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SEMI-ANNUAL TECHNICAL REPORT FOR THE PERIOD

January 1, 1972 to June 30, 1972

GLASSY CARBON, ALLOYS

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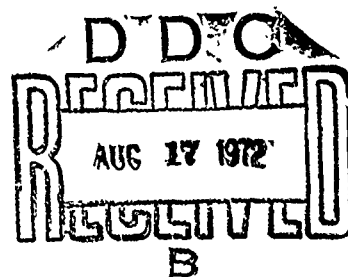
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Arlington, Virginia

July 27, 1972

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University Park, Pennsylvania 16802



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January 1, 1972 to June 30, 1972

GLASSY CARBON, ALLOYS

SUMMARY

Glassy carbons show promise of having a wide use in defense and space applications -- as well as a number of civilian-oriented spin-offs. Artifacts can be made in large shapes. Glassy carbons have a range of properties which are of interest such as impermeability to gases, despite the fact that they have significant porosity. Obviously the porosity is closed. As a result of low permeability, the oxidation rate of glassy carbon is low. As a result of a low oxidation rate and the ability to produce artifacts in a single phase (rather than a composite), the ablation performance of glassy carbon, particularly at high pressures, is excellent. The considerable porosity in glassy carbon results in their having a reasonably low coefficient of thermal expansion and, hence, reasonably good thermal shock resistance. Again this is important in defense and space applications where materials undergo large, sudden changes in temperature.

In the case of inorganic glasses, it has been common to modify and improve their properties by the addition of other elements. For vapor deposited carbons, it is not uncommon to incorporate one or more additional elements to improve some property such as fracture strength -- for example, silicon addition to isotropic carbons. It is almost inconceivable that the desirable properties of glassy carbons have been optimized chemically at the pure element composition. Therefore, this research program has as one of its main objectives to determine the possibilities of ultimately modifying the structure and properties of glassy carbon by the addition of various elements to the starting organic precursors.

This laboratory has shown recently that the use of elevated pressure during carbonization of organic precursors is a powerful variable to yield both low and high temperature carbons of widely different structures and properties. Other workers have shown that polymerization of organic precursors under pressure (prior to their carbonization) can lead to polymers of variable and interesting morphology. Hence, another main objective of this research program is to study the effects of the application of pressure during polymerization and/or carbonization of glassy carbon precursors on the structure and properties of carbons

produced.

Several new facets for producing glassy or disordered carbons are also being explored. They are: i) production of spherical particles of polymer which can be carbonized as free particles or as an artifact after compaction of the particles and ii) production of films of binary mixtures of disordered carbon and carbide by sputtering.

* * * * *

The first semi-annual technical report on the program was written January 20, 1972 and covered the period June 1, 1971 to December 31, 1971. This report covers our studies over the period January 1, 1972 through June 30, 1972

For our studies concerned with the possibilities of modifying the structure of glassy carbon by addition of other elements, we continue to concentrate on the system iron-furfuryl alcohol. Iron has been added in the form of either vinyl ferrocene or ferrocene dicarboxylic acid. Specimens have been prepared, to date, at a maximum heat treatment temperature of 950°C. Previous studies showed that heat treatment above 600°C results in the separation of iron from a homogeneously dispersed state into irregularly spaced but well defined particles of iron-enriched carbon. Our recent studies show that the structure of glassy carbon, the formation of compounds between the foreign element and carbon, as well as the morphology of the compounds, are highly sensitive to the structure of the precursor polymer and the ferrocene derivative used in its preparation. Such effects carry over to the tensile strengths and magnetic properties of artifacts produced.

For our studies concerned with polymerization and carbonization under pressure, attention continues to be centered primarily on divinylbenzene as a precursor. It was previously reported that polymerization and carbonization under pressure leads to the production of spherical particles 1-10 microns in diameter, which are optically isotropic. It is now shown that the spherulite size and extent of spherulite coalescence can be modified by changing polymerization pressure. Further heat treatment of the pressure-carbonized spherulites has been studied up to 2000°C and atmospheric pressure. Isotropic spherulites persist, with only a small decrease in diameter. With initial formulations containing ferrocene compounds, heat treatment to 2000°C leads to the formation of complex spheroid-descoid shapes.

It is now shown that spherical particles, 10-40 microns in diameter, can also be produced by the polymerization of furfuryl alcohol in water in the presence of an emulsifying agent. These particles can be pressed into pellets at room temperature, cured, and carbonized to give artifacts possessing a macropore system between particles and pores of molecular dimensions within the particles.

In line with one of the original major objectives of this program, that is to produce disordered carbons containing a homogeneously dispersed metal phase, we have commenced a study of producing fibers by the binary and concurrent sputtering of vitreous carbon and metal carbides.

SEMI-ANNUAL TECHNICAL REPORT FOR THE PERIOD

January 1, 1972 to June 30, 1972

GLASSY CARBON, ALLOYS

INTRODUCTION

During the period, work has been performed in the following areas:

1. Compositional and Structural Modifications of Glassy Carbon
2. Polymerization and Carbonization of Glassy Carbon Precursors Under Pressure
3. Glassy Carbons with open Macroporosity
4. Magnetic Characterization of Glassy Carbons Containing Iron
5. Binary Carbide Glasses

Details of our progress in these areas are given in the following sections of the report.

1. COMPOSITIONAL AND STRUCTURAL MODIFICATION OF GLASSY CARBON BY ADDITION OF IRON

(R. Kammerer and M. Nakamizo)

1.1 Introduction

Glassy carbons containing the element iron were prepared by pyrolysis in an inert atmosphere from copolymers of furfuryl alcohol (PFA) and organo-metallics such as ferrocene dicarboxylic acid (FDA) and vinyl ferrocene (VF) at temperatures from 500°C to 970°C. The purpose of this study was to determine the possibilities of ultimately modifying the structure and properties of glassy carbon by the addition of organometallic derivatives of the element iron to organic precursors of glassy carbon. In this report, our attention will be directed toward the study of the distribution of iron and its effects on the morphology and mechanical properties of the glassy carbon matrix as a function of pyrolysis temperature and iron content.

1.2 Experimental

Two series of samples of glassy carbon were prepared from the polymeric carbon precursors with an average ferrocene content of about 1 wt % and 3 wt % from PFA-FDA and 1 wt %, 3 wt %, and 10 wt % from PFA-VF. All specimens were in rod form with a diameter of approximately one-eighth inch and a length of two inches, and were heat treated to 500°C, 700°C, and 950°C to allow investigation of the influence of HTT on the distribution and behavior of iron in the carbon matrix and the mechanical properties of the composite material. The precursors were prepared in rod-shaped molds by acid catalyzed polymerization of the monomers at 70°C for 48 hours, followed by a gradual temperature increase to 250°C during a time period of equal duration in nitrogen under reduced pressure. In this manner uniformly cured samples were obtained and the formation of bubbles in the material was avoided. The samples were then heated at atmospheric pressure and in purified nitrogen at a rate of 6.6°C/hour to a temperature of 700°C and from there at a rate of 25°C/hour to 950°C.

1.3 Results and Discussion

Our previous findings on the structure characteristics of glassy carbons obtained from PFA-FDA resins, heat treated at temperatures from 500°C to 950°C, indicated the separation of iron from a homogeneously dispersed state at 550°C to 600°C into irregularly spaced but well defined whiskers of iron-enriched carbon. These whiskers consist of pure Fe_3C and are cylindrical in shape with a diameter of 1.0 μ in length. The results of the scanning electron microprobe

analysis indicates a decrease in the concentration of highly dispersed background iron in the carbon matrix surrounding the Fe_3C domains accompanied by an increase in the size of the domains with increasing HTT and soak time. Table 1 and Figure 1 show the results of the scanning electron microprobe analysis on glassy carbon from PFA - 1% FDA and PFA - 1% VF copolymers. The data in Table 1 were obtained from a statistical analysis of the detector response from background iron in scanning time increments of 10 seconds. In the PFA - 1% FDA system, the content of dispersed background iron decreases with increasing heat treatment temperature and becomes negligible at 970°C in spite of increase of total iron content (Figure 2).

TABLE 1
INTENSITY OF HIGHLY DISPERSED BACKGROUND IRON IN
GLASSY CARBON MATRIX BY SCANNING ELECTRON MICROPROBE ANALYSIS

HTT	500°C	700°C	950°C
PFA - 1% FDA	55.4 ± 3.7*	32.5 ± 1.9	3.8 ± 2.0
PFA - 1% VF	18.7 ± 3.1	42.1 ± 2.9	49.1 ± 2.5

*Confidence limits at 95% certainty.

Our recent work has produced substantial evidence to show that the structure of glassy carbons, the formation of compounds between the foreign element and carbon, as well as the morphology of the compounds, are highly sensitive to the structure of the precursor polymer and the ferrocene derivative used in its preparation. In the case of glassy carbons from PFA-VF, the content of background iron increases, in contrast with the case of PFA-FDA, with increasing heat treatment temperature, and the total iron content is nearly constant at temperatures from 500°C to 970°C. This constancy of the total iron content in the glassy carbon from PFA and VF over the temperature range from 500°C to 970°C indicates the partial weight loss of iron at a rate proportional to that of the weight loss of the carbon matrix due to thermal cracking, and, therefore, the existence of a thermally unstable iron compound which is released from the carbon matrix at temperatures above 550°C. Figures 3 to 7 show transmission electron micrographs of representative sections of glassy carbons from PFA-VF with an average content of ferrocene iron of 10 wt %. Figure 3 shows the formation within the carbon matrix of thin, square-shaped crystallites which occur in samples heat treated to 550°C and a

Figure 1. Scanning electron microprobe analysis of iron in glassy carbons.
(HTT 970°C)

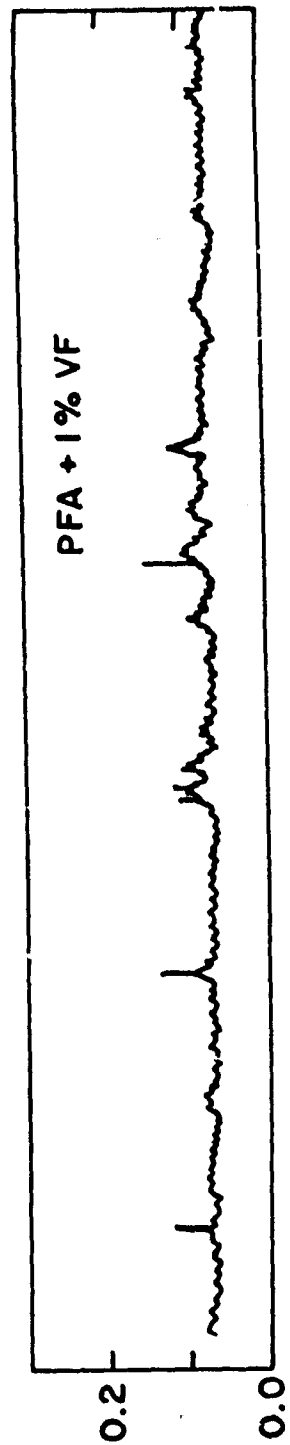
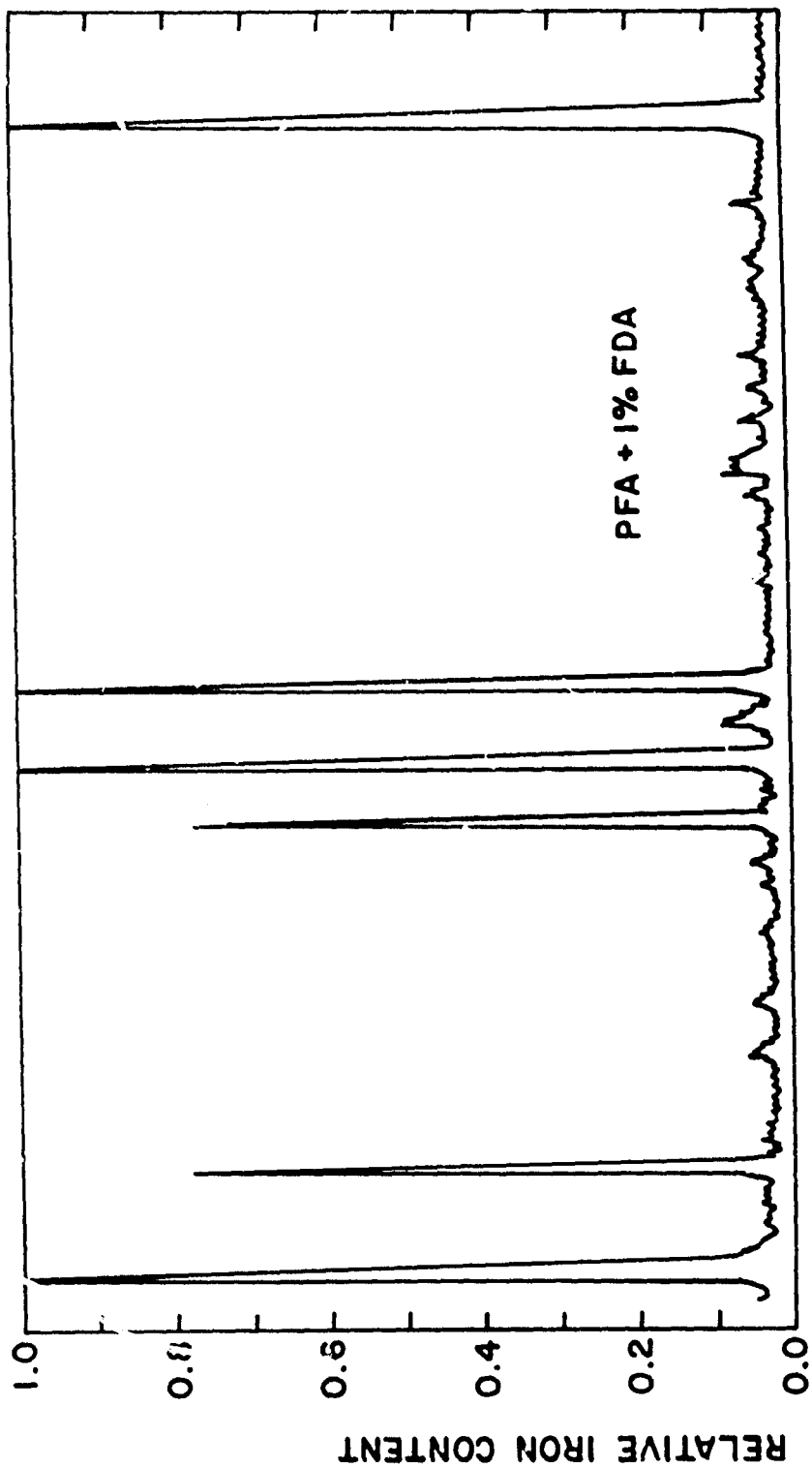


Figure 2. Relative change of total iron in glassy carbons with HTT.

