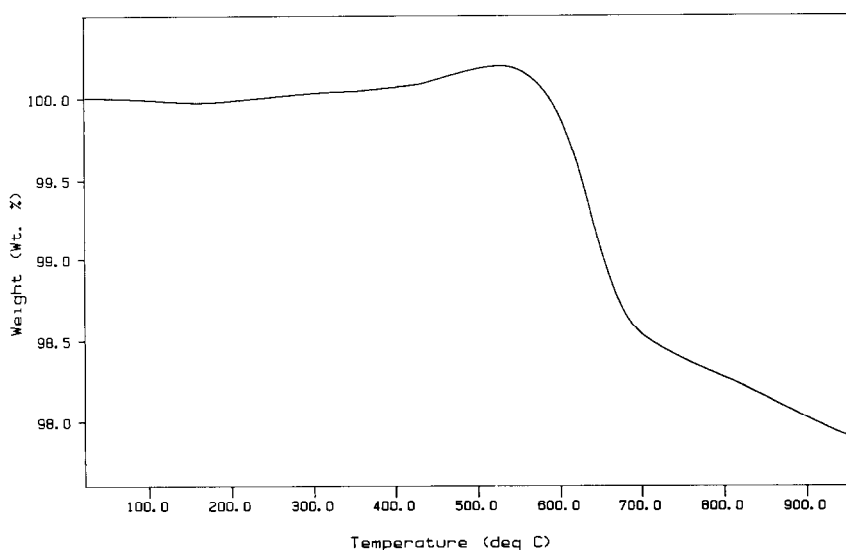


Fig. 2. TG curve for CIP.

Thermomagnetometry and differential thermal analysis

Figure 3 shows TM curves for iron nitride and iron carbide. For iron nitride, two well defined Curie transitions can be seen, at 255°C (probably the Fe_3N phase) and 480°C (Fe_4N phase) [7]. Above 600°C the iron nitride started to convert to pure iron, as shown by the regaining of specific magnetization around 670°C, yielding a Curie transition at 770°C of pure iron. For iron carbide, the Curie transition of cementite (Fe_3C) at 210°C was clearly revealed by TM. However, this sample retained a strong ferromagnetic character even after the transition. This indicated the presence of α -iron, producing a major Curie transition at around 740°C. This result is different from that obtained in an earlier work, where pure Fe_3C was used [8].

The TM curve for the CIP sample is shown in Fig. 4. The initial apparent weight gain which is related to the specific magnetization of the CIP sample (40–50%) is lower than that of iron nitride (54%), iron carbide (60%) or pure iron (100%). As the temperature increased, minor transitions from 200°C to 250°C (Fe_3N , Fe_3C and Fe_2C phases), and at approximately 350°C (Fe_2C phase), 470°C (Fe_4N phase) and 570°C (Fe_3O_4 phase) can be seen in the derivative curve. The transition at around 600°C cannot be attributed to any component and is probably related to the evolution of nitrogen or other impurities which would temporarily disrupt the magnetic domains of the CIP. As the temperature continued to increase, the magnetic moment increased immediately after this transition (as indicated by the increase in apparent weight). This suggests that after the release of the nitrogen (or

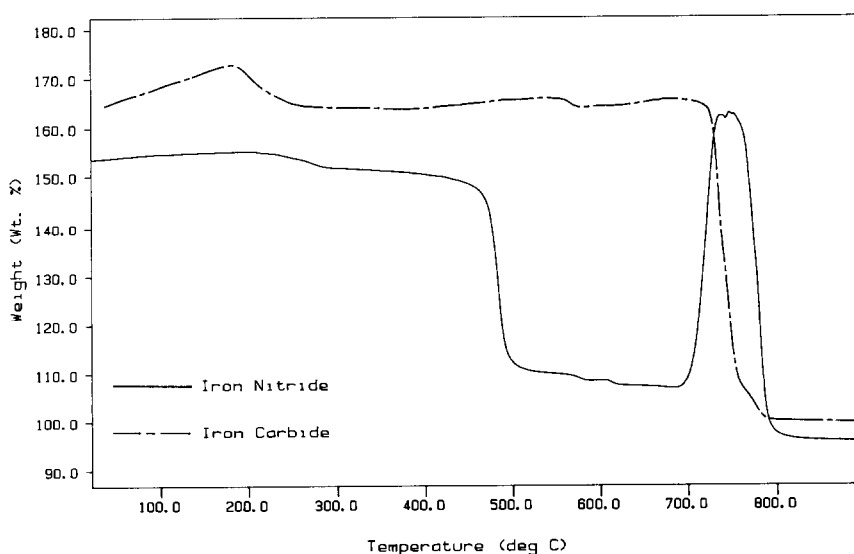


Fig. 3. TM curves for iron nitride and iron carbide.

