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STRUCTURE AND PROPERTIES OF IRON CONTAINING GLASSY CARBONS

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Abstract—Glassy carbons containing iron were prepared from copolymers of furfuryl alcohol and ferrocene derivatives at heat-treatment temperatures from 500°C to 2500°C. The copolymerization produced a highly dispersed state of iron in carbonaceous matrices at least in the early stage of pyrolysis. Above 500°C, the homogeneously dispersed iron separated into irregularly spaced domains consisting of cementite, pure iron and iron compounds of unknown composition. Addition of iron resulted in a local graphitization of the glassy carbon at heat-treatment temperatures above 1000°C. At heat-treatment temperatures between 500°C and 800°C, electrical resistivities of the iron-doped carbons were much smaller than those of unmodified polyfurfuryl alcohol carbons but followed more or less the behavior of the latter for heat-treatment temperatures above 800°C.Measurements of mechanical properties indicated a remarkable increase in tensile strength of the low temperature carbons (500°C) with increasing iron content but the strength of the iron containing carbons decreased at higher carbonization temperatures.

1. INTRODUCTION

Studies by Fitzer and co-workers have shown that some of the properties of glasslike carbons perpared from three different thermosetting resins were nearly independent of the chemical structure of the starting resins[1]. This indicates the difficulty of obtaining desirable properties of glassy carbon at the pure element composition by chemical treatment only. The addition of very small amounts of platinum salt to the raw material led to a marked increase in flexural strength of the resultant glassy carbons, unaccompanied by any change in the X-ray diffraction parameters[2]. A large number of studies have been done on the structural modification of glassy carbon and the improvement of its properties by the addition of various metallic elements[3]. So far, the metallic elements have been added in the form of pure metal or ionic compound to an already carbonized matrix or polymerized resin[4–6]. Therefore, a homogeneous dispersion of the added metal could not be obtained throughout the carbon matrix.

The objective of the present work is to determine the possibilities of modifying the structure and properties of glassy carbon by the addition of iron to the starting organic precursor to obtain glassy carbons containing iron in a highly dispersed state. In this work, glassy carbons were prepared by the copolymerization of furfuryl alcohol and ferrocene derivatives such as ferrocene dicarboxylic acid and vinyl ferrocene in order to obtain a highly dispersed state of iron in the glassy carbon matrices.

2. EXPERIMENTAL

2.1 *Preparation of samples*

Furfuryl alcohol commercially obtained was distilled at 60°C under reduced pressure. The ferrocene derivatives were dissolved in

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purified furfuryl alcohol monomer and then copolymerized at 70°C for 48 hr in the presence of an acid catalyzer, 2N HCl, followed by a gradual temperature increase to 250°C under reduced pressure. Two series of samples of copolymers were prepared from solutions of furfuryl alcohol containing 1 per cent (by weight) and 3 per cent of ferrocene dicarboxylic acid (FDA) and 1 per cent, 3 per cent and 10 per cent of vinyl ferrocene (VF). All of the specimens were in rod form with a diameter of approximately 1/8 in. and a length of 2 in.; on occasion, plate shaped specimens were prepared of 1/16 in. in thickness and one inch square. They were heat-treated in purified nitrogen at atmospheric pressure with a heating rate of 6°C/hr to a temperature of 700°C, from there with a rate of 25°C/hr up to 970°C. Specimens obtained at 970°C were further heat-treated to 1500°C, 2000°C and 2500°C in a graphite resistance furnace with a positive flow of argon at a heating rate of 3·3°C/min. Soaking time at the maximum temperature of each heat-treatment ranged from 1 to 1·5 hr. The specimens heat-treated at 2000°C and 2500°C were slowly cooled down to 1500°C, held at 1500°C for 30 min and again cooled to 1300°C. From there, they were furnace-cooled for 2 hr. Control samples, without the ferrocene additives, were also prepared and heat-treated under the same conditions. Specimens of copolymers containing different amounts of the ferrocene additives were heat-treated at the same time to allow for a meaningful analysis of their properties, and in separate sample containers to avoid contamination between different samples.