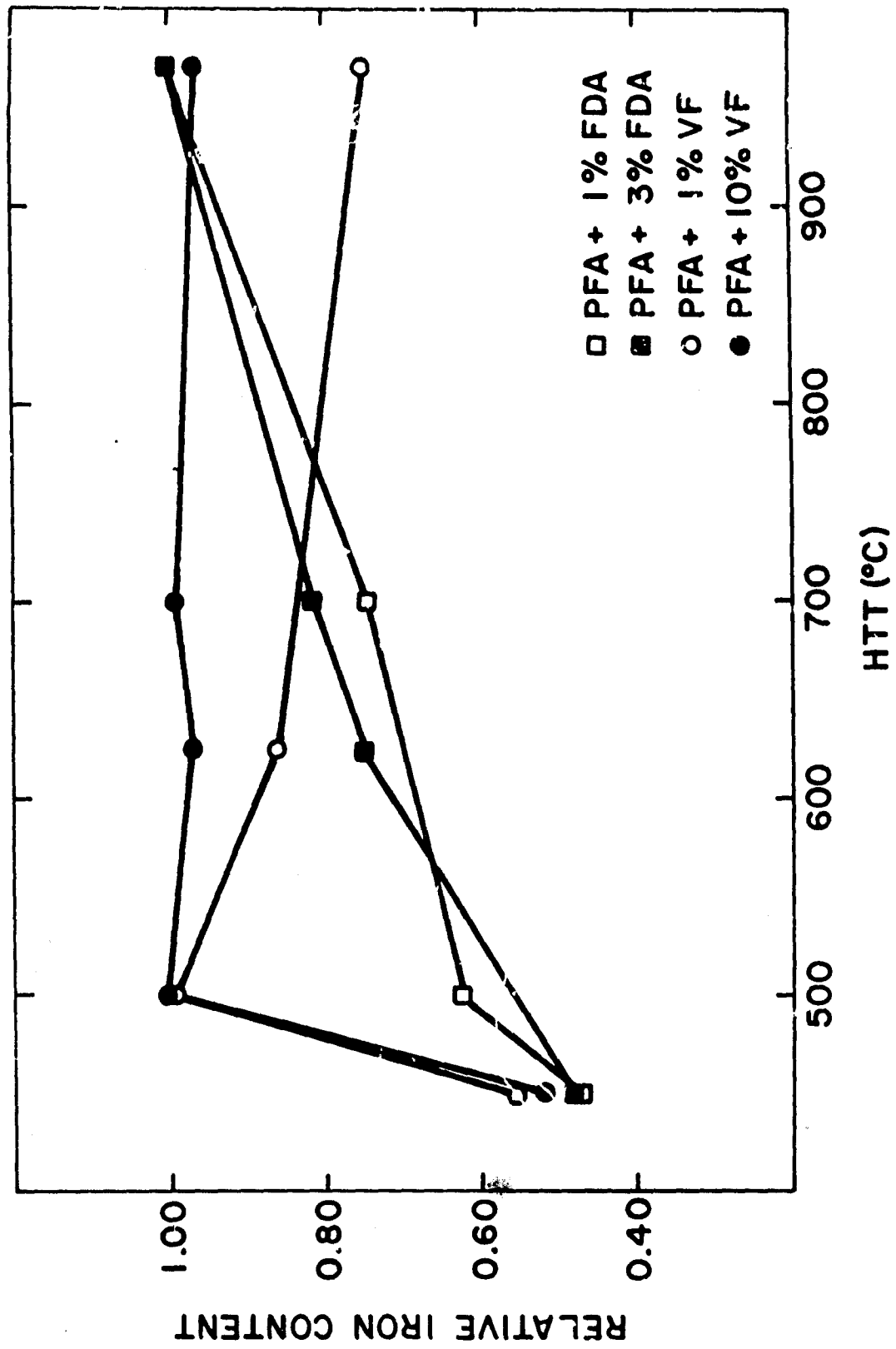


Figure 3. Transmission electron micrograph of glassy carbons from PFA-10% VF showing the appearance of square-shape crystallites at 550°C HTT. Pictures were taken from the core of rod-shaped specimens.

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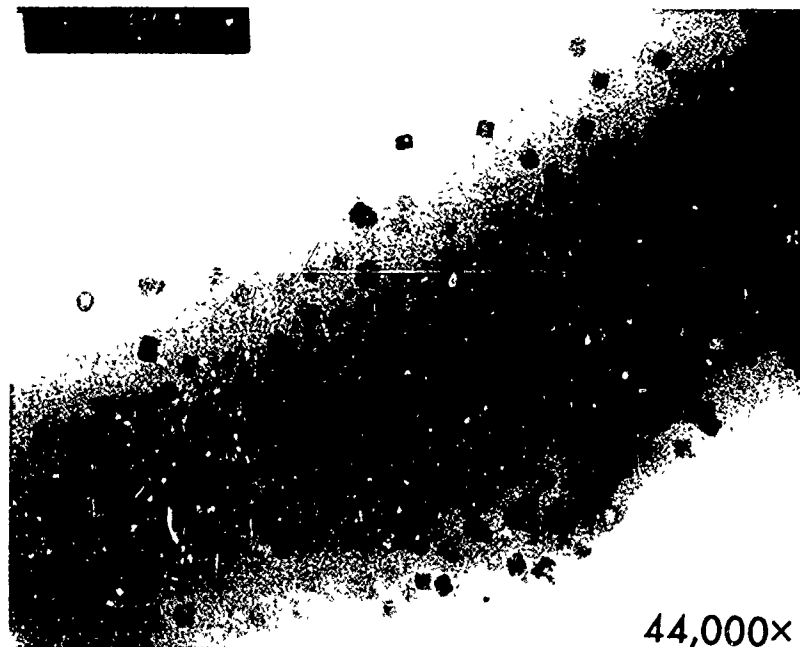


Figure 3

Figures 4 and 5. Replication of crystallites in the carbon matrix produced from PFA - 10% VF for 625°C HTT. Pictures were taken from the core of rod-shaped specimens.



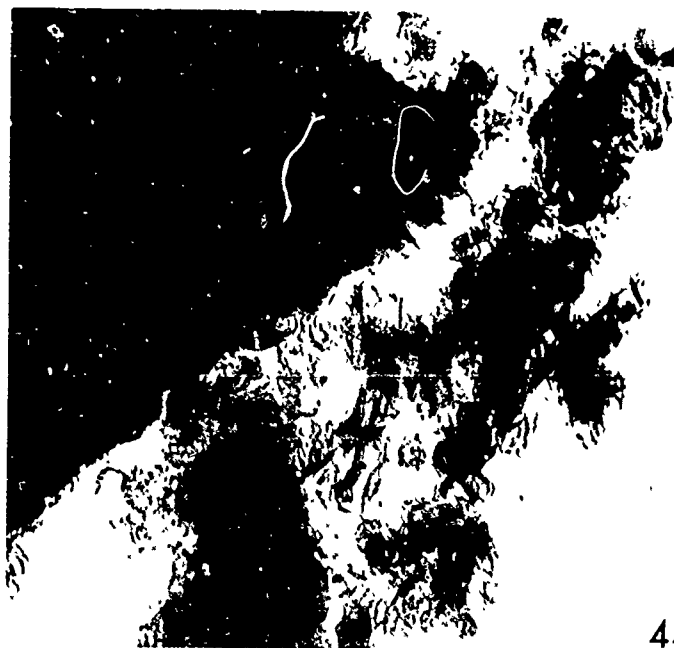
Figure 4

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Figure 5

Figure 6. Transmission electron micrograph of glassy carbon, HTT 970°C, from PFA - 10% VF. The picture originated from the surface of a rod-shaped specimen.



44,000x

Figure 6

Figure 7. Transmission electron micrograph of a γ -iron crystal contained in glassy carbon, HTT 970°C, from PFA - 10% VF.

Figure 8. Selected area electron diffraction pattern obtained from the crystal shown in Figure 7.

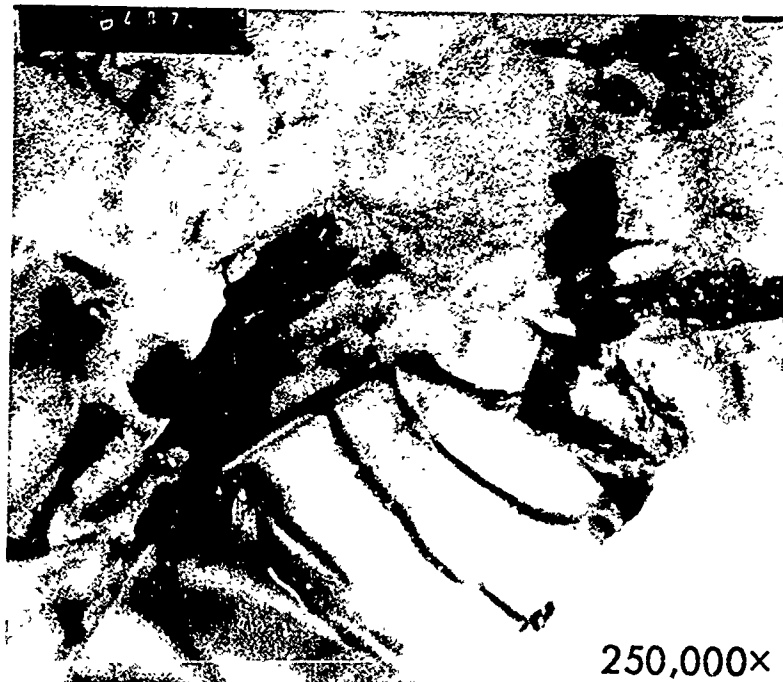


Figure 7

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Figure 8

soak time of one hour. Some of these crystallites are released from the carbon surface upon an increase in HTT to 625°C and leave their trace behind (Figure 4). Heat treatment temperatures above 600°C produce a lustrous core of concentric circles in the carbons containing ferrocene iron of 10 wt %. Figure 5 shows a micrograph taken from the section inside the core. Whisker-like iron carbides are formed, which have been observed in glassy carbon from PFA-FDA. The outside portion of the core reveals the typical band structure of glassy carbon (Figure 6). When the sample is heated to 970°C, the formation of massive aggregates can be observed (Figure 7). Selected area electron diffraction (SAD) of the aggregates shows a highly crystalline material as seen in Figure 8. This is identified as a crystalline elemental iron of the γ -type with fcc unit cell.

As is evident from the above observations, in the case of glassy carbons from PFA-VF, the iron separates at heat treatment temperatures above 550°C into amorphous phases consisting of mixtures of iron carbides, highly crystalline elemental iron of the γ -type, and thin, square-shaped crystalline materials of as yet unknown composition.

Uniaxial tensile strength measurements were carried out on all of the samples of glassy carbons obtained from PFA-FDA and PFA-VF copolymers heat treated at 500°C, 700°C and 970°C with a soak time of one hour. Both ends of a specimen of glassy carbon in rod form are embedded in brass tubes with an outside diameter of 5/16 inch, an inside diameter of 1/8 inch, and 3/4 inches in length. All the measurements were made with a crosshead speed of 0.02 in/min. Glassy carbons obtained from PFA containing no iron show a remarkable increase in tensile strength with increasing HTT. On the other hand the specimens of glassy carbon containing iron become more brittle and generally indicate a trend of tensile strength. However, the specimens obtained at 500°C reveal a striking increase of the tensile strength with increasing iron content.

