JOURNAL OF SOLID STATE CHEMISTRY 2, 218–224 (1970)

Magnetic Susceptibility and Electron Spin Resonance of Ultrafine Graphite

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Received December 19, 1969

An ultrafine, reactive form of graphite is produced when bulk graphite is subjected to conditions involving high-speed rubbing or wearing in an inert atmosphere. The diamagnetic susceptibility of ultrafine graphite increases with increasing heat-treatment temperature from 0.2 emu/g to 6.2 emu/g after 3000°C heat treatment. This behavior is similar to that observed for most cokes and carbon blacks. The electron spin resonance of ultrafine graphite heated below 900°C has a *g* value of 2.0023 ± 0.0001 and follows Curie's law. The *g* shifts observed after it is heated above 1600°C strongly suggest that the spin resonance in the high temperature materials originates from conduction electrons. The susceptibility and ESR results, complemented by X-ray and surface property measurements, lead to the conclusion that the high speed wearing process *degraphitizes* graphite to a material which can then be *regraphitized* by subsequent heat treatment.

Introduction

This paper presents the results of experimental investigations of the unusual magnetic properties of ultrafine graphite. We use the term *ultrafine graphite* to denote a material which has an average particle size less than 0.2μ, a surface area of 200–500 m^2/g, and which is also pyrophoric upon first exposure to air. This form of graphite (also known as wear-dust) was first studied by Savage (*1, 2, 3*) and is of practical interest in applications where it may be used as a lubricant, as an inert gas purifier, and as a possible filler in special carbon applications. The conditions necessary for the production of ultrafine graphite apparently are (1) a high rubbing velocity and (2) an inert atmosphere or a vacuum. Conventional grinding of graphite, if done in air, produces a decidedly coarser material with a much lower surface area and lower reactivity.

A number of studies of the adsorption and structural properties of finely divided carbons and graphites have been reported. Zarifyanz and coworkers (*4*) measured adsorption isotherms and heats of adsorption of freshly cleaved graphite surfaces prepared in a vibratory mill. They concluded that most of the chemically active centers were not free radicals. Vastola and Walker (*5*) also measured the kinetics of the reactions of ball-milled graphite with carbon dioxide and oxygen at low pressures. The existence of surface complexes was postulated. Walker and Seeley (*6*) considered the structural changes in finely ground graphite. They found that Ceylon graphite ground in the submicron range had crystallite sizes considerably less than particle dimensions.

The high purity and extreme state of disorganization of our ultrafine graphite samples make them particularly suitable for studies of structural changes which occur during heat treatment. In this study, we have determined the diamagnetic susceptibility, electron spin resonance (ESR), and X-ray properties of a number of ultrafine graphites. We have also investigated the effects of heat treatment and of chemical treatment on these properties.

Experimental

Sample Preparation

The preparation and treatment of the ultrafine graphite samples are summarized in Table I. In each case, the starting material was a lampblack-base graphite similar to that studied previously (*7*).

Apparatus G is a chamber-enclosed grinding wheel in which a block of lampblack-base graphite

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TABLE I

PREPARATION AND HEAT TREATMENT OF ULTRAFINE GRAPHITE SAMPLES

Series	Apparatus	Atmosphere	Heat Treatment
1	G	Nitrogen	None
2	G	Nitrogen	In chlorine, at intervals from 250°–3000°C
3	G	Argon	None
4	G	Argon	In vacuum, at intervals from 250°–1000°C
5	V	Vacuum	None

rubs on a wheel of the same material in an inert atmosphere at a velocity of approximately 1200 cm/sec. Relatively large amounts of ultrafine graphite from Series 2 and Series 4 were used for heat treatment at each temperature. Portions of each of the heat treated samples were then used for measurements of diamagnetic susceptibility, ESR, and X-ray diffraction. A number of surface property measurements were also made with the Series 2 ultrafine graphite.

The essential parts of the vacuum apparatus (V) are shown in Fig. 1. A magnetically driven shaft is employed to avoid sealing problems, permitting ultrafine graphite to be produced at a pressure of 5×10^{-6} Torr. The fine particles fall into the long glass tube which has the same diameter as the standard ESR sample tubes. Small sections of the tubing can be removed by sealing off with a torch without disturbing the vacuum. Due to the relatively low torque developed in this apparatus, only small amounts of ultrafine graphite can be produced in a reasonably short time. Only a limited number of ESR and X-ray measurements were made on the ultrafine graphite prepared in apparatus V.