2.2 *Experimental measurements*

The specimens heat-treated at various temperatures were analyzed by transmission electron microscopy, scanning electron probe, selected area electron diffraction and X-ray diffraction methods. After each heat-treatment, the total iron content in glassy carbon matrices was determined by wet chemical analysis and the dispersion of iron examined by scanning electron probe. Structural changes of the samples with heat-treatment temperature and total iron content were followed using an X-ray diffractometer with FeKα radiation. On occasion, nickel-filtered CuKα radiation was used for the specimens containing no iron.

Electrical resistivities of rod-shaped specimens were measured at room temperature employing a potential probe method which utilizes two extra electrodes to eliminate errors due to contact resistance. The potential drop due to the resistance of the specimen was measured at zero current through a known distance of sample between potential probe electrodes having point contact with the specimen surface. The temperature dependence of the resistivity was measured in a silicon oil bath at temperatures ranging from 20°C to 120°C in order to obtain activation energies of iron containing glassy carbons.

Uniaxial tensile strength measurements were performed on samples of all glassy carbons obtained at 500°C, 700°C and 970°C with a soak time of 1 hr. All the measurements were made with a crosshead speed of 0·02 in./min.

3. RESULTS AND DISCUSSION

3.1 *Morphology of iron*

Preliminary experiments on copolymerization showed that the ferrocene derivative could not be solvent extracted from the resin produced from the polymerization of furfuryl alcohol containing the ferrocene derivatives. This indicates that the organic derivative of iron is incorporated by covalent bonds into the polymer matrix. The precarbonization temperature of 300°C, while converting the copolymer into a rigid matrix, does not result in the decomposition of the ferrocene derivative. Thus, by delaying the release of the foreign element from its organic structural cage until a rigid carbon matrix is formed, it can be expected that its aggregation into distinct phases is prevented and that

its initial molecularly dispersed state is maintained.

The results of the electron microprobe analyses of furfuryl alcohol FDA copolymers heat-treated at temperatures from 500°C to 970°C indicate that the separation of iron from a homogeneous iron-carbon macrostructure existing below 600°C into irregularly spaced domains of iron-enriched carbon increases with increasing heat-treatment temperature and soak time. These domains are composed of cylindrical whiskers of 0·1 μm in diameter and up to several microns in length as shown in Fig. 1. They were identified as a highly crystalline cementite (Fe_3C) by selected area electron diffraction (SAD). Andreev *et al.*[7] studied the thermal stability of ferrocene and found it decomposes at temperatures between 400° and 470°C into metallic iron and carbon as well as gaseous products consisting of hydrogen and low molecular weight hydrocarbons. At these temperatures they reported the absence of iron–carbide type compounds among the decomposition products. The formation of amorphous and microcrystalline iron carbides occurs at temperatures of 540°–550°C in the pyrolysis of pure ferrocene as reported by Gray *et al.*[8].

Table 1 and Fig. 2 show the results of the electron microprobe analysis on glassy carbons prepared from copolymers of furfuryl alcohol with 1 per cent FDA and 1 per cent VF, respectively. The data in Table 1 were obtained from a statistical analysis of the detector response from background iron in scanning time increments of 10 sec. The peaks in Fig. 2 correspond to the domains of iron-enriched carbon. In the PFA—1 per cent 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 as shown in Fig. 3. In the case of glassy carbons from PFA–VF, the content of background iron increases, with increasing heat-treatment

Table 1. Intensity of highly dispersed background iron in glassy carbon matrix by Scanning Electron Microprobe analysis

Sample	Microprobe intensities for different HTT 500°C	700°C	970°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 per cent certainty.