In the case of glassy carbons from PFA-VF, the tensile strength cannot be reliably determined for samples with average contents of ferrocene iron of 3 wt % and 10 wt %, as well as samples heat treated at 700°C and 970°C because of their low strength and excessive scattering of data points. The remarkable decrease in tensile strength with increasing heat treatment temperature and iron content may be ascribed to the inhomogeneity of the glassy carbon matrix along with the variation in composition of the iron domains. The increase of heat treatment temperature and the inhomogeneity of the matrix

may produce internal strain which cause the decrease in the overall tensile strength. This coincides with the fact that the samples containing large amounts of iron are easily shattered during carbonization.

TABLE 2
TENSILE STRENGTH OF IRON-CONTAINING GLASSY CARBONS

(Kg/cm²)*

<u>HTT</u>	<u>500°C</u>	<u>700°C</u>	<u>970°C</u>
PFA	80	148	442
PFA + 1% FDA	-	-	132
PFA + 3% FDA	253	275	200
PFA + 1% VF	96	166	244
PFA + 3% VF	150	-	51
PFA + 10% VF	288	-	-

*Average of five determinations.

2. POLYMERIZATION AND CARBONIZATION OF GLASSY CARBON PRECURSORS UNDER HIGH PRESSURES

(F. Dachille, S. Hirano and M. Miller)

2.1 Introduction

In common with the experience of general chemical processes, almost all prior work in the preparation of glassy carbon precursors has been restricted to compositional and temperature parameters. The present work is concerned with the use of pressure, the next most important fundamental parameter, as a variable in this area. This project's semi-annual report, dated January 20, 1972, covered compositions and procedures used and typical results obtained, so that only a brief summary will be given here for convenience.

Polymerization of furfuryl alcohol (FA) or divinyl benzene (DVB), with or without small amounts of organo-metallic complexes, was carried out in thin-walled sealed capsules under hydrostatic pressures of up to 60,000 psi. Gold seal hydrothermal pressure vessels were used for the reactions. The polymers so formed were carbonized at temperatures up to 900°C in flowing nitrogen at 1 atmosphere, or in sealed capsules up to pressures of 30,000 psi. The results showed that the reactions were highly responsive to all the variables, both with respect to the "chemistry" and morphology of the final products. Many of these results are evident in the scanning electron micrographs included in the semi-annual report.

Perhaps the most notable result was the occurrence of a botryoidal carbon during the carbonization of poly DVB under pressure. This material was in the form of free spherules, 1 to 10 microns in diameter, and identical in appearance with the "mesophase" spherules which are receiving so much attention in the area of graphitizing carbons. The spherules produced from the PDVB were, however, optically isotropic and amorphous to x-rays. It was also evident that the formation and character of the spherules could be modified by conditions used or the initial DVB + organo-metallic compound formulation.

2.2 New Experimental Results

2.2.1 Polymerization of DVB Under Pressure

DVB was polymerized at 300°C in thin-walled Pd-Ag capsules at pressures up to 60,000 psi. Densities, infrared spectra and refractive indices were determined, and these are shown in Figures 9-12. The results are compared with those from a polymer prepared at one atmosphere and room temperature in the presence of a catalyst.

Figure 9. Density of DVB polymerized at 300°C under pressure.

Figure 10. Refractive index of polymers of DVB prepared under pressure and at 200 or 300°C. The index of a DVB polymer prepared at room temperature and pressure and using AlB nitrile as a catalyst is plotted on the ordinate axis.

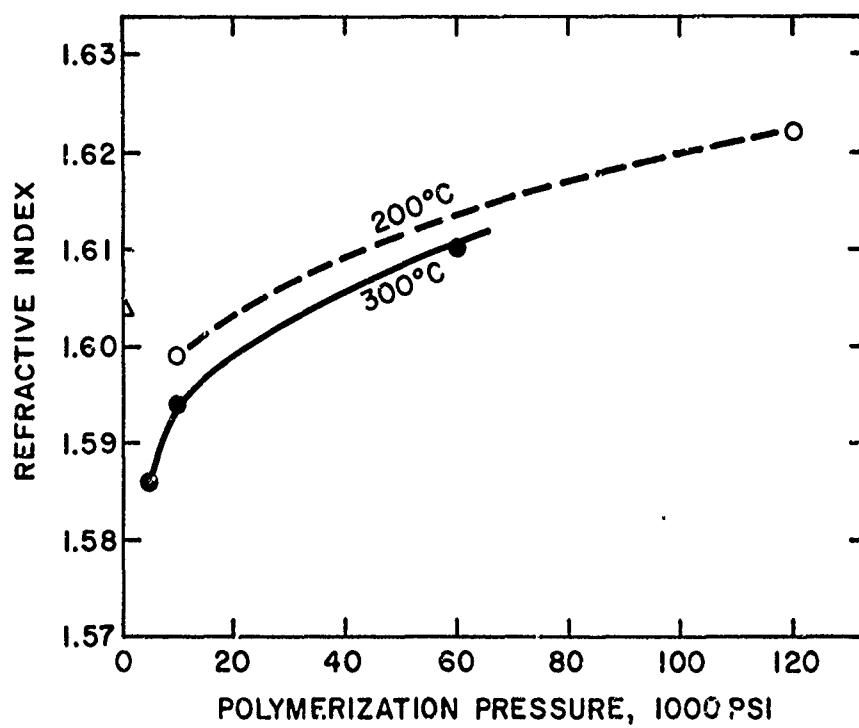
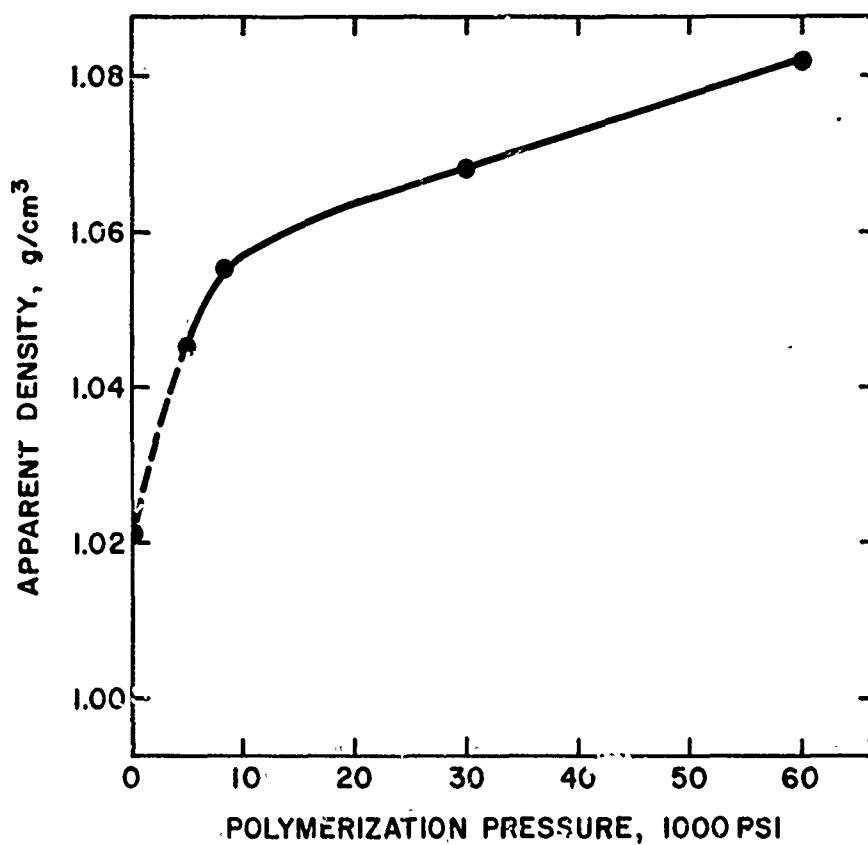


Figure 11. Portions of infrared absorption spectra of the catalyzed-room temperature DVB polymer and of the DVB polymers formed under pressure at 300°C. Note the progressive decrease with pressure of the absorption of the vinyl functional groups at 985 and 1630 cm^{-1} and the increase in what is believed to be absorption by a butyl functional group at 1370 cm^{-1} . An assignment for 1685 cm^{-1} has not been determined, but it is not related to a carbonyl group.

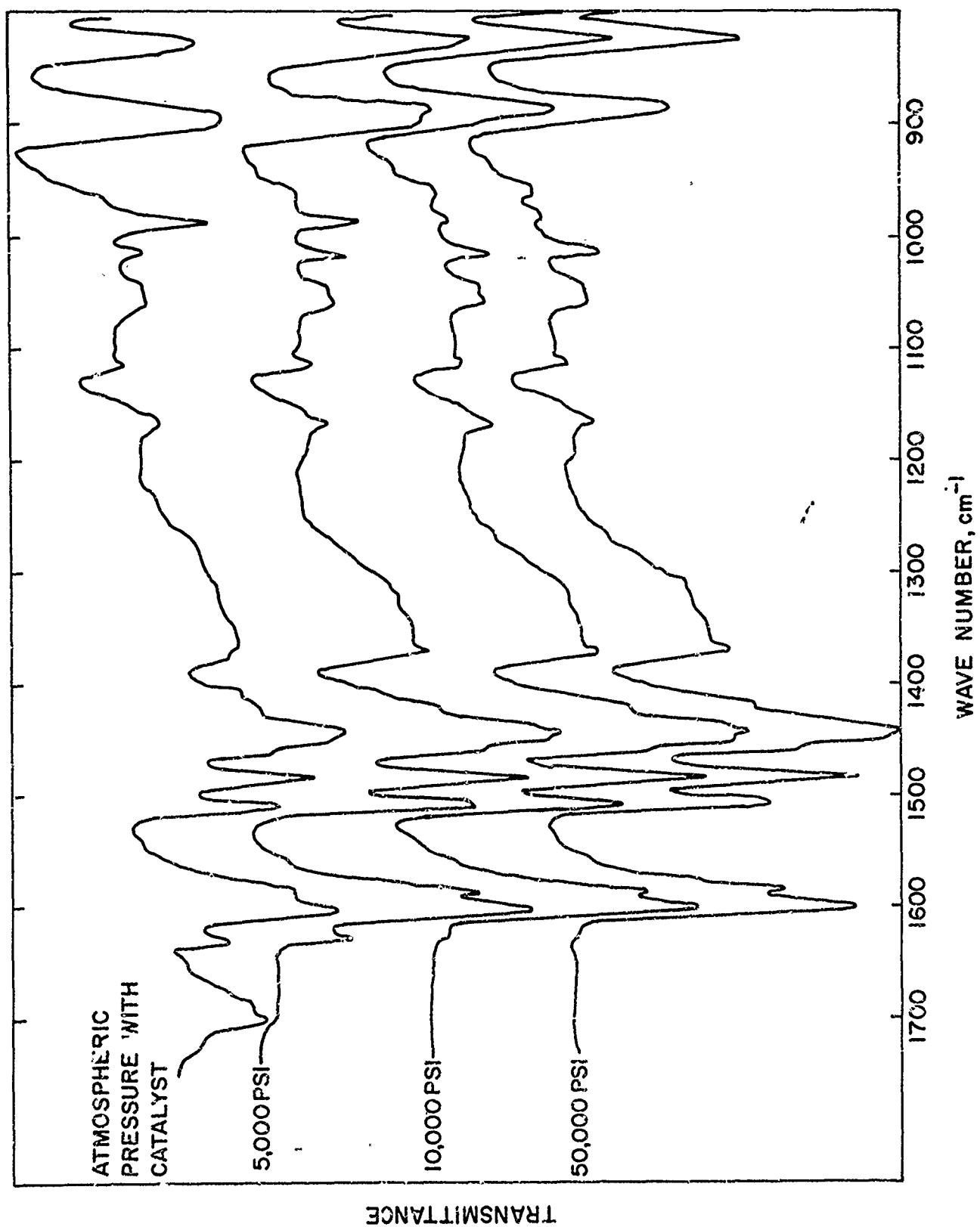
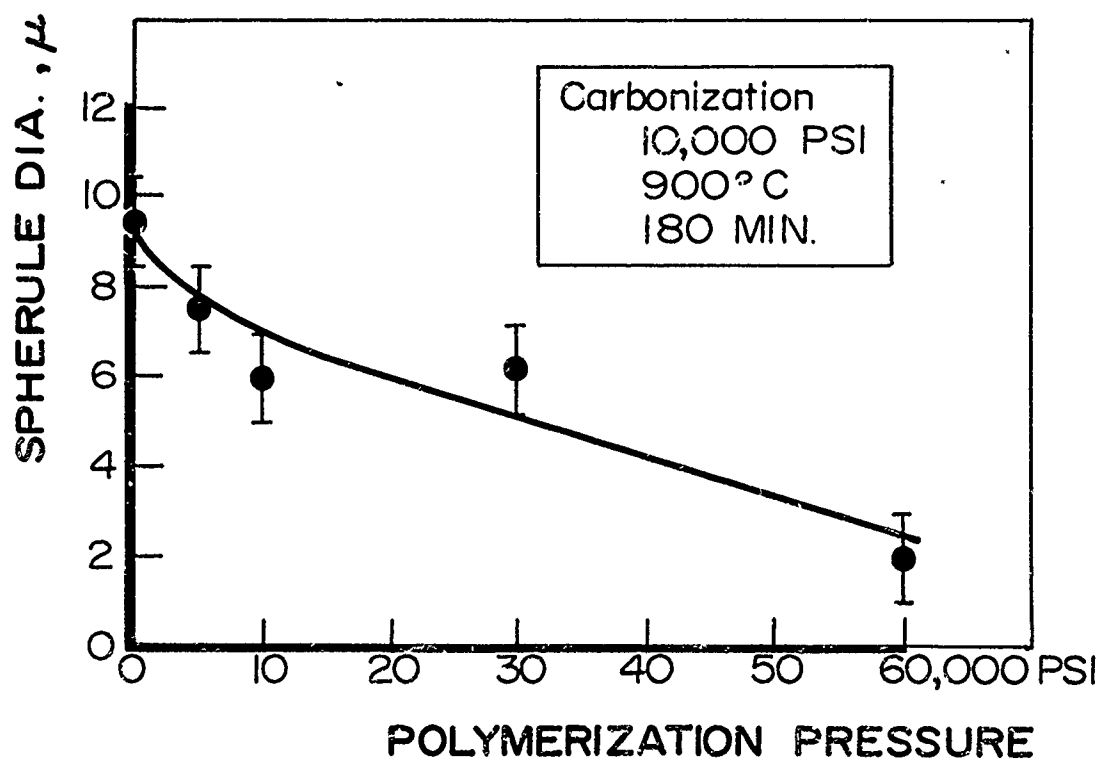
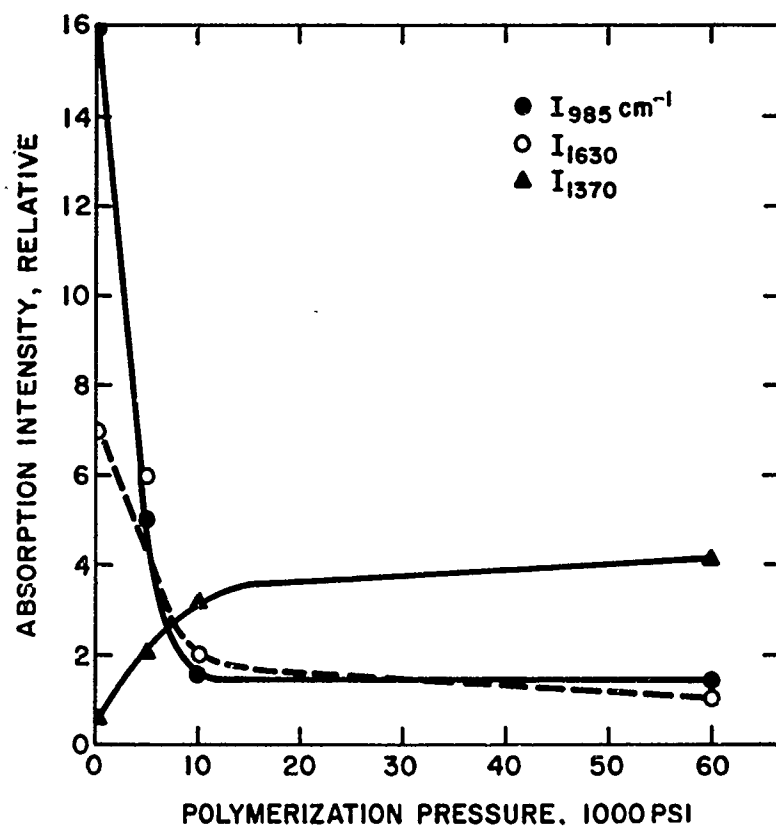