Diamagnetic Susceptibility

It has been well established that the diamagnetic susceptibility of carbons and graphites is sensitive to crystallite size and structure and, thus, to the degree of graphitization (*8*). It was, therefore, of interest to compare the susceptibility of ultrafine graphite with that of the bulk starting material, as well as to follow the evolution of magnetic properties with heat treatment.

The measurements of the Series 1 and 2 ultrafine graphites were made in air by the Faraday method with an apparatus constructed by Soule, Nezbeda, and Czanderna (*9*). The sensitivity of the balance was 1×10^{-9} emu/g, and the accuracy of individual measurements was estimated to be 1%. All samples were found to be isotropic within 2%. Field dependence measurements up to 20 kG showed that ferromagnetic impurities were absent.

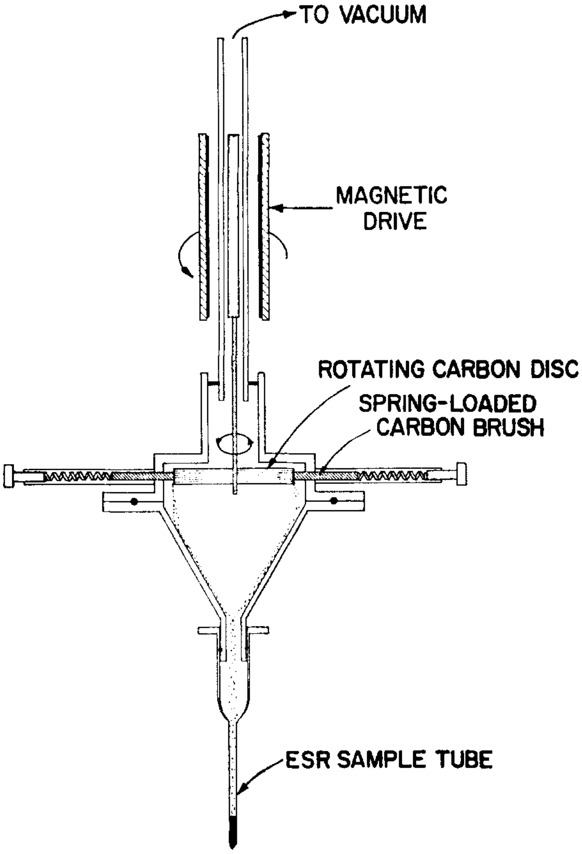

FIG. 1. Apparatus (V) for preparing ultrafine graphite in vacuum.

The variation of the diamagnetic susceptibility of Series 1 or 2 ultrafine graphite with heat-treatment temperature is shown as the solid line in Fig. 2. The dashed curve represents the data of Kiive and Mrozowski for heat treated lampblack (*10*). The generally close correspondence of the two curves is evident, but two regions of possibly significant dissimilarity exist. The diamagnetic susceptibility of ultrafine graphite is lower than that of lampblack for heat-treatment temperatures up to 500°C. Unpublished work by G. Wagoner indicates that the disparity between the two curves in this region may be caused principally by physically adsorbed oxygen. Above 2000°C, the diamagnetic susceptibility of lampblack increases more rapidly with increasing temperature than does that of the ultrafine graphite. A possible explanation for the diverg-

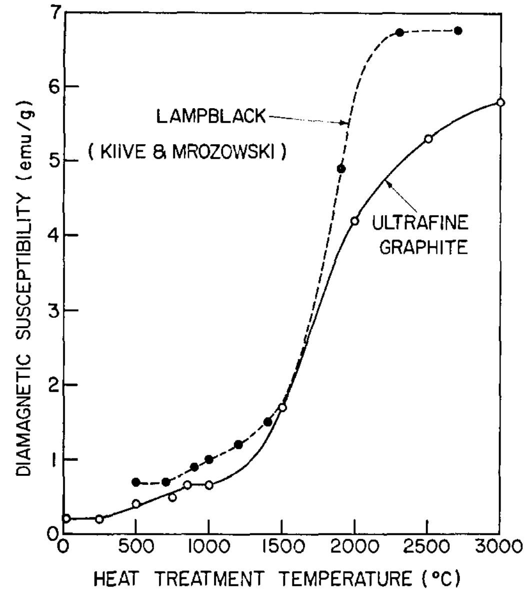

FIG. 2. Comparison of diamagnetic susceptibility versus heat treatment temperature for lampblack (Kiive and Mrozowski) and ultrafine graphite.

