

NOVEL DISPERSIONS OF IRON IN AMORPHOUS GLASSLIKE CARBONS:^{*}
EXPLORATORY MAGNETIC STUDIES

Alan W. Thompson, P.L. Walker, Jr. and L.N. Mulay⁺

Materials Research Laboratory and the Solid State Science Program, The Pennsylvania State University, University Park, Pa. 16802

INTRODUCTION AND EXPERIMENTAL

One of us (LNM) reported extensive studies on the superparamagnetic behavior of dispersions of iron species (atoms, ions) in the silicate¹⁻³ and zeolite type matrices⁴. In a search for novel methods for dispersing iron, this author noticed the possibility of dispersing Fe species in a diamagnetic carbon host lattice. As such this exploratory work was undertaken. A number of samples of amorphous glasslike carbon containing iron were supplied to us by Professor R. Kammareck⁺⁺ and Dr. Nakamizo. A schematic of their synthesis is shown in the following diagram⁺⁺.

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⁺All inquiries should be addressed to this author.

⁺⁺Details of the synthesis will be presented separately at the 11th Biennial Carbon Conference (Gatlinberg, TE) and published in its proceedings. We are very grateful to our distinguished polymer chemists for supplying these samples.

Schematic of Synthesis

(FA) copolymerize with (FDA)* or (VF)*

[at 60°C under acid catalysis]

(Product-I)

[cured in vacuum at 250°C, 48 hrs]

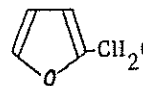
(Product-II)

[pyrolysis in inert atmosphere up to 970°C

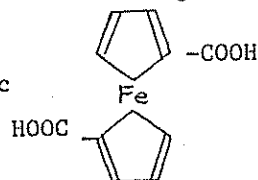
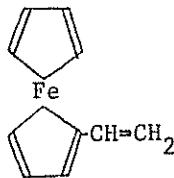
rate of temperature increase from 5°C/hr to 60°C/hr]

(AMORPHOUS GLASSLIKE CARBONWITH DISPERSION OF Fe)

FA = furfuryl alcohol



(polymerizes to poly(furfuryl alcohol) (PFA))

FDA = { ferrocene
dicarboxylic
acidVF = { vinyl
ferrocene

*Note: The concentrations of FDA varied from 1 to 3% and that of VF from 1 to 10% by weight.

TABLE I: SAMPLES STUDIED AND TYPE OF MEASUREMENTS

Sample	Preparation Temperature			
	500°C	625°C	700°C	970°C
PFA	M	M	M	M
PFA + 1% FDA	M	M	M	M
PFA + 3% FDA	-	M,S	M	M,S
PFA + 1% VF	M	M	-	M
PFA + 10% VF	M,S	M,S	M,S	M,S

The particular samples studied are given in Table I. In this table, M indicates magnetization measurements, and S indicates susceptibility measurements.

The vibrating sample magnetometer technique was selected because of its ability to furnish rather quickly the magnetization as a function of the field and temperature, especially for samples with large magnetic moments. A magnetometer of this type, manufactured by the Princeton Applied Research Laboratory, Princeton, N.J., was employed for all magnetization measurements reported here. Several high temperature susceptibility measurements (from room temperature to 750°C) were carried out in the Chemistry Department at the University of Pittsburgh* using an automated Faraday balance described by Butera, et al.⁵ The sensitivity of this particular balance was fairly low. This limited the samples to be measured to those with high iron content and to those available in large quantity. The large amount of sample rendered the absolute measurement of the susceptibility to be somewhat ambiguous. Thus, only relative susceptibilities are reported here. However, the Curie points of the materials were accurately established.

*We are grateful to Drs. W.E. Wallace and R.S. Craig for providing these facilities.

MAGNETIC PROPERTIES AND DISCUSSION

Magnetization versus field measurements were made on all samples. The samples that contained iron displayed weak ferromagnetism. For all samples save one, saturation occurred at 5-6 K gauss. The 500°C VF sample saturated at 2-3 K gauss. The saturation magnetization per gram (σ) of Fe for various samples containing iron was measured. Results are shown in Figure 1a.

