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December 1982

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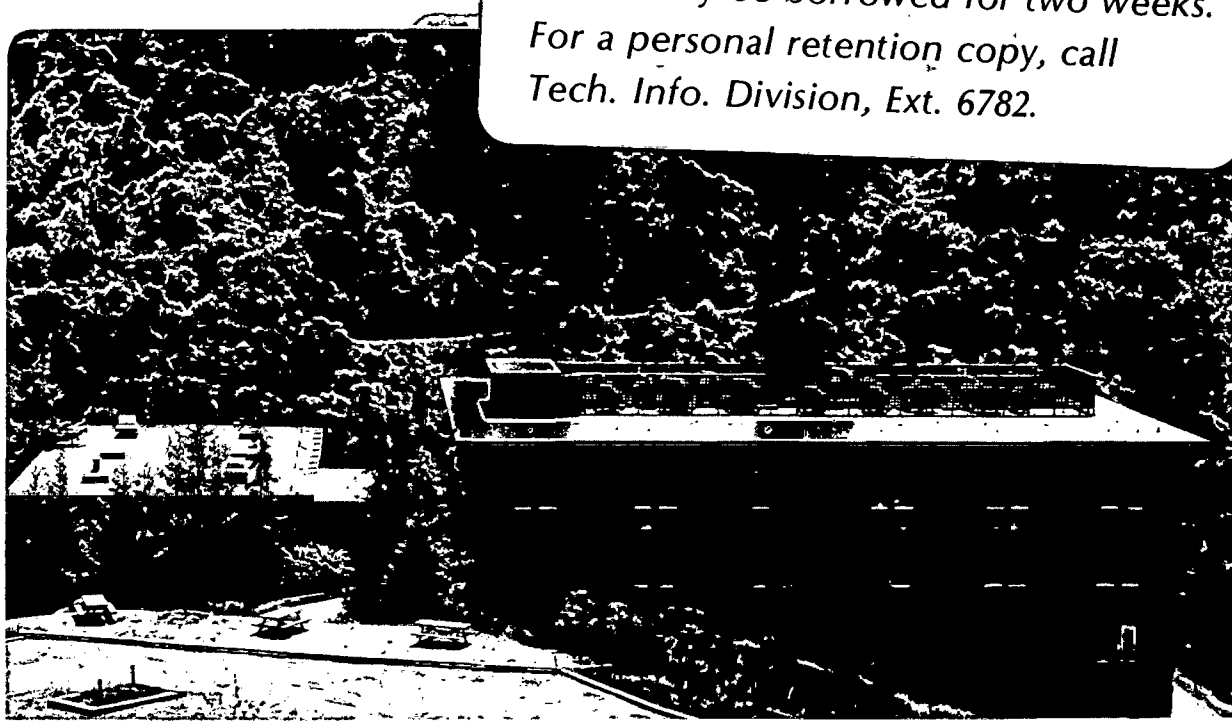

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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ABSTRACT

A negative $T^{-1/2}$ dependence of a component of the electrical conductivity, indicative of one-dimensional transport, was found in glassy carbon heat treated at temperatures less than 2200°C. The microstructure, as examined in lattice images in the transmission electron microscope, the Porod law dependence obtained in small angle scattering, and the decrease in the d_{002}-spacing interlayer as measured by x-ray diffraction (above this critical temperature) support this thesis.

PACS : 72.15.Cz.

Received:

There has been increased interest in the electrical conductivity of solids restricted to less than three dimensions, as in thin wires,[1-6] thin sheets[7] such as MOSFET channels,[8-10] and in some organo-metallic materials.[11-12] We believe that we have found an example of one-dimensional conductivity in glassy carbon. Our results empirically agree with theory and the case for one-dimensionality is supported by the observed microstructure.

Glassy carbon,[13] a prototype non-graphitizing bulk carbon, is prepared by thermally decomposing a thermosetting resin, typically a mixture of phenol formaldehyde and furfuryl alcohol. The as received material had been given a final one hour processing at 1000°C in inert atmosphere. It was heat treated further for three hours in a graphite furnace under an inert gas at temperatures ranging from 1200 to 2700°C. Specimens were ground, polished to uniform thickness and ultrasonically cut into a four probe bar configuration. Electrical conductivity measurements were made under isothermal conditions at temperatures from 3 to 300°K.

The results can be divided into two classes according to the behavior of the low temperature conductivity. For high heat treatment temperatures, greater than about 2200°C, the conductivity decreases with temperature to a shallow minimum (Fig. 1(a)). Of more interest in this letter, for low heat treatment temperatures the conductivity continues to decrease more rapidly with decreasing temperature as shown in Fig. 1(b).