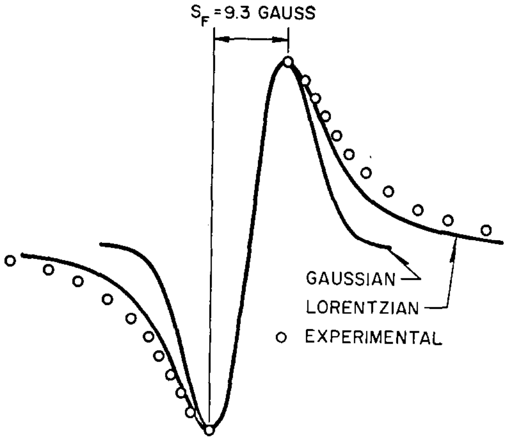

FIG. 3. ESR lineshape for a typical sample of ultrafine graphite.

ence of the two curves in the high temperature region is that the ultrafine graphite is not completely graphitized even at 3000°C. The X-ray results confirm this interpretation.

Electron Spin Resonance (ESR)

The ESR properties of carbons and graphites are also indicative of crystallite size and structure (*11*, *12*). For example, the starting bulk material (lampblack-base graphite) exhibits a *g* value and temperature-independent spin susceptibility typical of the conduction electron resonance in fairly small crystallite-size polycrystalline graphite (*12*). On the other hand, the ESR properties of the ultrafine graphite samples were totally different from those of the bulk starting material. In fact, they behaved more like low-temperature cokes or carbon blacks (*11*).

The ESR measurements were made in the spectrometer described previously (*12*). The measurements included (1) paramagnetic spin susceptibility and its temperature dependence, (2) relaxation time and oxygen effects, (3) chemical treatment experiments, and (4) heat treatment experiments.

Paramagnetic Spin Susceptibility and its Temperature Dependence. The temperature dependence of the ESR was determined between 100°K and 300°K. A typical ESR curve for ultrafine graphite at room temperature is shown in Fig. 3. The *g*-factor is 2.0023 ± 0.0001. No signal was observed at a field corresponding to the *g* value of the starting material, viz., 2.013 (*12*). The line has a slight cusp shape, i.e., the curve drops off more slowly in the wings than a Lorentzian curve. The complete absence of asymmetry in the lineshape due to skin effects is also noteworthy (*12*). A spin susceptibility of 2.1×10^{-7} emu/g was calculated, based on a comparison of the ESR signal with that from a single crystal of $CuSO_4 \cdot 5H_2O$ by using the ruby signal as a secondary standard (*13*). Since this value was calculated from the peak-to-peak linewidth (S_F) assuming a Lorentz shape, the calculated susceptibility is only approximate. However, the slight cusp shape indicates that the computed value is a lower limit and is probably not in error by more than 20%. The room-temperature spin susceptibility for the conduction electrons in similar lampblack-base graphite is, according to previous measurements, more than a factor of 10 smaller than this value, viz., 1.1×10^{-8} emu/g (*12*).

The ESR was measured at several temperatures between 100–300°K. Although the linewidth increased by a factor of two between 100–300°K (Fig. 4), lineshape analyses of the curves at 106 and 172°K were indistinguishable. Figure 5 shows the spin susceptibility results. There is some spread in the data; however, the results indicate a Curie law temperature dependence of susceptibility. Assuming spins of 1/2, the spin susceptibility corresponds to an effective spin concentration of 1.0×10^{20}/g.

Relaxation Time and Reversible Oxygen Effects. The linewidth and relaxation behavior of the ESR in ultrafine graphite is further evidence for the similarity of the material to a low temperature coke or char. The ESR for all the ultrafine graphite samples broadened reversibly in air by a factor of

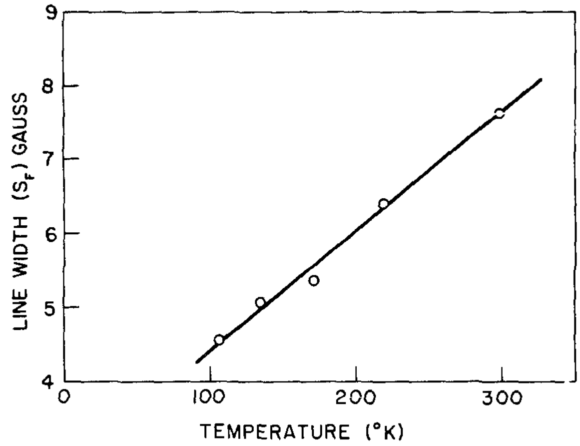

FIG. 4. ESR linewidth as a function of temperature for ultrafine graphite.