Figure 12. Trend of the intensities of the absorption bands at 985, 1630, and 1370 cm^{-1} referred to in Figure 11. Pressures of 10,000 to 15,000 psi appear to be enough to achieve most of the polymerization under pressure.

Figure 13. Spherule diameter of glassy carbon after a standard pressure carbonization as a function of pressure of polymerization.



That the intimate structure of the polymer is influenced by polymerization pressure is further demonstrated in subsequent carbonization. For example, Figure 13 shows that the spherulite size of glassy carbon formed under one set of carbonization conditions decreases steadily with increasing pressure of polymerization. It was also observed that the lower pressure polymers could lead to spherules which would coalesce in part.

2.2.2 Pressure Pyrolysis and Carbonization of PDVB

The finding of the spherulitic glassy carbon precursor led to an exploration of the P-T conditions under which this behavior could be expected. Further, the expectation that new morphologies might be encountered, including what is termed a periodic minimal surface (Donnay and Pawson) supported such an exploration. Figure 14 outlines the results of the pressure pyrolysis of DVB polymerized at 300°C and 10,000 psi. Of course, the figure is not an equilibrium diagram but does serve to indicate the long-time trends of a closed reaction system. Figures 15-18 display typical morphologies. The vesicular and spherulitic morphologies obtained on pyrolysis at 700°C and in the respective pressure regions are made up of optically isotropic material. Very recent examinations of the more complex morphologies like that of Figure 17, which begins to approach the periodic minimal surface form, indicate that these morphologies may be made up of a material which is anisotropic. The fact that the solid lattice work is quite fine, on the order of one micron diameter, is suggestive that high pressures may have a strong orienting effect on the high molecular weight species of the carbonization products.

Another interesting result is that the spheroidal form of glassy carbon is appreciably denser than commercial grades in plate form. For example, the Tokai "1000" and "2000" grades have apparent or bulk densities which fall between 1.47 and 1.51 gm/cm³, but the spherulites resulting from pressure carbonization at 900°C have a density of 1.68. On heating the spherulites to 2000°C, the density increases to 1.79 gm/cm³. Further, the x-ray densities as determined from the 900°C and 2000°C products (3.58 and 3.44A) are about 2.07 and 2.22 gm/cm³. This means that the porosities of these samples are slightly less than 20%, which compare with porosities in the Tokai glassy carbons of 25-34%.

2.2.3 High Temperature Heat Treatment

Some results of high temperature heat treatment of the products of pressure pyrolysis are covered in the discussion above concerned with densities. Another finding was that the isotropic spherules made from "straight" PDVB

Figure 14. Quenched products of DVB, polymerized at 10,000 psi and 300°C, related to the pressures and temperatures of carbonization. The carbonization was in sealed capsules, heating to temperature at a standard rate of 6.5°C/min and held at temperature for 3 hours.

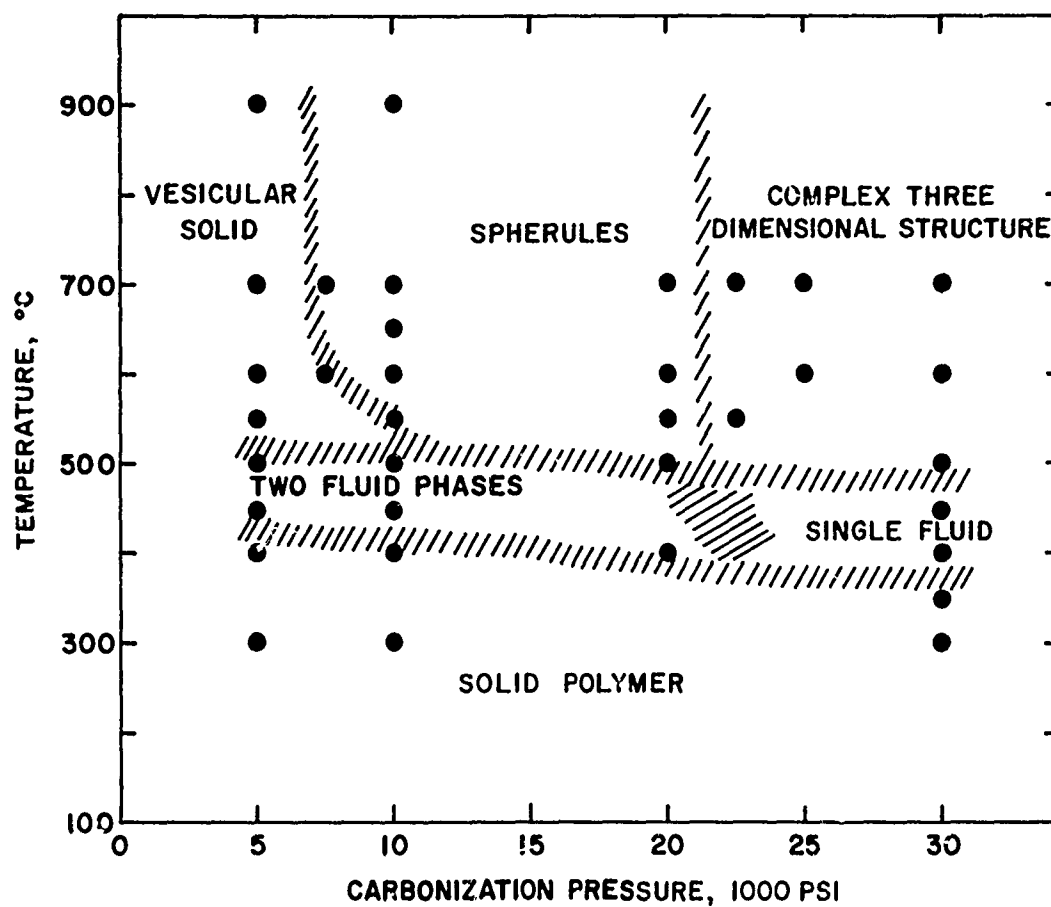


Figure 15. Vesicular solid from DVB.

Figure 16. Spherulites from DVB.

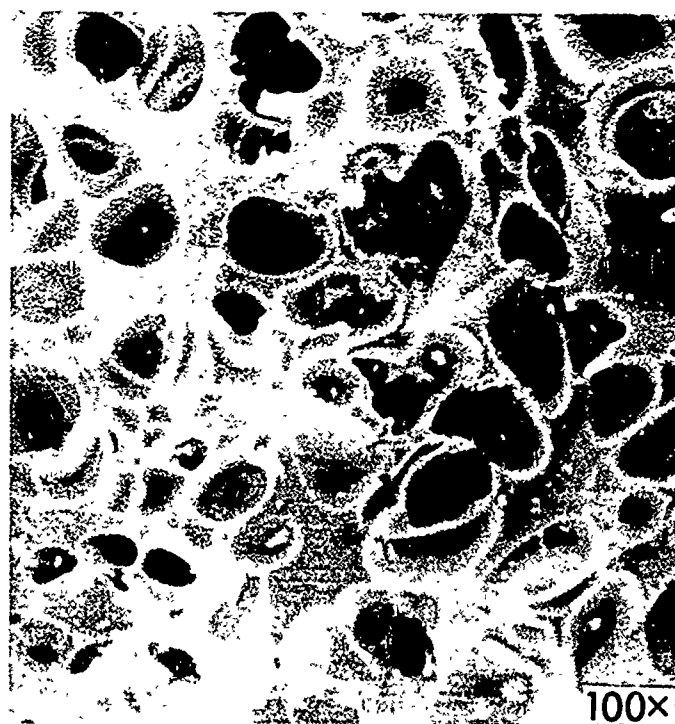


Figure 15

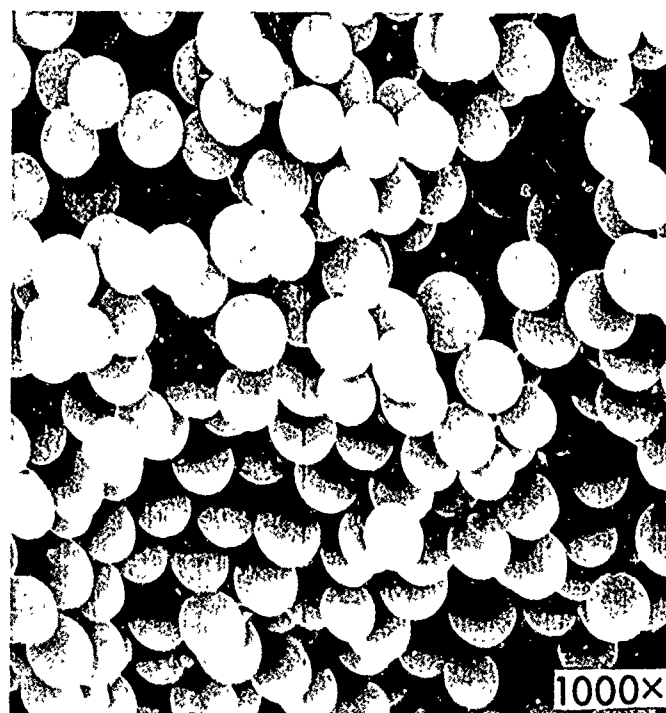


Figure 16

Figure 17. Complex rods approaching a 3-d structure from DVB.