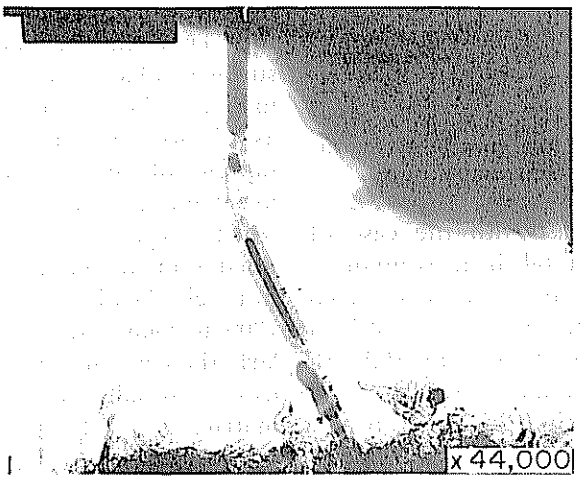

Fig. 1. Electron micrograph of glassy carbons from polyfurfuryl alcohol–FDA obtained at 950°C, showing whiskers of cementite (Fe_3C).

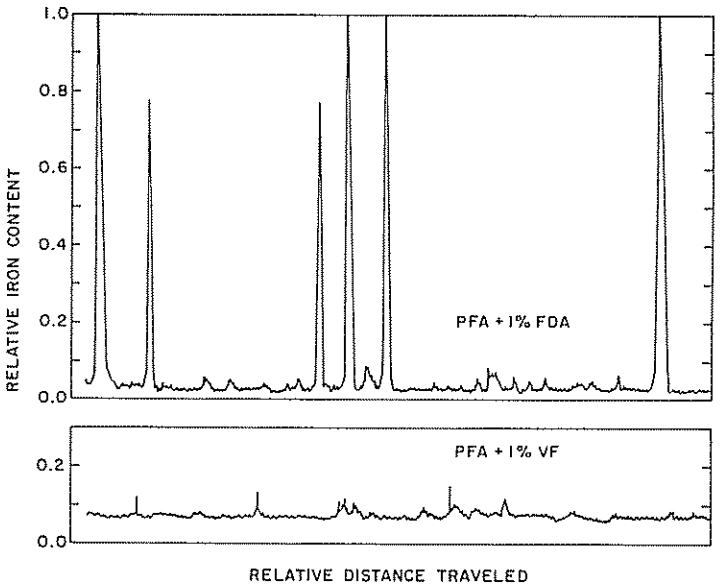

Fig. 2. Scanning electron microprobe analysis of iron in glassy carbons (HTT, 970°C).

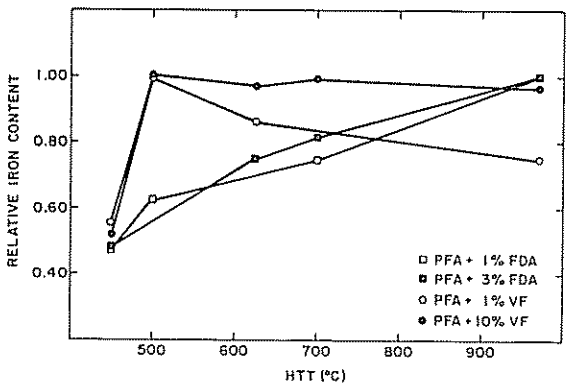

Fig. 3 Relative change of total iron in glassy carbons with heat-treatment temperature.

temperature, in contrast with the case of PFA–FDA, and the total iron content is nearly constant at temperatures from 500°–970°C. This constancy of the total iron content in the glassy carbon from PFA–VF over the temperature range from 500°–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 4 and 5 show transmission electron micrographs of representative sections of glassy carbons from PFA–10 per cent VF. Figure 4 shows the formation within the carbon matrix of thin, square-shaped crystallites which occur in samples heat-treated to 550°C. Upon an increase in heat-treatment temperature to 625°C, some of these crystallites are released from the carbon surface and leave traces behind as can be seen in Fig. 5. The exact nature of these crystallites, as of now, has not been determined. In samples obtained at 970°C, the formation of massive aggregates can be observed (Fig. 6), which consist of a crystalline material identified as elemental iron of the γ-type with fcc unit cell. At high temperatures, going from 1000° to 2500°C, the iron compounds, particularly the cementite whiskers, decompose and iron eventually disappears from the carbon matrix.