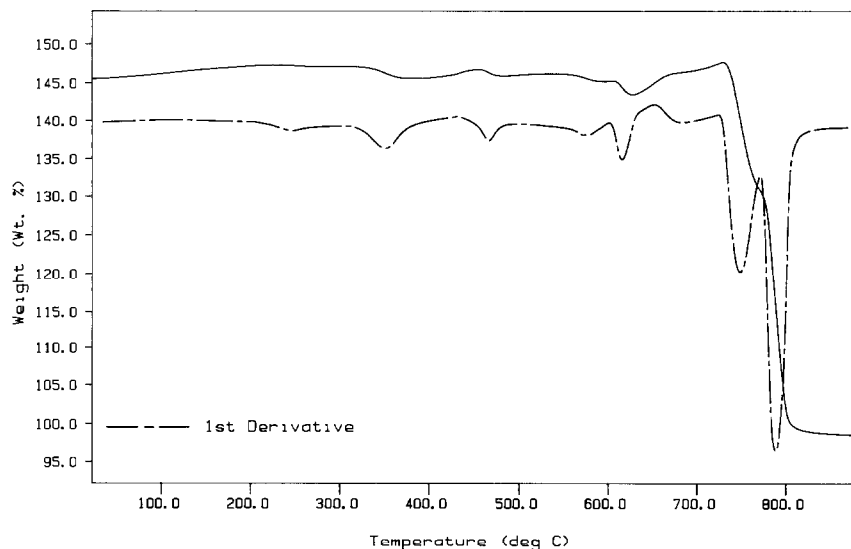


Fig. 4. TM curve for CIP.

other impurities) α -iron domains were able to grow, increasing the magnetic properties of the CIP.

Figure 5 shows the TM curve for the pure iron powder. A well defined Curie point can be seen at around 770°C. A minor transition at around 570°C also occurred. This is believed to be the Curie point of magnetite (Fe_3O_4) [7], which can be formed during heating as a result of imperfect

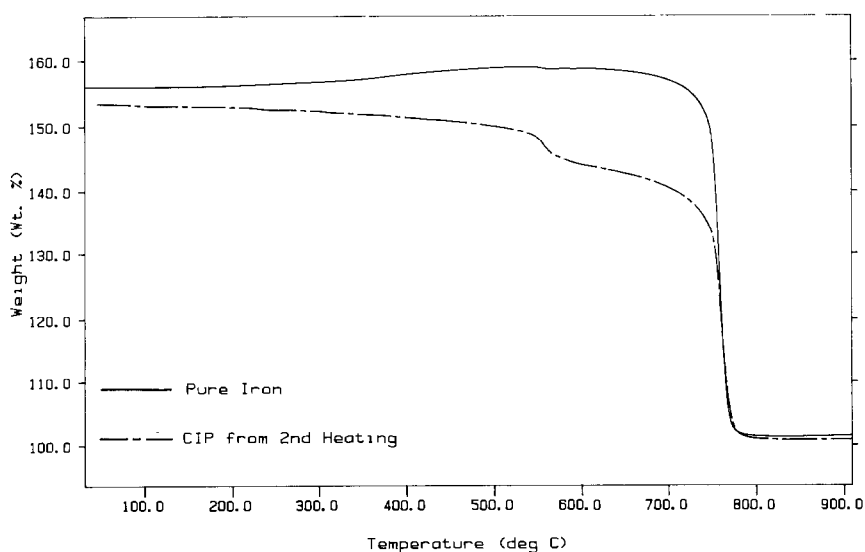


Fig. 5. TM curves for pure iron powder and CIP from the second heating cycle.

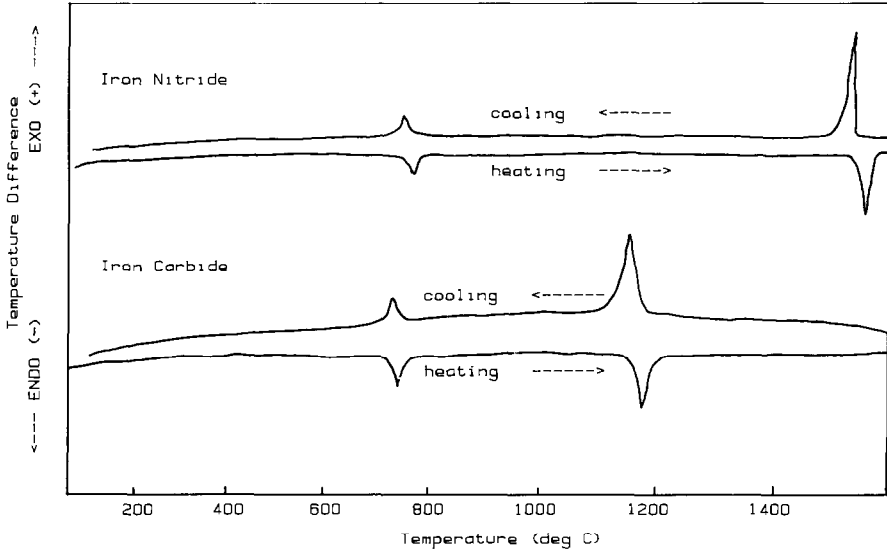


Fig. 6. DTA curves for iron nitride and iron carbide.

sealing of the instrument. This minor transition also appeared in the TM curves for the iron carbide, iron nitride and CIP samples. Figure 5 also shows the TM curve for CIP during the second heating cycle. Most of the minor transitions have disappeared. This is believed to be due to elimination of most of the impurities (which are responsible for the minor phases) after heating to 900°C in the first heating. In fact, this curve is almost the same as that obtained for pure iron.