Figure 18. For comparison with Figures 15-17. A LVB polymer, formed at 10,000 psi and 300°C, then carbonized to 700°C at a heating rate of 6.5°C/min under nitrogen at one atmosphere.

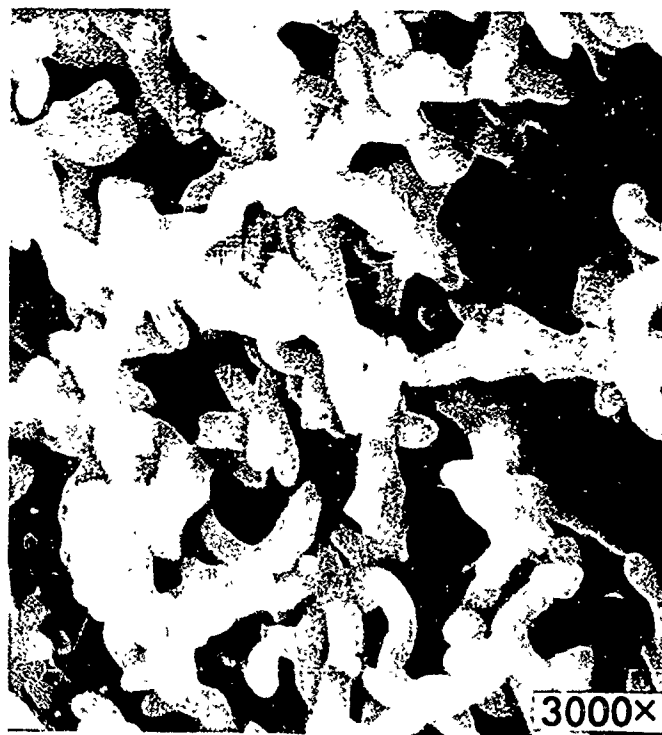


Figure 17

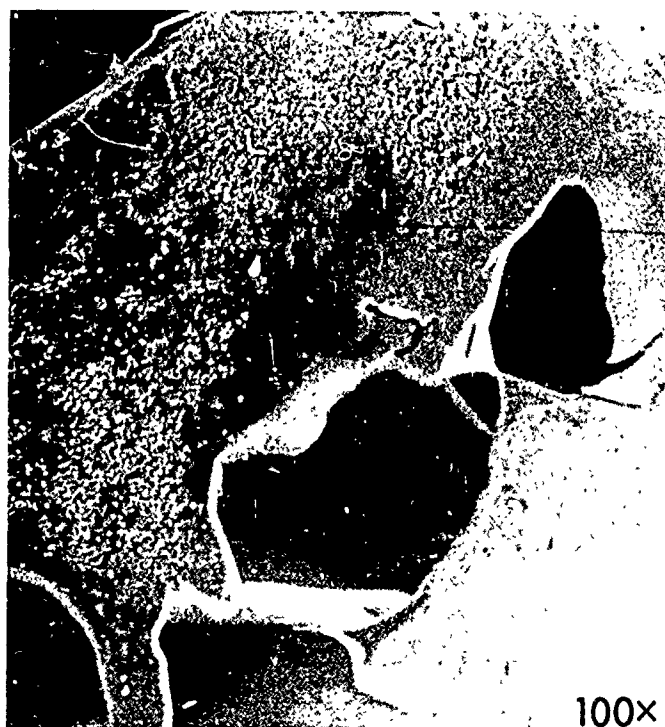


Figure 18

remained so and showed only a small decrease in diameter under heat treatment to 2000°C. However, with the formulations containing the ferrocene compounds, the spherulites were converted to complex spheroid-discoid shapes. Such changes in morphology are presumably related to the presence of ferrocene "carbon-cages" in the 900°C spheroidal products and to their subsequent collapse with the diffusion of iron out of the matrix at 2000°C. Figures 19 and 20 picture typical results.

It is note-worthy that both samples remained x-ray amorphous after this treatment, although the formulation including ferrocene demonstrated some 3-dimensional crystallinity in electron diffraction and was definitely optically anisotropic. See Figures 21 and 22. The x-ray diffraction maxima for the 900°C and 2000°C treated products are shown in Figure 23. Note the definitely sharper and more symmetrical peak at 3.44Å with no trace of the graphitic (002) diffraction maximum. For comparison is shown Figure 24 which is of a spherulitic graphite produced in a similar manner from the precursor, anthracene.

In Table 3 are summarized some density and x-ray diffraction measurements which allow an approximate comparison with two Tokai glassy carbons.

TABLE 3
SELECTED PROPERTIES OF TOKAI GLASSY CARBONS
AND THOSE PRODUCED FROM DVB

	<u>Tokai's ~ C.</u>	<u>Present Work</u>
900°C		
Lc ₀₀₂	12A	18A
La	unmeasureable	unmeasureable
2000°C		
Lc ₀₀₂	23A	160A
La	30A	unmeasureable
Apparent Density		
900°C	1.48 to 1.51 g/cm ³	~1.68 g/cm ³
2000°C	1.47 to 1.50 g/cm ³	~1.79 g/cm ³

Figure 19. DVB, polymerized at 10,000 psi and 300°C, carbonized at 10,000 psi and 700°C, then further carbonized to 2000°C in flowing atmospheric helium.

Figure 20. DVB plus vinyl ferrocene (2%), polymerized, etc. as sample for Figure 19.

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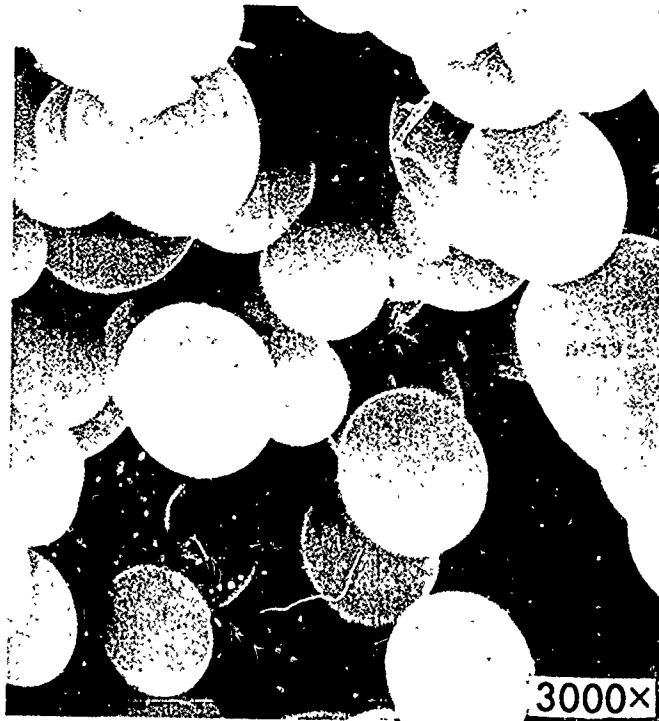


Figure 19

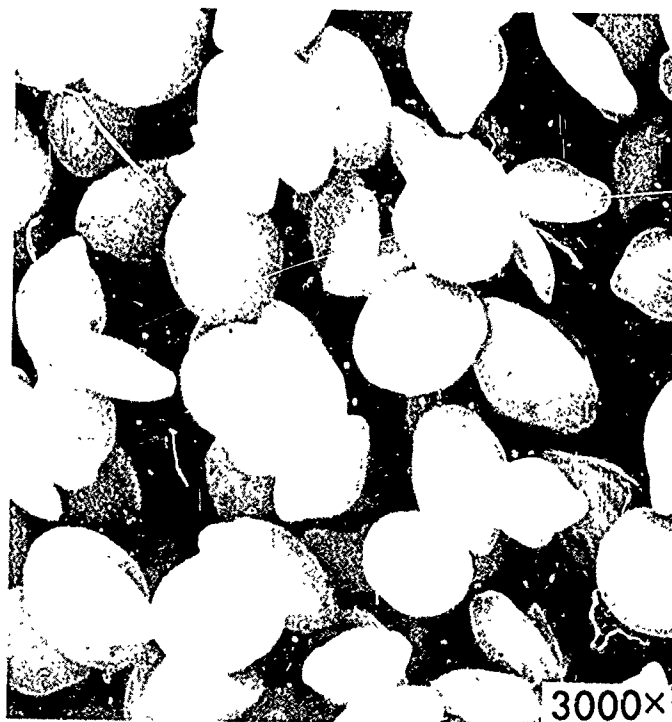


Figure 20

Figure 21. Electron diffraction of 2000°C carbonized PDVB - sample of Figure 19.

Figure 22. Electron diffraction of 2000°C carbonized PDVB plus vinyl ferrocene - sample of Figure 20.

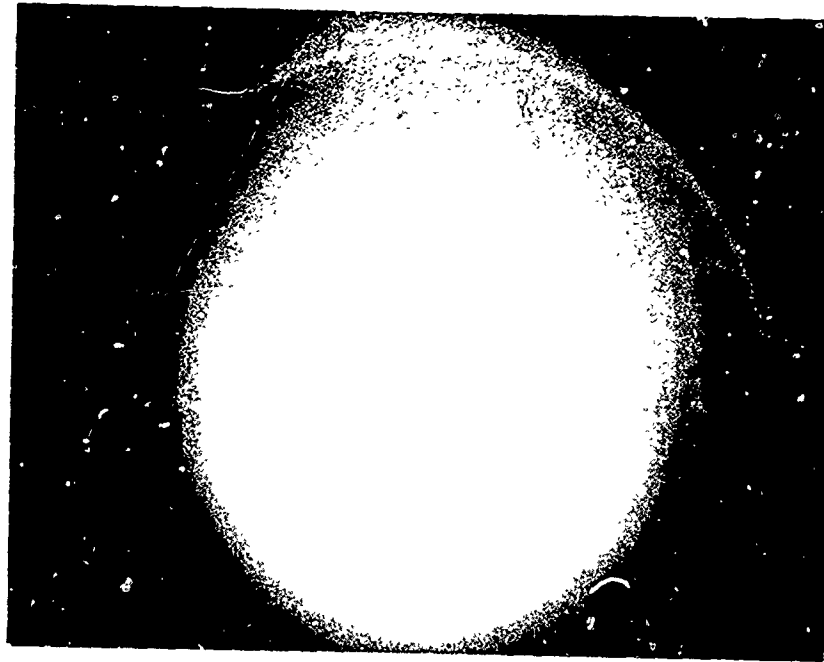


Figure 21

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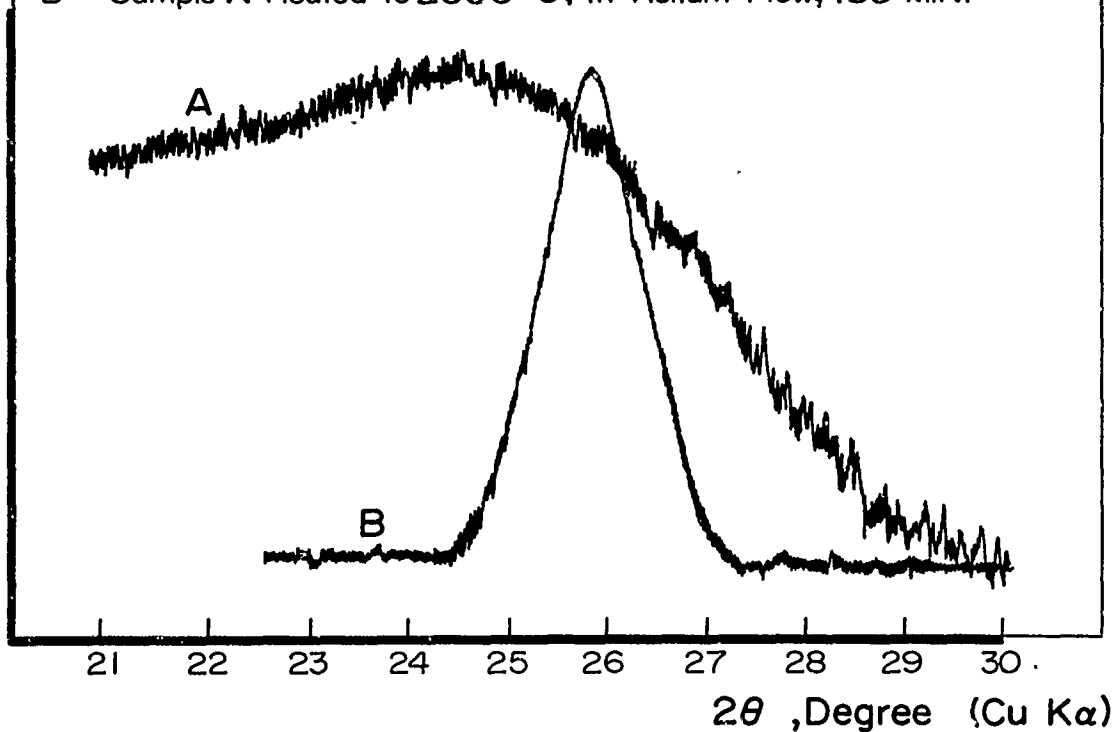