approximately two. The spin-lattice relaxation time T_1 also decreased reversibly when the samples were exposed to air. When the T_1 for the ultrafine graphite samples was compared with that for a single crystal of DPPH, the T_1 for ultrafine graphite in vacuum was determined to be $\sim 5 \times 10^{-8}$ sec. Since the linewidth was approximately 10 G ($T_2^* = 6 \times 10^{-9}$ sec), it is apparent that T_1 is an order of magnitude longer than T_2^*. This situation is analogous to that observed for many low-temperature chars (*11*).

An approximate calculation can be made of the broadening expected from simple magnetic dipole-dipole interactions in these ultrafine graphites (*14*, *15*). For a spin concentration of 10^{20} per gram in a solid having a density of 2 g/cm^3, a linewidth of 7 G is calculated. The approximate agreement with the observed linewidth suggests that exchange interactions do not determine the linewidth of the ESR in ultrafine graphite.

Chemical Treatment Experiments. Since the temperature dependence and relaxation time results suggested the presence of *localized* unpaired spins in ultrafine graphite, it was of interest to determine if the spins were associated with easily attacked surface groups. Several ultrafine graphite samples were treated with acetyl chloride, 1:1 HCl, and 5 M NaOH, and none of these reagents had an effect on the ESR. Also, no irreversible effects on the ESR were observed when ultrafine graphite was heated to 200°C in O_2. At 250°C, combustion occurred.

The most conclusive evidence that the unpaired spins in ultrafine graphite are not affected by surface reactions was obtained from a sample of pyrophoric ultrafine graphite. The sample had been prepared and sealed in an ESR sample tube under vacuum (apparatus V). An ESR signal similar to that in Fig. 3 was observed. When the sample was exposed to air, a dull red glow due to the rapid oxidation reactions was observed. After reevacuation at room temperature, the ESR signal was the same as that observed in the original sample.

Heat Treatment Experiments. The evolution of the properties of a carbonaceous material heat treated at various temperatures up to 3000°C is indicative of the structural nature of the starting material and also the completeness of the transformation of carbon to graphite (*8*, *10*, *11*). In the first experiment, a typical sample of ultrafine graphite, which had been prepared in argon, was successively heat

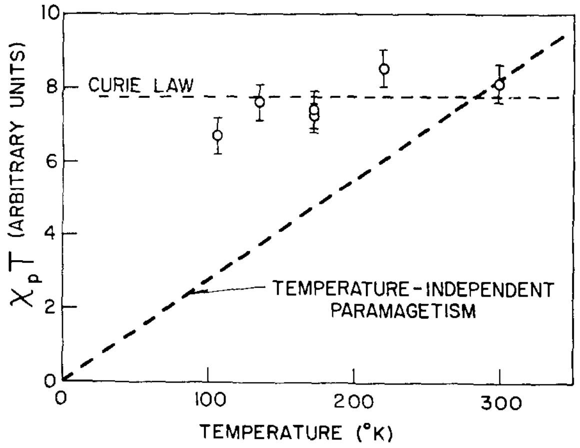

FIG. 5. Temperature dependence of the spin susceptibility of ultrafine graphite.

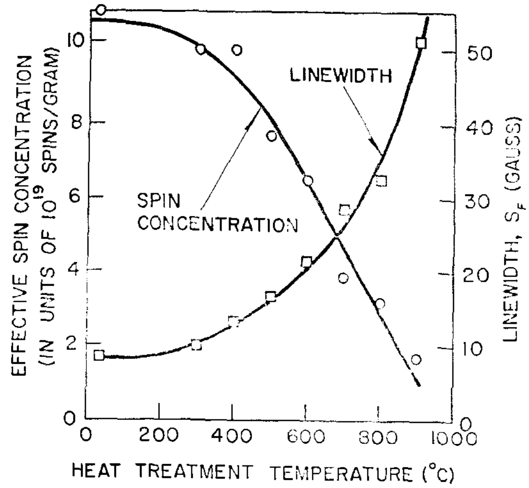

FIG. 6. Spin concentration and linewidth as a function of heat treatment temperature of ultrafine graphite.