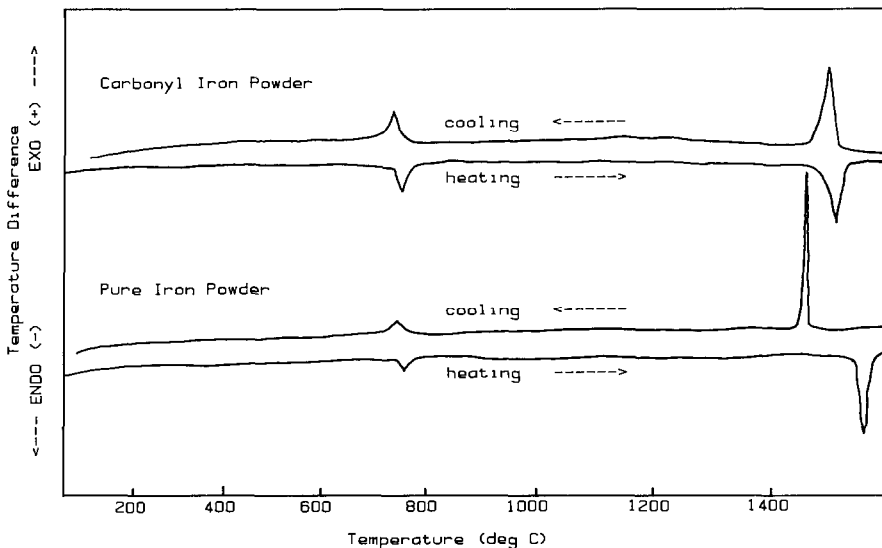


Fig. 7. DTA curves for CIP and pure iron powder.

DTA curves for the four samples (CIP, pure iron, iron nitride and iron carbide) are shown in Figs. 6 and 7. There are no minor transitions to be seen in any of these DTA curves. DTA seems to be insufficiently sensitive to detect the existence of minor phases. For example, the DTA curves are almost the same for pure iron, CIP and iron nitride, with the Curie transition of α -iron at 750°C and melting of iron at around 1550°C. For iron carbide, the DTA curve (Fig. 6) shows the Curie transition of α -iron at 745°C and the eutectic point at 1175°C for the mixture of λ -iron, carbon and Fe_3C [9].

CONCLUSIONS

(1) The actual weight loss in TG of CIP is attributable to the elimination of elemental impurities (i.e. carbon, nitrogen, oxygen). Iron nitride can be converted to pure iron, while iron carbide loses weight only partially between 500 and 900°C, as determined by TG in an inert atmosphere (helium).

(2) DTA can detect the Curie transition of α -iron, but the technique is not sensitive enough to detect Curie transitions in iron nitride or iron carbide, or the nitride and carbide phases in CIP.

(3) XRD at ambient temperature cannot detect nitride or carbide phases in CIP, presumably because of the smallness of the crystallite size.

(4) TM is by far the most sensitive, direct and convenient technique for the detection of all the Curie transitions (of major and minor phases) in CIP, iron nitride and iron carbide. From the appearance of their Curie transitions in CIP, the presence of nitride and carbide phases has been confirmed. Changes in the magnetic properties of CIP owing to factors other than phase transitions (e.g. elimination of impurities, formation and disruption of magnetic domains) can also be followed using TM.

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REFERENCES

1. A. Taylor, in C.E. Richards and A.C. Lynch (Eds.), *Soft Magnetic Materials for Telecommunications*, Interscience, New York, 1953, p. 202.

- 2 G. Bohm, *Fach. Heeten. Metall.*, 20 (3) (1982) 146.
- 3 H. Borchers, N. Haberland and V. Haberland, *Arch. Eisenhuettenwes.*, 38 (3) (1967) 241.
- 4 F.L. Ebenhoech, Carbonyl iron powder: production, properties and applications, Annual Meeting of the Metal Powder Industry Federation, Boston, MA, 1986.
- 5 P. Selwood, *Magnetochemistry*, Interscience, New York, 1956, p. 3.
- 6 Powder Diffraction File, Alphabetical Index, Inorganic Phase, International Center for Diffraction Data, 1981, p. 430.
- 7 P. Selwood, *Magnetochemistry*, Interscience, New York, 1956, pp. 38, 312.
- 8 R.G. Charles, L.N. Yannopoulos and P.G. Hauerlack, *J. Inorg. Nucl. Chem.*, 32 (1970) 447.
- 9 D. Nicholls, in *Comprehensive Inorganic Chemistry*, Vol. 3, Interscience, New York, 1973, Chap. 40, p. 988.