Figure 22

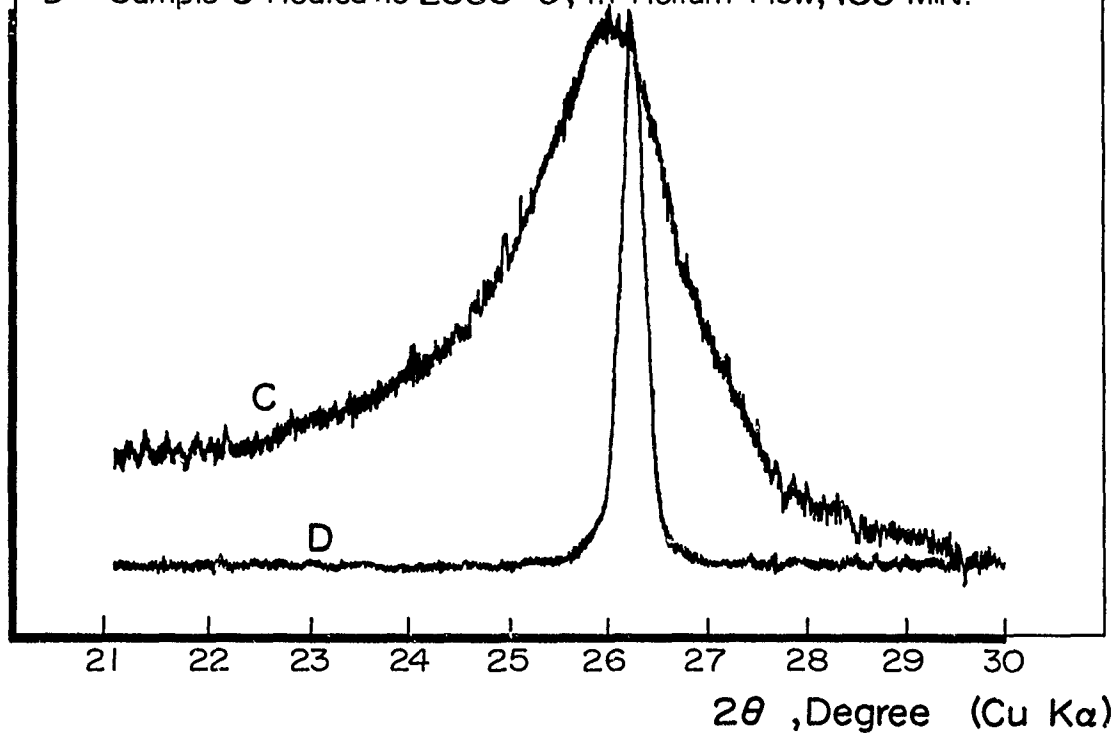
Figure 23. Typical x-ray diffraction maxima of DVB or DVB plus vinyl ferrocene after pressure polymerization and pressure carbonization to 900°C, followed by atmospheric pressure heating to 2000°C.

Figure 24. Typical x-ray diffraction maxima of anthracene carbonized under pressure at 15,000 psi and 600°C, followed by atmospheric heating to 2000°C (courtesy P. W. Whang).

A - DVB Carbonized at 900°C, 10,000 PSI, 180 MIN.
B - Sample A Heated to 2000°C, In Helium Flow, 180 MIN.



C - Anthracene Carbonized at 600°C, 15,000 PSI, 60 MIN.
D - Sample C Heated to 2000°C, In Helium Flow, 180 MIN.



2.2.4 Pressure Studies Using Furfuryl Alcohol

Continued work in this area showed that coarse and irregular vesiculation was too readily encountered during pressure carbonization. This no doubt is a direct consequence of the large amount of the water from the condensation reactions. However, it was felt that a glassy carbon foam might have a desirable combination of properties. To this end experiments have been started in which polymerization is conducted under argon pressures of 2000 to 10,000 psi, followed by various carbonization procedures. The results are only preliminary and not conclusive, but they do indicate that vesiculation may be controllable. Samples of bulk density of about 0.55 gm/cm^3 and with very low to zero permeability have been obtained with these methods. The bulk density is much too high to be of special interest, but it is hoped that manipulation of process variables will lead to much lower bulk densities and a good foam structure.

2.3 Discussion

There is evidence that pressure influences the polymerization of DVB, plainly seen in the behavior of the density, infrared absorption and refractive index data. One cannot be sure, however, that these effects are unambiguous indicators of more complete cross-linking in the polymer with pressure, although this is not an unreasonable expectation. It is hoped that these pressure effects will carry through the high temperature carbonizations and so result in denser, stronger and more impervious glassy carbons. At such time a study of the influence of pressure on mechanisms or details of polymerization may be considered.

In the interest of allowing a greater margin for demonstrating the effect of pressure on polymerization and the final glassy carbon, a few polymers are being prepared under 120,000 to 130,000 psi.

Figure 14 summarizes the behavior of a sealed PDVB system under pressure and temperature. From the point of view of this project, the tendency of the carbon precursor to drift away from being an isotropic material at pressures over 25,000 psi is a disappointment in that the carbon may prove to be graphitizable when heated to 2000°C or so (Figure 25). In any event, the behavior on carbonization to these temperatures will be determined.

It has been observed that within the P-T area for the formation of spherulitic glassy carbon conditions can be varied to yield more or less coalesced or sintered contacts between spherules. Such behavior, although it may not lead to an ideal interlinking of solid and pore space such as is

Figure 25. Electron diffraction from the carbon of complex form (see Figure 17) showing orientation but not crystallinity.

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Figure 25

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found in a periodic minimal surface, should still help produce glassy carbon artifacts for special needs having high porosity and permeability together with appreciable strength.

In reviewing the work of the past year, it appears that the objectives have been fairly met. Two major polymeric materials leading to glassy carbons have been investigated over a very large P-T area; five metal-organic complexes have been studied and used in conjunction with these polymers; and one, or perhaps two new forms of carbon have been prepared. With regard to the last, reference is made to the spherulitic form and to the complex form of Figure 17 which may end up as an intermediate between glassy and graphitic carbons.

All this ties in with the aim for the next year. It is intended to follow significantly different polymers through pressure carbonization and high temperature heat treatment, evaluating the glassy nature of the carbon and properties such as hardness, density, microporosity and permeability, and the influence of one or two organo-metallic additives. An ultimate goal will be the formation of small pieces suitable for use in mechanical, electrical, magnetic, and chemical testing.

3. GLASSY CARBONS WITH OPEN MACROPOROSITY

(I. R. Harrison and M. Schulman)

Two methods of achieving an artifact with a porous macrostructure whose internal surfaces would exhibit molecular sieve characteristics were explored; sintering small particles of polymer and polymerizing as a gel.

Resin particles were produced by polymerizing furfuryl alcohol (FA) in water in the presence of an emulsifying agent, propylene glycol alginate. At higher monomer contents (33-50% of the emulsion) the resin agglomerated before it reached a rubbery, non-tacky state. By lowering the FA to 5% and increasing the amount of emulsifier a stable emulsion was maintained long enough to harden the resin. The resin was filtered, washed and dried. The particles are spherical in shape with irregular surfaces. The diameter of the spheres runs from 10-40 microns, but there are agglomerates of a number of spheres with dimensions over 100 microns. It is unknown whether this agglomeration takes place in the emulsion or during filtering.

The particles were pressed into pellets, cured and carbonized to temperatures from 700°C to 900°C. Hand pressures of 80,000 psi, and 160,000 psi were used. Adsorption of CO₂ and n-butane, and shrinkages of the pellet during carbonization of about 20% was the same for all pressures. Adsorption is maximum at 700°C or 800°C and decreases at 900°C. Though there was shrinkage of the material, the particles remained bound and retained their pressed shape. On pressing the powder under pressure, a tarry residue was observed on the surface of the pellets and die. This was found to be soluble in acetone. The resin powder was extracted with acetone and pressed into pellets. These pellets gave similar adsorption of CO₂ and n-butane but higher yields during carbonization (complete data can be found in Table 4). When care is taken in pressing, the pellets are free from observable cracks, but scanning electron microscope pictures reveal severe cracking of many of the particles. It was observed that particles as small as 10-20 microns in diameter were cracked, though others of similar size appear intact. This cracking may be due to gas pressure in the particle during carbonization or thermal or mechanical stresses.

Gels have been prepared at 50% solids with tetrahydrofurfuryl alcohol as the solvent. In the initial attempts there has been some macro-cracking and wrinkling during the initial curing and solvent removal. Despite a few large cracks, the gels retain their shape and integrity during carbonization at 7-1/2°C/min to 800°C. No other evidence of an open structure exists at this time. Experiments are now in progress to eliminate the large cracks.

TABLE 4

CARBONS FROM POLYFURFURYL ALCOHOL

Conditions			Carbonization Temperature (°C)	Yield (%)	Density (Carbonized) g/cc	Adsorption (m ² /g)			
Precursor	Pressure	Cure *				CO ₂ (P/P ₀ = 0.5, -78°C)	n-Butane(P/P ₀ = 0.5, 0°C)		
						One Hour	Two Hours	One Hour	Two Hours
E-16	Hand	Vac.	800	41	0.66	---	472	0	0
E-16	80,000 psi	Vac.	800	41	0.83	---	453	0	0
E-16	16,000 psi	Vac.	800	41	0.73	467	472	0	0
E-16	80,000 psi	Vac.	700	41	--	456	456	0	0
E-16	80,000 psi	N ₂	300	42	0.83	427	437	0	0
E-16	80,000 psi	N ₂	900	42	--	374	382	0	0
Acetone Extracted									
E-16	80,000 psi	N ₂	800	51	0.86	475	481	23	23
Bulk PFA	80,000 psi	Vac.	800 (-400 msh)	56	--	479	485	0	0
	80,000 psi	N ₂	800 (-400 msh)	---	--	464	468	10	15

*Cures were for 16 hours at 200°C

*Heat rate 7-1/2°C/min, soak time at temperature one hour

4. MAGNETIC CHARACTERIZATION OF GLASSY CARBONS

CONTAINING IRON

(L. N. Mulay and A. Thompson)

4.1 Introduction

The applicability of magnetic techniques to the characterization of various systems has been clearly demonstrated by Mulay, et. al. over the past several years. These systems include (i) various carbons and graphites [J. J. Santiago, P. L. Walker, Jr. and L. N. Mulay, Abstracts Tenth Biennial Conference on Carbon, p. 271, 1971; J. J. Santiago, Ph.D. Thesis in Solid State Science, Pennsylvania State University, June 1972], (ii) amorphous superparamagnetic systems [D. W. Collins and L. N. Mulay, J. Amer. Ceram. Soc., 53, 74 (1970); 54, 1 (1971); 54, 69 (1971); IEEE-Magn. Trans., 4, No. 3, 470 (1968)] and (iii) organometallics [L. N. Mulay, "Magnetic Susceptibility: Characterization of Organometallic Compounds", Chapter in Characterization of Organometallics, Vol. II, Ed. Tsutsui, Interscience, New York, 1971].

In view of this work, various magnetic measurements were employed to characterize glassy carbons, particularly those where iron has been incorporated into the structure. Two types of measurement have been used: magnetization versus field at room temperature and susceptibility versus temperature from room temperature to about 750°C.

The samples used were prepared by R. Kammereck and M. Nakamizo using polyfurfuryl alcohol (PFA) as a precursor. Iron was added by mixing in an organometallic, namely ferrocene dicarboxylic acid and vinyl ferrocene. These mixtures were heated to temperatures ranging from 500°C to 970°C. The samples studied and the types of measurements made on them are summarized in Table 5.

TABLE 5

SAMPLES STUDIED

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
PFA + 1 % VF	M	M	-	M
PFA + 10 % VF	M,S	M	M	M,S

In the Table, FDA is ferrocene dicarboxylic acid, VF is vinyl ferrocene, M refers to the magnetization versus field measurements and S is the susceptibility versus temperature measurement.

4.2 Experimental

Various techniques for measuring magnetization or magnetic susceptibility as a function of the field and/or temperature have been described recently in detail by Mulay [L. N. Mulay, "Techniques for Magnetic Susceptibility", Chapter VII in Physical Methods of Chemistry, Part I, Vol. IV, Eds. Weissberger and Rossiter, Wiley, New York, 1972]. The vibrating sample magnetometer technique was selected here because of its ability to obtain 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 measurements reported here.

The sample to be measured is mounted securely between the poles of a homogeneous magnetic field and attached from a transducer. The transducer vibrates at a frequency of 82 Hz. Also in the magnetic field are two pick-up coils. As the sample is vibrated, a voltage proportional to the induced magnetization is generated in the coils. This voltage is applied to one end of a differential transformer. The resulting signal is amplified and phase detected by a lock-in amplifier where it is measured. This voltage is also applied to the damping capacitor and the resulting signal is then applied to the other end of the differential transformer. Electrical damping is then provided, cancelling spurious signals produced by the vibrating sample. The magnet is a Varian 12 in electromagnet controlled by a Varian Fieldial field regulator. The maximum field produced is 19 K gauss. The magnetometer was calibrated with a standard sample of nickel.