The FDA samples show similar behavior with an approach at the high temperature end to the saturation magnetization of Fe_3C (cementite), which was found in these carbons by a combination of electron microscopy and x-ray diffraction. It is interesting to note that the "dilute" (1% FDA) sample shows relatively higher saturation magnetization than the "concentrated" (3% FDA) sample over a wide range of their preparation temperatures. Thus it may be surmised that the 1% FDA sample has relatively small particles (probably superparamagnetic) of iron species, which are more difficult to saturate. In both cases, the final product obtained by preparing the samples at a higher temperature ($\sim 1000^\circ\text{C}$) turns out to be Fe_3C , which is formed by the conglomeration of such particles,

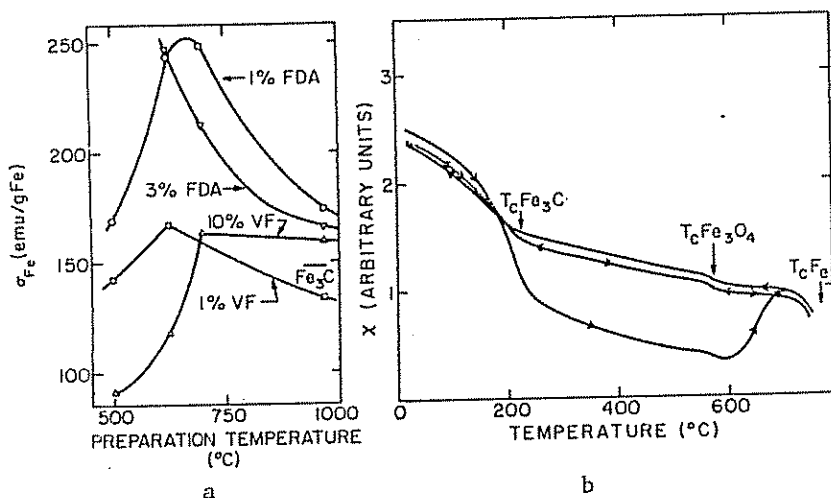


Figure 1. (a) Saturation magnetization measured at 19K gauss and 25°C for various glassy carbon samples as a function of their preparation temperature. (b) Magnetic susceptibility in arbitrary units as a function of temperature for the glass-like carbon prepared with 10% VF (970°C).

large or small, existing at preceding temperatures of preparation.

While the 1% VF and 10% VF samples show a similar trend over the low temperature region of preparation (500 to 700°C) this trend is reversed over the higher range (700 to 1000°C). This is suggestive of an unusual mode of conglomeration for the VF system, which is quite different than the FDA system.

In any case, it is noteworthy that the 10% VF system also approaches the formation of Fe_3C . The 1% VF samples appear to show the same trend as the FDA sample; however, the magnetization at 970°C is below that of Fe_3C . This may be due to incomplete conglomeration of fine particles to form bulk Fe_3C .

Electron micrographs of the 500°C, 10% VF sample show small "cubic" areas of high density material. Micrographs of the samples treated at higher temperatures show the material in these areas to have migrated out. It is apparent that the trend in magnetization reflects this migration. However, this species as of now has not been identified.

Despite the large error involved in measuring diamagnetic magnetization on the magnetometer, a definite trend to larger diamagnetic magnetization with increasing preparation temperature was observed. This increase in the diamagnetic magnetization is probably due to a decrease in paramagnetic centers (i.e. free radicals) with heat treatment.

SUSCEPTIBILITY MEASUREMENTS

Susceptibility versus temperature measurements were made on several of the samples, temperatures not exceeding the preparation temperatures. Except for the 500°C - 10% VF and 625°C - 10% VF samples, the samples all displayed similar behavior. The samples were heated and cooled several times as susceptibility measurements were being made. Figure 1b shows the observed behavior. Besides the Curie point for Fe_3C at 222°C, the curve also shows a Curie point at about 565°C, that for magnetite (Fe_3O_4). As the samples were heated above 600°C, there was observed an increase in the susceptibility with a turnover above 700°C indicating the Curie point of metallic iron at 770°C. Cooling back to room temperature, a marked decrease in the amount of Fe_3C is observed. Since Fe_3C is an unstable compound, it must be concluded that the iron in Fe_3C is being decomposed to metallic iron when heated above 600°C. This is interesting, since these samples, in

their preparation, have previously been heated, in some cases, to above this temperature. In some way, the preparation method forces the formation of Fe_3C . It has been thought that these glasslike carbons have closed pores, thus being impervious to gases. This may not be so, since these materials have been stored in air for six months or better before susceptibility measurements were made. During this time, air may have entered the pores or some gas produced during the preparation may have escaped.