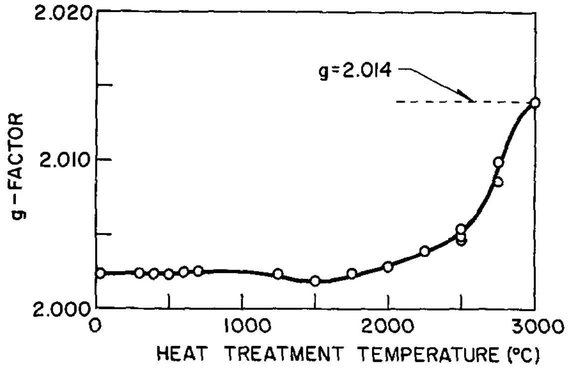

FIG. 7. *g* Factor of ultrafine graphite as a function of heat treatment temperature.

treated in vacuum to 1000°C, and its room-temperature ESR properties were measured. Figure 6 shows the spin concentration and linewidth results. Note that the effective spin concentration drops more than a factor of 5, whereas the linewidth increases by approximately the same factor. These results closely parallel those for carbon blacks heat-treated over the same temperature range (*16*, *17*).

For heat-treatment temperatures between 1000–3000°C, a chlorine atmosphere was maintained to prevent the diffusion of impurities into the graphite during heat treatment. The presence of even minute amounts of impurities in graphite is known to produce broadening of the ESR (*12*). The *g* factor results for the entire temperature range are shown in Fig. 7. Again, the similarities with heat-treated carbon blacks are apparent (*16*, *17*). The *g* of 2.014 observed for the 3000°C heat-treated ultrafine graphite is the same, within experimental error, as that for lampblack-base graphite for which electron motion effectively averages out the g-anisotropy (*12*).

When one considers the data in Table II as well as the other observations, the results of the ESR experiments can be summarized as follows:

(a) For ultrafine graphite, the *g* value, relaxation time, intensity, and temperature dependence are totally different from the corresponding properties of the conduction electron resonance observed in the starting material.

(b) The unreactive character of the unpaired spins indicates that they are not associated with surface groups but are an intrinsic part of the aromatic carbon skeleton.

(c) The high-spin concentration, Curie law temperature dependence, and relaxation properties are similar to those observed in many cokes and carbon blacks.

(d) The behavior of the *g* factor on heat treatment is also similar to that observed for carbon blacks and indicates that regraphitization occurs at 3000°C.

X-Ray

To see if the magnetic properties of ultrafine graphites were consistent with their structural characteristics, we carried out X-ray measurements on several Series 1 and Series 2 samples. The Debye patterns for various heat-treatment temperatures are shown in Fig. 8, along with the Miller Index assignments of the observed reflection peaks. In its initial state, ultrafine graphite is apparently a highly amorphous material which responds to heat treatment in much the same way as carbon black.

Direct application of the Debye formula for the calculation of crystallite dimensions cannot yield

TABLE II

COMPARISON OF ESR PROPERTIES OF BULK GRAPHITE AND ULTRAFINE GRAPHITE

	Lampblack-Base Graphite	
ESR Property	Bulk Sample	Ultrafine Graphite
Paramagnetic spin susceptibility at 25°C	$\chi_p = 1.1 \times 10^{-8}$ emu/g	$\chi_p = 2.1 \times 10^{-7}$ emu/g
Effective spin concentration at 25°C	$N_{eff} = 5.3 \times 10^{18}$/g	$N_{eff} = 1.0 \times 10^{20}$/g
Temperature dependence of χ_p	~ Independent	$\chi_p \propto 1/T$
g Factor	2.013	2.0023
Relaxation times	$T_1 \approx T_2^*$	$T_1 \gg T_2^*$
Effect of oxygen	None	Reversibly decreases T_1 and T_2^*