This magnetometer is equipped with a Dewar operating in the range 4° - 300°K. Currently efforts are being made to install a high temperature furnace for reaching temperatures up to 900°C.

4.2.2 Susceptibility vs. Temperature Measurements

Several high temperature susceptibility measurements were carried out in the Chemistry Department at the University of Pittsburgh* using an automated Faraday balance described by Butera, et. al. [R. A. Butera, R. S. Craig and L. R. Cherry, Rev. Sci. Instr., 32, 708 (1961)]. The principle of this

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

technique is the same as outlined in our ARPA Report on Glassy Carbon, Alloys [January, 1972]. The temperature range of the apparatus was from room temperature to 750°C, the limit of the equipment. A magnetic field of about 8 K gauss was used. 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.

4.3 Results and Conclusions

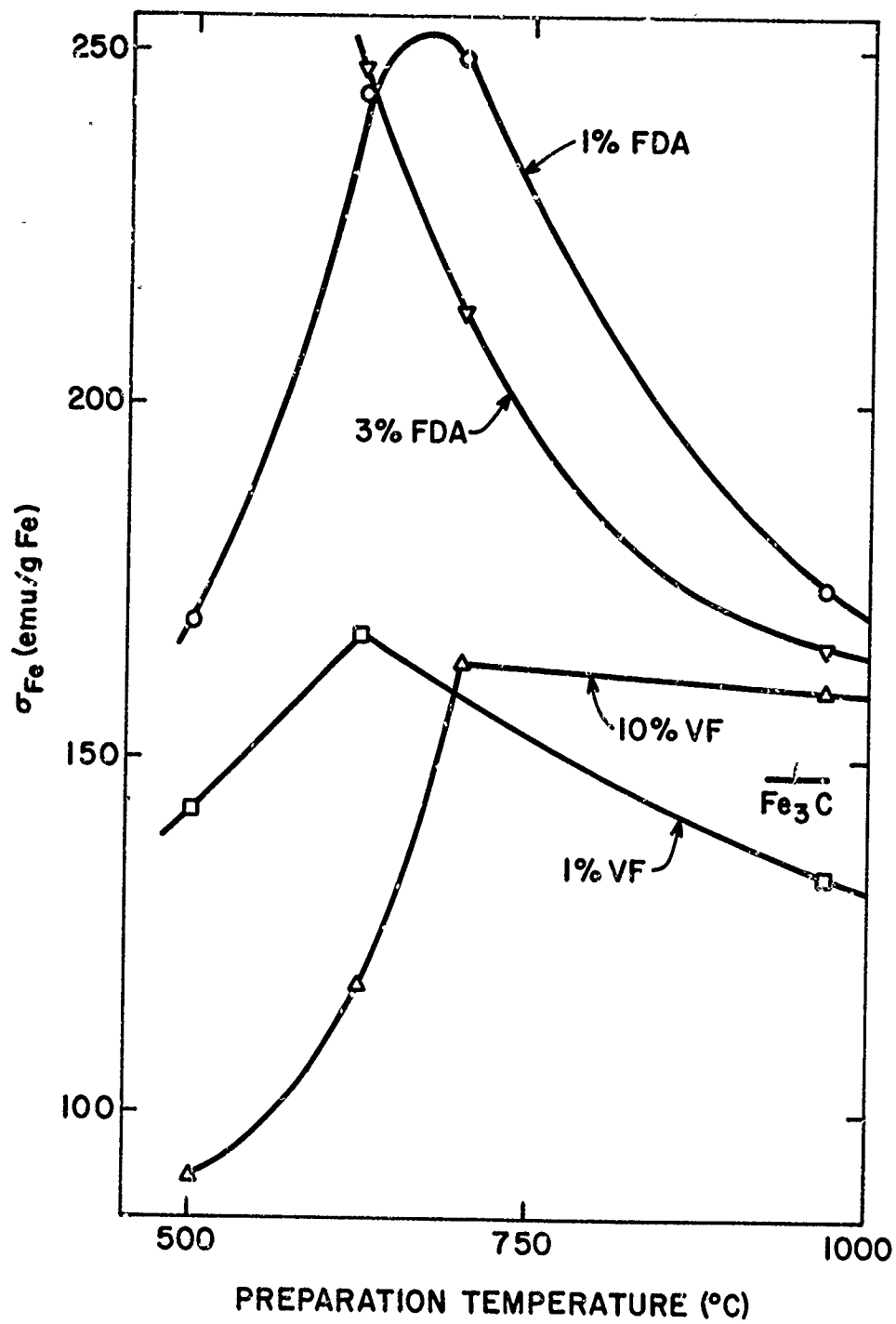
4.3.1 Magnetization Measurements

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 of Fe for various samples containing iron was measured. Results are shown in Figure 26.

The FDA samples show similar behavior with an approach at the high temperature and 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 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, 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 ($500^\circ - 700^\circ\text{C}$), this trend is reversed over the higher range ($700^\circ - 1000^\circ\text{C}$). 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 have migrated out. It is apparent that the trend in magnetization reflects this migration. However, this species as of now has not been identified.

Magnetization measurements of the samples containing no iron were made to correct for the diamagnetic susceptibility of the carbon matrix in the other samples. Despite the large error involved in measuring diamagnetic magnetization, a definite trend is observed. Figure 27 summarizes this. The increase in diamagnetic magnetization at higher heat treatment temperatures is probably due to a decrease in paramagnetic centers (i.e. free radicals) with heat treatment. In a series of related experiments, we established that the control samples of PFA (that is, without the addition of ferrocene) under various experimental conditions produce free radicals in sufficient quantity to give measurable magnetization.

4.3.2 Susceptibility Measurements

Susceptibility versus temperature measurements were made on three of the samples. Figure 28 shows the 625°C, 3 % FDA and 970°C, 10 % VF samples. These two samples have a definite Curie point which corresponds to that of Fe_3C , 222°C. It is also quite evident that there is a greater amount of Fe_3C in the 970°C sample than in the 625°C sample. The residual paramagnetism is quite a bit higher, which may be due to highly dispersed paramagnetic iron species in the sample.

The 970°C, 10 % VF sample was also heated to about 750°C and allowed to cool to room temperature as susceptibility measurements were being taken. A marked temperature hysteresis was observed and is shown in Figure 29. Besides the Curie point for Fe_3C at 222°C, the curve also shows an approach to the Curie point of iron at 770°C. The reason for the increase in susceptibility, a change from the paramagnetic to the ferromagnetic state as the temperature increased to above 500°C must be related in some way to the decomposition of Fe_3C to iron. Electron micrographs of this material show the existence of small volumes of γ (FCC) iron at room temperature. This form of iron is known to exist in the metallic state only at temperatures above 900°C. Thus, being above the Curie point of iron, γ iron is only known to be paramagnetic. However, since only one temperature hysteresis cycle was run, it is difficult to assign the hysteresis to a chemical, a structural phase change, or a magnetic phase change, or perhaps to a combination of such effects.

Figure 27. Diamagnetic magnetization as a function of temperature for the PFA glassy carbon with no ferrocene derivatives.

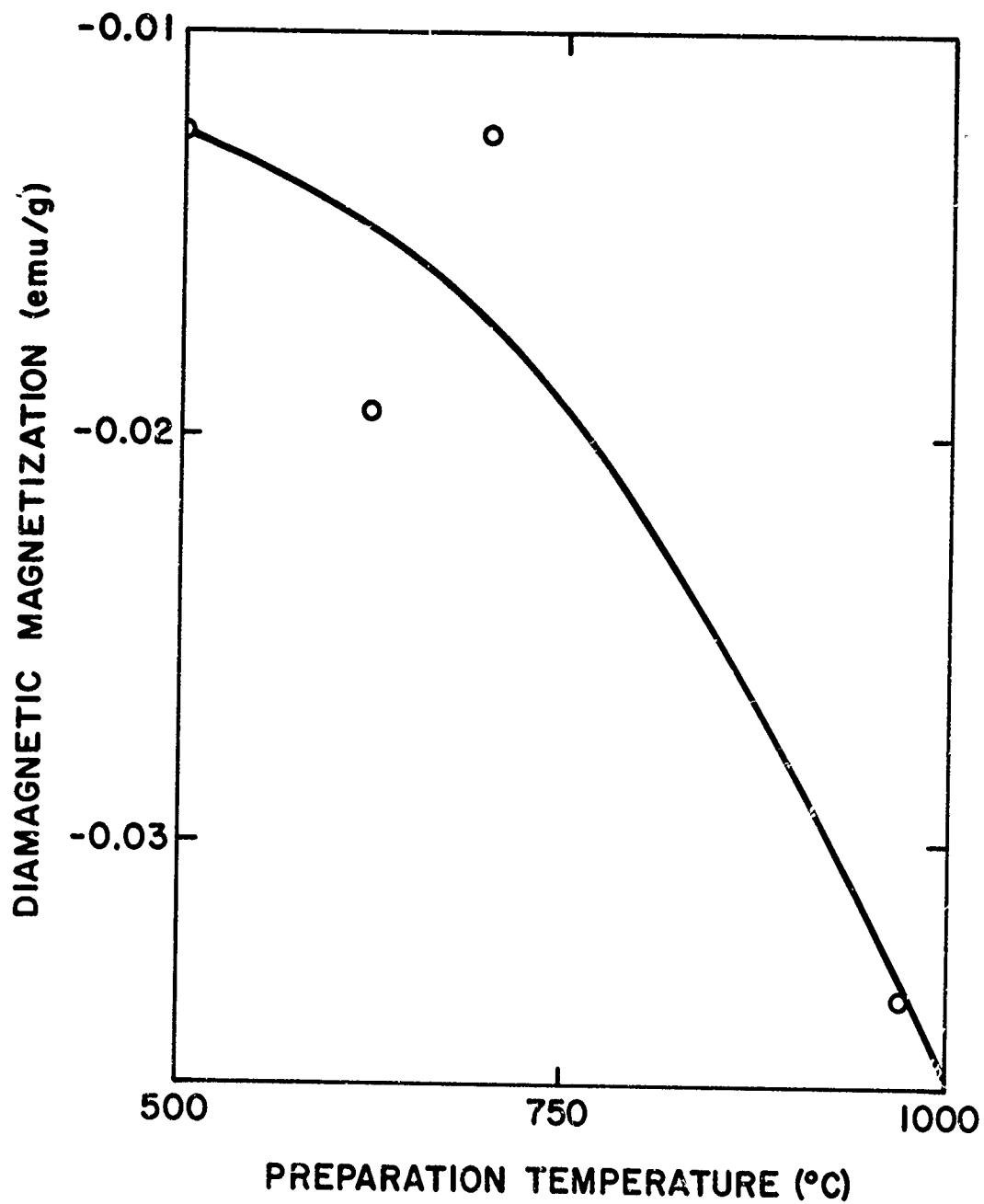


Figure 28. Magnetic susceptibility in arbitrary units as a function of temperature for the PFA glassy carbons, prepared with 10 % VF (970°C) and 3 % FDA (625°C).