The susceptibility of the 500°C-10% VF and the 625°C-10% VF samples (Figure 2) both showed similar behavior, somewhat different from the other samples. The Curie points observed are those for Fe_3C and Fe_3O_4 . Unlike the previous samples, the Fe_3C decomposes to Fe_3O_4 instead of iron. Here again, the heat treatments during preparation have forced Fe_3C formation. However, the small cubic areas of high density material revealed by electron microscopy cannot be determined from the data.

Further work along the lines indicated here is being continued in the hope of producing good superparamagnetic systems.

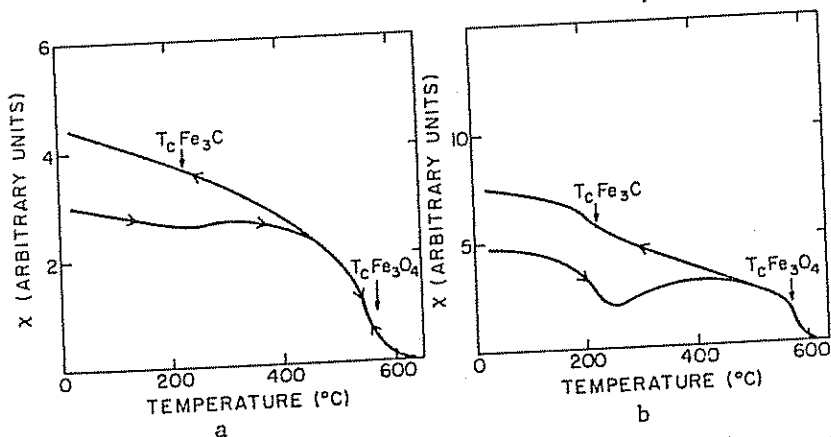


Figure 2. Magnetic susceptibility in arbitrary units as a function of temperature for the glasslike carbon prepared with 10% VF (a-500°C, b-625°C).

REFERENCES

1. D.W. Collins and L.N. Mulay, *J. Amer. Ceram. Soc.* **54**, 69 (1971); **54**, 52 (1971); **53**, 74 (1970).
2. D.W. Collins, L.N. Mulay and W.F. Fisher, *Bull. Amer. Soc.* **44**, 343 (1965); *Jap. J. Appl. Phys.* **6**, 1342 (1967).
3. D.W. Collins, J.T. Dehn and L.N. Mulay, "Superparamagnetism and Mössbauer Spectroscopy," in *Mössbauer Methodology*, Vol. III, Ed. I.J. Gruverman, Plenum Press, New York, 1967.
4. Another paper on the dispersion of iron in zeolite appears in this Proceedings volume.
5. R.A. Butera, R.S. Craig and L.R. Cherry, *Rev. Sci. Instr.* **32**, 708 (1961).

DISCUSSION

C.W. Rector: In the glassy carbons would you estimate the sample bulk density of the spherules as compared to the thread-like structures?

L.N. Mulay: I don't remember these figures, but I have a report with me and I would be happy to look up the values and give them to you.*

E.J. Siegel: Have you ever made glassy carbon with a high nitrogen content?

L.N. Mulay: No. The other variable which I neglected to mention in the synthesis of glass-like carbons is that some work is being done by Professor Dachille, at Penn State University, under high pressures which again produces all kinds of porosity.

*Spherules, (1.68-1.79 g cm⁻³); thread-like structure, (1.47-1.5 g cm⁻³). These values are extracted from the ARPA Semi-Annual Report (Contract DAH-15-71-C-0290) "Glassy Carbon, Alloys", July 27, 1972, (P.L. Walker, Jr.), Penn State University, University Park, Pa. 16802.