3.2 *X-ray diffraction data*

The glassy carbons were examined by X-ray diffraction to determine crystallite size

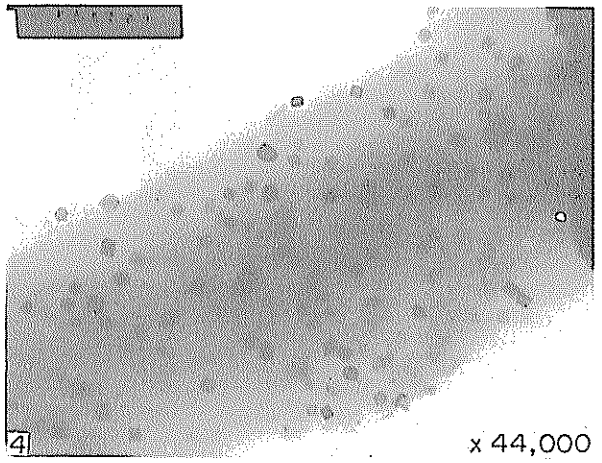

Fig. 4. Electron micrograph of glassy carbons from polyfurfuryl alcohol–10 per cent VF showing the appearance of square-shaped crystallites at 550°C.

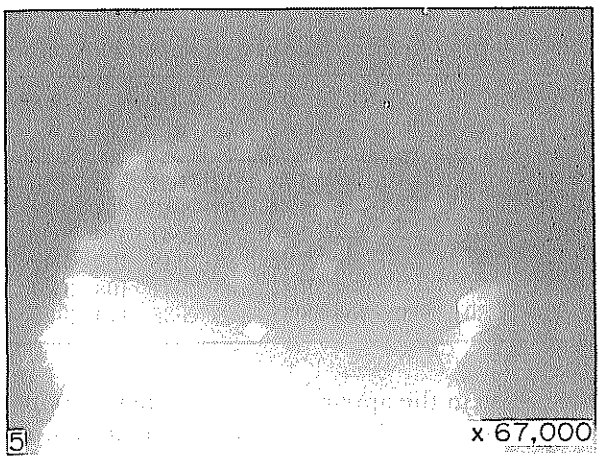

Fig. 5. Electron micrograph of glassy carbons from polyfurfuryl alcohol–10 per cent VF at 625°C.

and interlayer spacing. Figure 7 shows diffraction profiles from (002) plane. The addition of iron produces a marked increase in the intensities of (002) diffraction peak and the narrowing of the linewidth. The interplanar spacing (d_{002}) and apparent crystallite size (L_c) normal to the (002) planes are shown as a function of heat-treatment temperature in Table 2. The X-ray diffraction data listed in Table 2 were obtained using manganese-filtered FeKα radiation for samples heat-treated up to 2000°C and nickel-filtered CuKα radiation for samples prepared at 2500°C. These data indicate that catalytic graphitization of glassy carbons from polyfurfuryl alcohol increases with increasing heat-treatment temperature and concentration of the ferrocene derivative. The degree of catalytic graphitization for the PFA–VF system is nearly equal to that for the PFA–FDA system. The inclusion of a small amount of iron in glassy carbon matrices re-

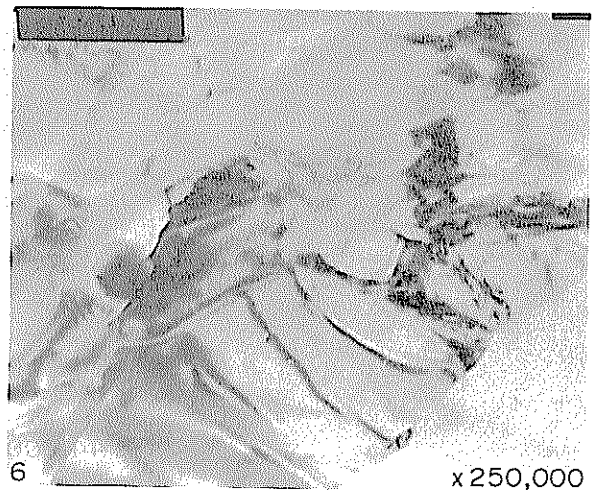

Fig. 6. Electron micrograph of glassy carbons from polyfurfuryl alcohol–10 per cent VF at 970°C.