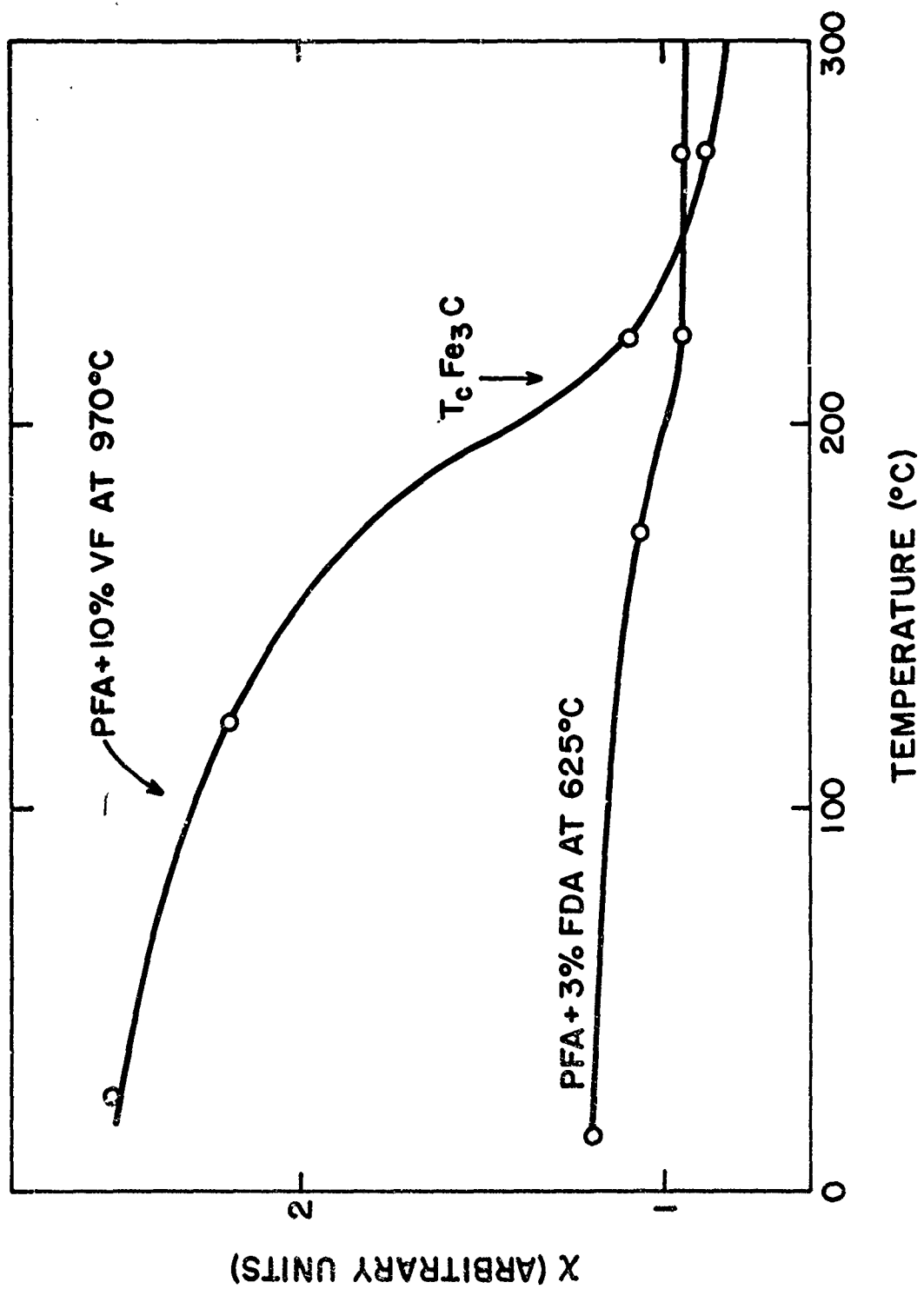
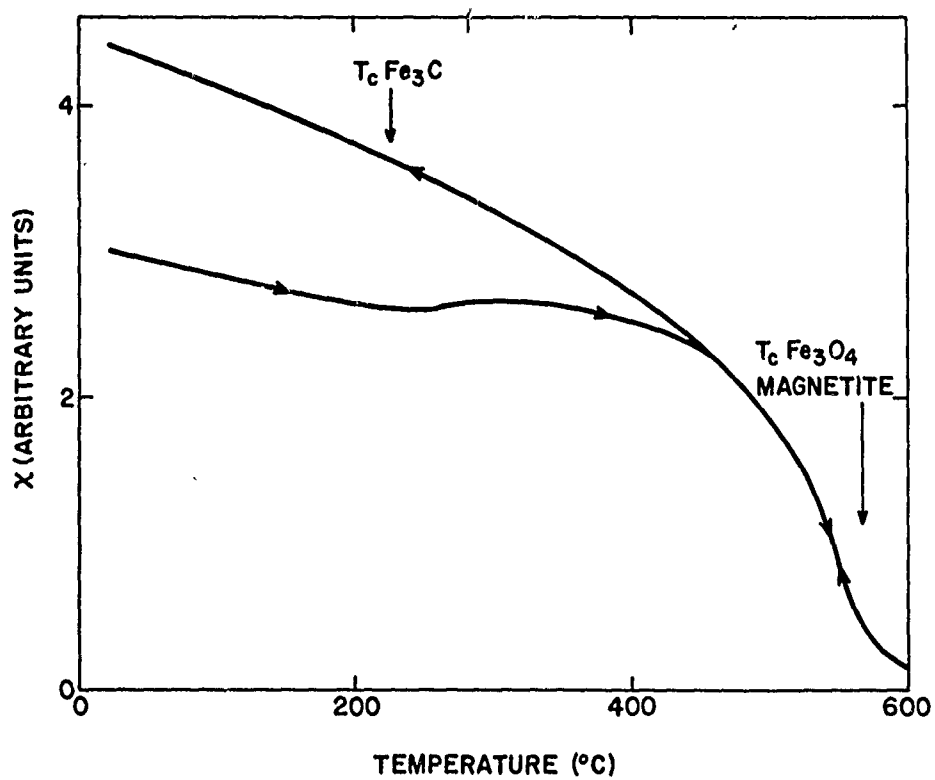
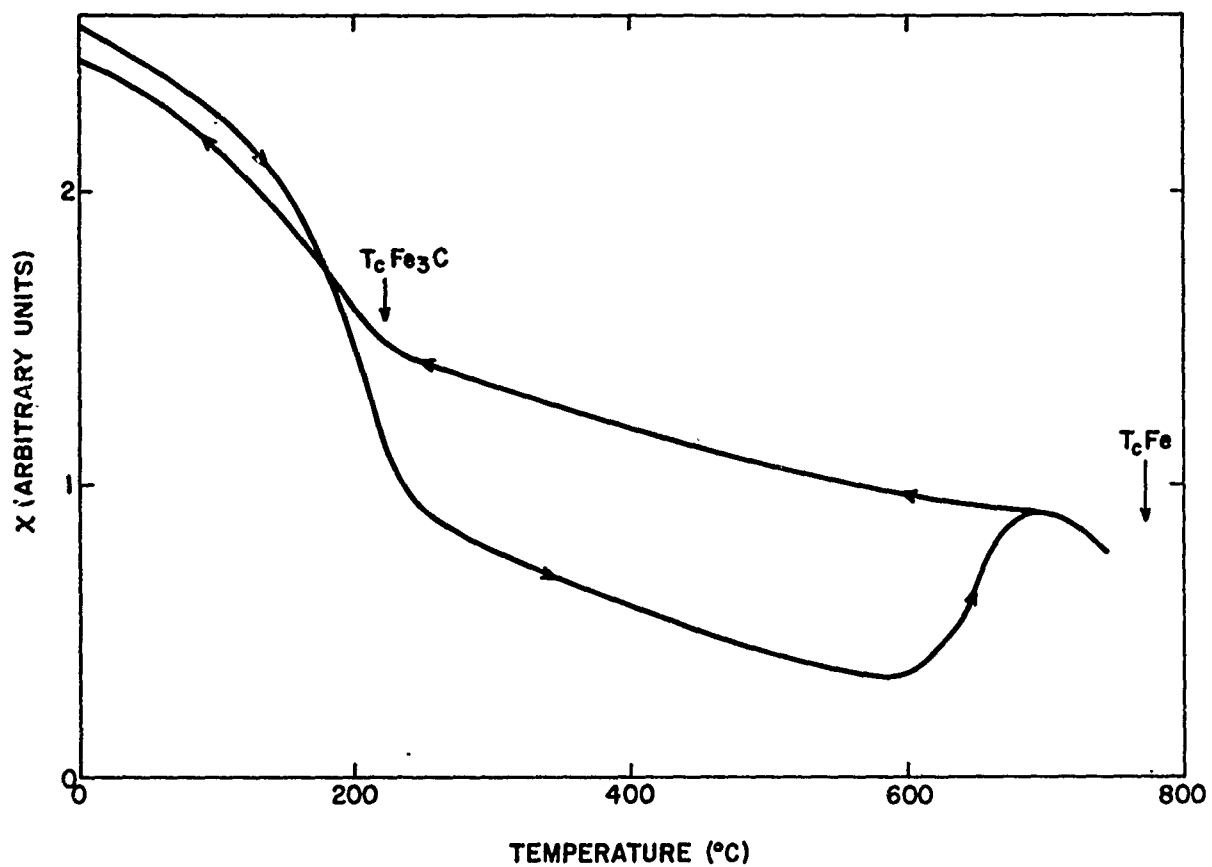


Figure 29. Magnetic susceptibility in arbitrary units as a function of temperature for the PFA glassy carbon prepared with 10 % VF (970°C).

Figure 30. Magnetic susceptibility in arbitrary units as a function of temperature for the PFA glassy carbon prepared with 10 % VF (500°C).



The susceptibility of the 500°C, 10 % VF sample was measured in the same way as the 970°C, 10 % VF sample, except the maximum temperature was restricted to about 640°C, just above the observed Curie point. Figure 30 shows this curve and the observed hysteresis. It was necessary to heat the sample to above its preparation temperature to measure the Curie point of the sample. This Curie point corresponds to the reported value of Fe_3O_4 (magnetite). However, since there is a transition in the susceptibility, it cannot be stated with certainty that the high density species observed in the electron micrographs is Fe_3O_4 . It is interesting to note that the residual paramagnetism is quite low, possibly indicating that there is no dispersed iron in the sample.

4.4 Conclusions

The iron species in various glassy carbons appears to eventually produce Fe_3C (cementite). It also seems reasonable to assume that some of the iron is dispersed as paramagnetic or superparamagnetic particles. For the FDA samples prepared at 625°C and above, the quantity of Fe_3C increases as the dispersed iron decreases and is reflected in the total magnetization curves for these compounds.

The observations on the VF samples are further complicated by the presence of other iron species. Hence, it is difficult to attribute the observed Curie point for the 500°C material to that of the high density "cubic" material, revealed in the electron micrographs. The dispersion of this material and the appearance of γ iron in the 970°C sample cannot be analyzed any further, because the magnetic properties of γ iron are unknown below its metallic transition temperature.

5. BINARY CARBIDE GLASSES

(S. A. Gallagher and R. Roy)

One of the two principal aspects of the proposal made for this project was the concept that up to now all glassy carbons had dealt only with elemental carbon. In the ordinary silicate glass field this would be like restricting all work to pure SiO_2 .

For the last year we have attempted - as reported elsewhere in this report - to make such "solid solutions" via chemical means. In the meantime supported by a parallel ARPA grant on glass research, a beginning has been made in this direction nucleating an area in which we will make a major effort next year on this grant. The research deals with preparing such novel binary carbide glasses by RF-sputtering to study

- a) The range over which such glasses can be made
- b) How stable they are
- c) Some of their properties

5.1 Experimental

Sputtering of the unary systems was performed on the Material Research Corporation MRC, Model 8632 Rf/DC sputtering module. MRC, Model 8500 was used for the binary systems. Knoop hardness tests were performed on a Leitz Wetzlar Miniload hardness tester.

The range of conditions for the unary systems, SiC , B_4C , WC , and Vitreous carbon, are 15 to 30 millitorr argon and 25 to 200 watts with sputtering times of 20 to 810 minutes. For the binary systems, $\text{B}_4\text{C-C}$, SiC-C , $\text{B}_4\text{C-SiC}$, 7 to 30 millitorr argon, 50 to 200 watts, and 20 to 700°C were used for times ranging from 60 to 490 minutes. The systems were pumped to pressures of 3×10^{-7} torr to 2.2×10^{-6} torr with a substrate to target distance of 21 - 33 mm. The argon tank pressure was maintained at 5 psi. The unary targets were 2 inches in diameter and the D-shaped binary targets were 5 inches in diameter.

5.2 Results

The systems studied yielded stable glasses under all conditions when deposited on glass substrates. The sputtering rates for SiC were 100 Å/min at 18 millitorr Ar and 100 watts, and 250 Å/min at 15 millitorr and 200 watts. Vitreous carbon had a rate of 20 Å/min at 30 millitorr Ar and 200 watts. SiC can be prepared without peeling under all conditions with an occasional mosaic peeling. Peeling occurs in vitreous carbon at all pressures other than 30 millitorr Ar.

WC and B_4C were sputtered in the presence of O_2 . The rates were 10A/min at 30 millitorr and 25 watts and 350 A/min at 30 millitorr Ar and 200 watts for WC. For B_4C the only rate determined was 83 A/min at 30 millitorr Ar and 100 watts. The B_4C samples showed signs of deterioration after several months. Knoop hardnesses for WC were 280 kp/mm^2 at 30 millitorr Ar and 100 watts and 400 kp/mm^2 30 millitorr Ar, 200 watts. B_4C showed a hardness of 100 Kp/mm^2 at 15 millitorr Ar and 25 watts, and 450 Kp/mm^2 at 30 millitorr Ar and 200 watts.

Binary sputtering was performed on a newly purchased machine with a substrate heater capable of reaching temperatures as high as 700°C . The sputtering rates are listed in Table 6 below.

TABLE 6
BINARY SPUTTERING CONDITIONS

		Argon Pressure millitorr	Power (Watts)	Temp. ($^\circ\text{C}$)	Sputtering Rate (A/min)
SiC-C	SiC	30	50	30	7.5
	rich	10	50	50	93
	slide				
	C	30	50	30	5
B_4C -C	rich	30	100	700	46
	slide				
	B_4C	30	100	300	5
	rich	30	50	700	25
	slide				
	C	30	100	20	2
SiC- B_4C	rich	30	100	700	17
	slide				
	SiC	30	100	60	15
	rich	30	150	80	47
	slide				
	B_4C	30	100	60	11
	rich				
	slide				

All sputtering rates listed are the minimum and maximum obtained.

Substrate heating has not been performed on the B_4C -SiC system at the present but this work is in progress. Other work in progress is the determination of the crystallization temperatures of the substances, while microprobe analysis will be done to determine the compositional changes across the binary systems.

ACKNOWLEDGMENTS

Those persons contributing directly to this report have been recognized by name. In addition, we appreciate the advice of Dr. P. A. Thrower on electron microscopy and Dr. J. H. Hoke on measuring tensile strength.