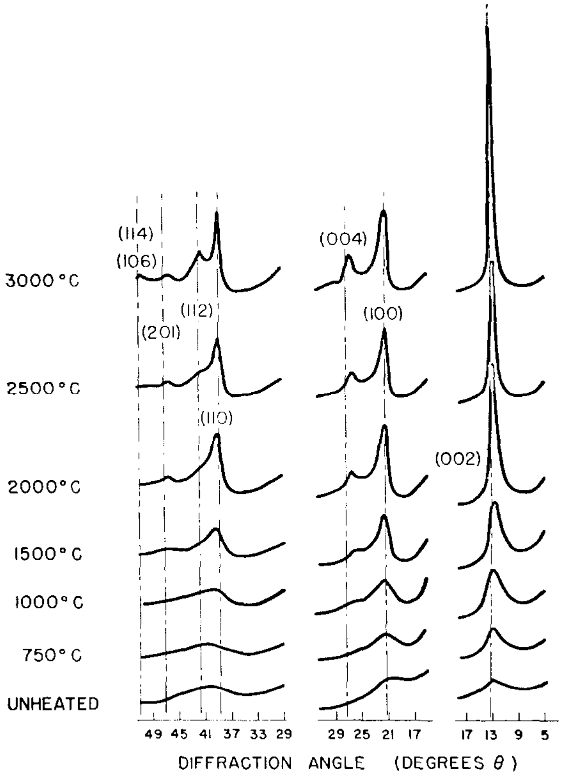

FIG. 8. X-Ray patterns for ultrafine graphite heat treated to various temperatures.

accurate results since most of the reflection peaks are asymmetric and there is undoubtedly a substantial contribution of both crystallite size and strain to the observed broadening. Consequently, only estimates of crystallite dimensions can be made. For the samples which were not heated above 500°C, the very poorly defined 002 peak indicates average crystallite thicknesses of, perhaps, two or three layers. The extremely broad planar reflections indicate layer diameters of, perhaps, 10–20Å.

The development of crystallinity seems to start at 750°C with a substantial ordering occurring by 1000°C. Above 1000°C, the structural development accelerates, although it never quite reaches the degree of order observed in the parent material. A similarly incomplete recovery of the full diamagnetism can be seen in Fig. 2.

Discussion and Conclusions

The high-speed rubbing or wearing of graphite in an inert atmosphere produces a material with structural properties and response to heat treatment closely resembling those of low temperature carbon blacks. Models for the structure of ultrafine graphite, unlike those for carbon blacks which contain many functional groups, must be capable of accounting for the observed response to heat treatment solely in terms of elemental carbon. Support for this view is obtained from experiments conducted with Series 5 ultrafine graphite samples which were prepared at 5×10^{-6} Torr and which exhibited the same ESR properties before and after exposure to air.

Two different models could account for the observations: *true crystallites* and *buckled crystallites*. The true crystallite model would be considered to consist of tiny platelets averaging 70 carbons in a layer plane and 200 carbons in a crystallite. The X-ray data in Fig. 8 indicate the presence of a very large number of such true crystallites in ultrafine graphite. Electron micrographs also support this conclusion. The observed unpaired spin concentration of 10^{20}/g corresponds to one spin per two crystallites. The unpaired spins would be stabilized by resonance through the comparatively large aromatic systems of approximately 30 fused rings. The persistence of the unpaired spins after chemical attack and also the fact that the paramagnetic resonance properties of ultrafine graphite are not changed by oxidation strongly suggest that the unpaired spins are an integral part of the aromatic carbon skeleton and are not localized at surface sites. Nevertheless, the true crystallite model appears rather unlikely because the onset of crystallite growth occurs at approximately 700°C, a temperature which is much too low to permit the fusion of true graphite crystallites. Furthermore, the specific surface area calculated for true crystallites consisting of approximately 200 carbon atoms per crystallite is far higher than the observed specific surface area.

An alternative model for the ultimate particles in ultrafine graphite which does not have these drawbacks is that of buckled crystallites. The particles are visualized as crumpled graphite planes in which the buckled areas are strained. Plane sections between buckled areas could have the dimensions of true crystallites. The number of carbon atoms in a buckled crystallite would be much larger than that in a true crystallite. An increase in crystallite size might then be expected to be observed at moderately low temperatures as the strained, buckled areas are relieved. Also, buckled crystallites would have a much smaller specific surface area, one closer to the observed value.

At this point, it is difficult to choose between these two models on the basis of the available observations. On the one hand, not enough strain can be introduced into a graphite crystallite to account for the exceedingly broad and diffuse planar X-ray reflections (*18*). On the other hand, it is not known whether strain alone could be responsible for the observed high concentration of unpaired spins. In the case of certain polymer fibers, mechanical deformation is known to produce free radicals (*19*). Whatever the correct model, the high-speed wearing process apparently degraphitizes graphite to a material which can then be regraphitized by subsequent heat treatment.

Acknowledgment

The authors thank Dr. G. Wagoner for many useful discussions.

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