Table 2. X-ray diffraction data of iron-doped PFA carbons

	625°C		700°C		970°C		1500°C		2000°C		2500°C	
	d_{002}(Å)	L_c (Å)	d	L_c	d	L_c	d	L_c	d	L_c	d	L_c
PFA	—	—	—	—	3·83	12	3·51	20	3·50	28	3·46	38
PFA–1% FDA	—	—	—	—	3·44	84	3·43	91	3·42	95	3·43	117
PFA–3% FDA	—	—	—	—	3·40	92	3·41	104	3·39	111	3·39	134
PFA–1% VF	—	—	—	—	3·43	86	3·43	100	3·42	100	3·39	123
PFA–3% VF	—	—	—	—	3·42	103	3·41	108	3·40	110	3·39	123
PFA–10% VF	3·38	130	3·38	164	3·37	166	3·38	170	3·38	181	3·37	201

sulted in a remarkable increase in the apparent cyrstallite size and a decrease in the interplanar spacing. For example, the PFA–1 per cent FDA carbon which contains 0·32 per cent by weight of iron after heat-treatment at 970°C for 1 hr had an L_c of 84Å and a d_{002} of 3·44Å, while the corresponding X-ray parameters for pure PFA carbon obtained under the same conditions are 12Å and 3·83Å, respectively.

3.3 *Properties of iron containing glassy carbons*

Uniaxial tensile strength and electrical resistivity measurements were carried out on samples of glassy carbons obtained from PFA–FDA and PFA–VF copolymers. Glassy carbons from pure PFA exhibit a pronounced increase in tensile strength with heat-treatment temperature. On the other hand, the specimens of glassy carbons containing iron become more brittle and generally have lower tensile strengths at elevated heat-treatment temperatures. However, the specimens obtained at 500°C reveal a striking increase in the tensile strength with increasing concentration of the ferrocene derivative, as shown in Table 3. The remarkable decrease in tensile strength at higher heat-treatment temperature may be ascribed to the inhomogeneity of the glassy carbon due to variation in composition of the iron domains and to the formation of graphitic structure in glassy carbon by the catalytic action of added iron. This matrix inhomogeneity may

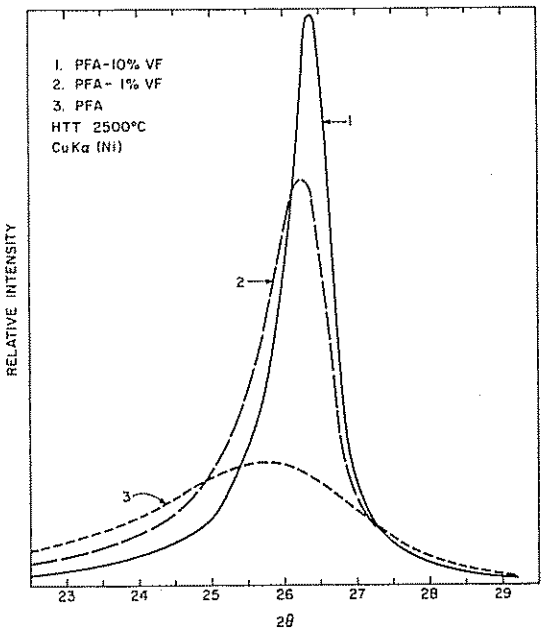

Fig. 7. X-ray diffraction profiles of glassy carbons from (1) PFA–10 per cent VF, (2) PFA–3 per cent FDA and (3) PFA at 2500°C.

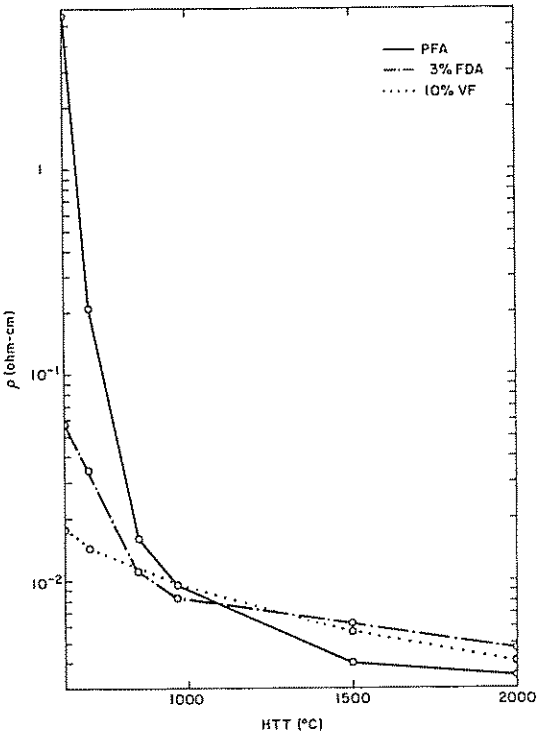

Fig. 8. Electrical bulk resistivity of glassy carbons PFA and iron-doped PFA.

Table 3. Tensile strength of iron-doped PFA carbons

Sample	Tensile strength (kg/cm²*) 500°C	700°C	970°C
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.

produce localized internal strain accompanied by a decrease in the overall tensile strength.

In Fig. 8 are shown electrical bulk resistivities of carbons from PFA and iron–organic PFA precursors as a function of heat-treatment temperature. In all cases inclusion of iron lowers the resistivity of the resultant carbon composite at heat-treatment temperatures below 800°C. Above this temperature the electrical resistivity follows more or less the behavior of unmodified PFA carbon. The influence of different functional groups attached to the ferrocene precursor on the properties of glassy carbons becomes apparent if resistivities are plotted versus total iron content. Carbons derived from PFA–VF show consistently lower resistivities than those derived from PFA–FDA at heat-treatment temperatures below 800°C, when compared at identical levels of iron, as can be seen in Fig. 9. This effect is not explainable at this time, but it is believed that it originates from differences in the copolymer structure of the precursor. Generally, resistivity depends not only on the degree of crystal disorder but also on geometrical factors such as porosity and the relative distribution of different conducting phases in the matrix. As is

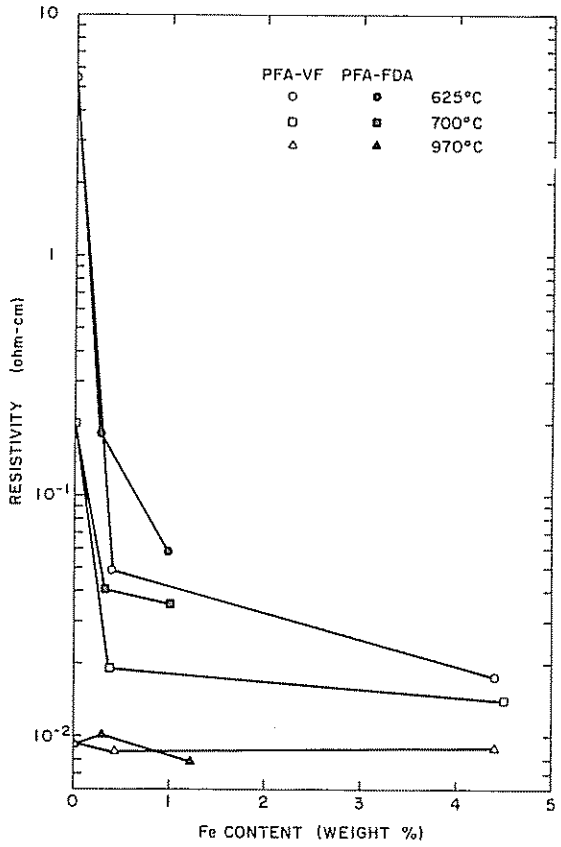

Fig. 9. Variation of electrical resistivity of iron-doped PFA carbons as a function of total iron content.

observed in semiconducting materials, the resistivity of all of these samples decreases with increasing measurement temperature. Table 4 shows activation energies obtained from the temperature dependence of resistivity, together with electrical bulk resistivities of glassy carbons prepared below 625°C. The activation energies of the samples decrease with an increase in heat-treatment temperature but are only slightly affected by iron addition.

Electronic properties of doped carbons by either titanium and manganese have been studied by Millet *et al.*[9]. Doping with these metallic elements resulted in a significant decrease of the electrical resistivity of the carbons heat-treated at a given temperature. This effect was entirely explained by graphitization catalysis, because all the values of resistivity from doped and nondoped carbons fell on the same curve when they were plotted as a function of the degree of graphitization. This does not apply to iron-doped PFA carbons which have nearly identical resistivities to those of nondoped PFA carbons at heat-treatment temperatures above 800°C, although the iron-doped glassy carbons contain more graphitic structure than the pure PFA carbons, as described in the preceding section. The lower resistivity of iron-doped PFA carbons obtained at temperatures between 500°C and 800°C may be ascribed to the presence of pure iron, cementite (Fe_3C) and magnetite (Fe_3O_4). These forms of iron were detected for iron-doped carbons by X-ray diffraction and selected area electron diffraction methods. The resistivities of iron and cementite are $9{\cdot}7\times10^{-6}\Omega$.cm and $45\times10^{-6}\Omega$.cm, respectively, and that of magnetite $3{\cdot}6\times10^{-2}\Omega$.cm[10]. Aluminum is a good electric conductor and one of the metallic elements which produce enhanced graphitization of amorphous carbons[11, 12]. However, addition of aluminum increases the resistivity

Table 4. Bulk resistivity and activation energy of carbons from polyfurfuryl alcohol and ferrocene derivatives

Sample	560°C		580°C		600°C		625°C	
	ρ(Ω·cm)	ΔE(eV)	ρ	ΔE	ρ	ΔE	ρ	ΔE
PFA	$6{\cdot}3\times10^{6}$	$7{\cdot}8\times10^{-2}$	$3{\cdot}8\times10^{6}$	$8{\cdot}3\times10^{-2}$	$6{\cdot}6\times10^{4}$	$6{\cdot}2\times10^{-2}$	5·4	$2{\cdot}8\times10^{-2}$
PFA–3% FDA	$3{\cdot}3\times10^{5}$	$8{\cdot}4\times10^{-2}$	$1{\cdot}8\times10^{5}$	$7{\cdot}5\times10^{-2}$	$3{\cdot}2\times10^{3}$	$6{\cdot}7\times10^{-2}$	$5{\cdot}8\times10^{-2}$	$4{\cdot}2\times10^{-3}$
PFA–10% VF	$1{\cdot}4\times10^{5}$	$8{\cdot}5\times10^{-2}$	$5{\cdot}6\times10^{4}$	$8{\cdot}1\times10^{-2}$	$2{\cdot}7\times10^{3}$	$6{\cdot}4\times10^{-2}$	$1{\cdot}8\times10^{-2}$	—

of pyro-polymer carbons heat-treated at temperatures from 800°C to 1200°C[13]. This has been explained by the presence of non-conducting aluminum carbides. The iron containing glassy carbons prepared in this study consist of small regions of highly graphitized carbon in the isotropic carbon matrix, as shown in the foregoing section. But, their resistivities are nearly equal to those of non-doped PFA carbons at heat-treatment temperatures above 800°C. This seems to indicate that the resistivity is dependent upon the nature of the material between regions of high conduction and on their relative distribution in the matrix.

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