Saxena and Bragg[14] were the first to formulate an empirical expression for the electrical conductivity of glassy carbon in the heat treatment temperature range of interest. In the present study,[15] the conductivity σ as a function of measurement temperature T is written as

$$\sigma = A + B\exp(-CT^{-1/4}) - DT^{-1/2}$$

where the first term is attributed to strongly scattering metallic conductivity independent of temperature and the second term to variable range hopping. Both terms have no strong dependence on the heat treatment temperature. The last and new term is a low temperature correction term to the metallic conductivity, and as shown in Fig. 2, is only important for heat treatment temperature less than about 2200°C.

Kaveh and Mott[16] have reviewed two approaches to a correction of the metallic conductivity. They are the localization approach by Abrahams, Anderson, Licciardello and Ramakrishnan[17] and the electron interaction approach by Altshuler, Aronov and Lee.[18] in the localization approach, the carrier is allowed to diffuse until an inelastic scattering event takes place (trapping by a localized state) and thus diffusion of the carriers is limited by the inelastic scattering time. In the electron interaction approach, the effective number of carriers is affected by the correlation between the shift of potential energy and the broadening of the momentum distribution of the carriers themselves as scaled by the physical dimensions. Both mechanisms may be operating simultaneously. They give identical results for conduction in two dimensions:

$$\delta\sigma = \frac{-e^2}{2\pi^2\hbar} \ln \frac{kT\tau}{\hbar}$$

where τ is the effective scattering time. The difference between the two approaches is seen in the Hall effect: The localization approach predicts no correction in the Hall effect but the interaction approach predicts that the relative change in the Hall coefficient will be twice that for the conduction.

The interaction approach has been used to predict a correction in three dimensions

$$\frac{\delta\sigma}{\sigma} = \left(\frac{kT}{(\hbar D)^3}\right)^{1/2} \frac{1}{N(E_F)}$$

and in one dimension

$$\delta\sigma = -\frac{e^2}{\hbar}\left(\frac{2}{\pi}\right)^2 \frac{1}{A}\left(\frac{\hbar D}{kT}\right)^{1/2}$$

where D is a diffusion coefficient related to the mean free path and A is the cross sectional area. Such a $-T^{-1/2}$ dependence for a component of the electrical conductivity indicates the possibility of one-dimensional transport in glassy carbon and is consistent with its structure.

Glassy carbon is primarily an elemental carbon material with perhaps trace amounts of hydrogen as an impurity. The microstructure is essentially the skeleton of its polymer precursors. Figure 3(a) shows direct 002 lattice images of glassy carbon heated at 2700°C. It

can be seen that ribbons or laths are imaged. However, Fig. 3(b) shows that imaging is less sharp in material heated at 2250°C and in Fig. 3(c) it is seen that hardly any lattice fringes can be obtained from material heated at 1800°C. By comparison with Fig. 2, it is inferred that there is a direct correlation between the presence of the one dimensional component of the conductivity and the inability to obtain lattice images. Small angle scattering results show that the micropores (10-20 Å) in low heat treatment temperature material have diffuse boundaries and that the Porod law is not obeyed.[17,18] However, for the high heat treatment temperatures the diffuse boundary scattering is absent and the Porod law is obeyed. Other changes in the microstructure occur at about 2200°C, the temperature where one-dimensional electrical conductivity ceases to be observed. In wide range x-ray diffraction, the d-spacing associated with the 002 graphitic planes in turbostratic carbons begins to decrease,[19,20] and the small (≈1 percent) weight loss during heat treatment becomes constant for higher heat treatment temperatures.[21] The nature of this transition, whether it is due to simply coarsening of the interlocking filaments, or if a phase transformation is taking place, has not been fully established.

In summary, the microstructure of glassy carbon heat treated below about 2200°C is best described as tightly interwound laths consisting of 5-10 layers of graphite-like ribbons of a width less than about 50Å which do not possess sufficient registry to resolve lattice images. This scale is minute enough to admit the possibility of a

one-dimensional electrical conductivity correction to the metallic conductivity having the observed $-T^{-1/2}$ dependence.

ACKNOWLEDGEMENTS

We gratefully acknowledge Dr. Ron Gronsky for his lattice imaging work and Dr. A. S. Rao for preparation of the microscope specimens.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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FIGURE CAPTIONS

Fig. 1. Electrical conductivity of glassy carbon heat treated at a) 2550 and b) 1200°C. The solid lines are calculated fitted lines from the empirical equation $\sigma = A + B\exp(-CT^{-1/4}) - DT^{-1/2}$.

Fig. 2. One-dimensional electrical conductivity component parameter D of glassy carbon as a function of heat treatment temperature.

Fig. 3. Transmission electron microscope 002 lattice images under identical conditions of glassy carbon heated at a) 2700, b) 2250, and c) 1800°C. The fringes imaged have a 3.4 Å spacing. The microscope work is courtesy of Dr. Ron Gronsky.

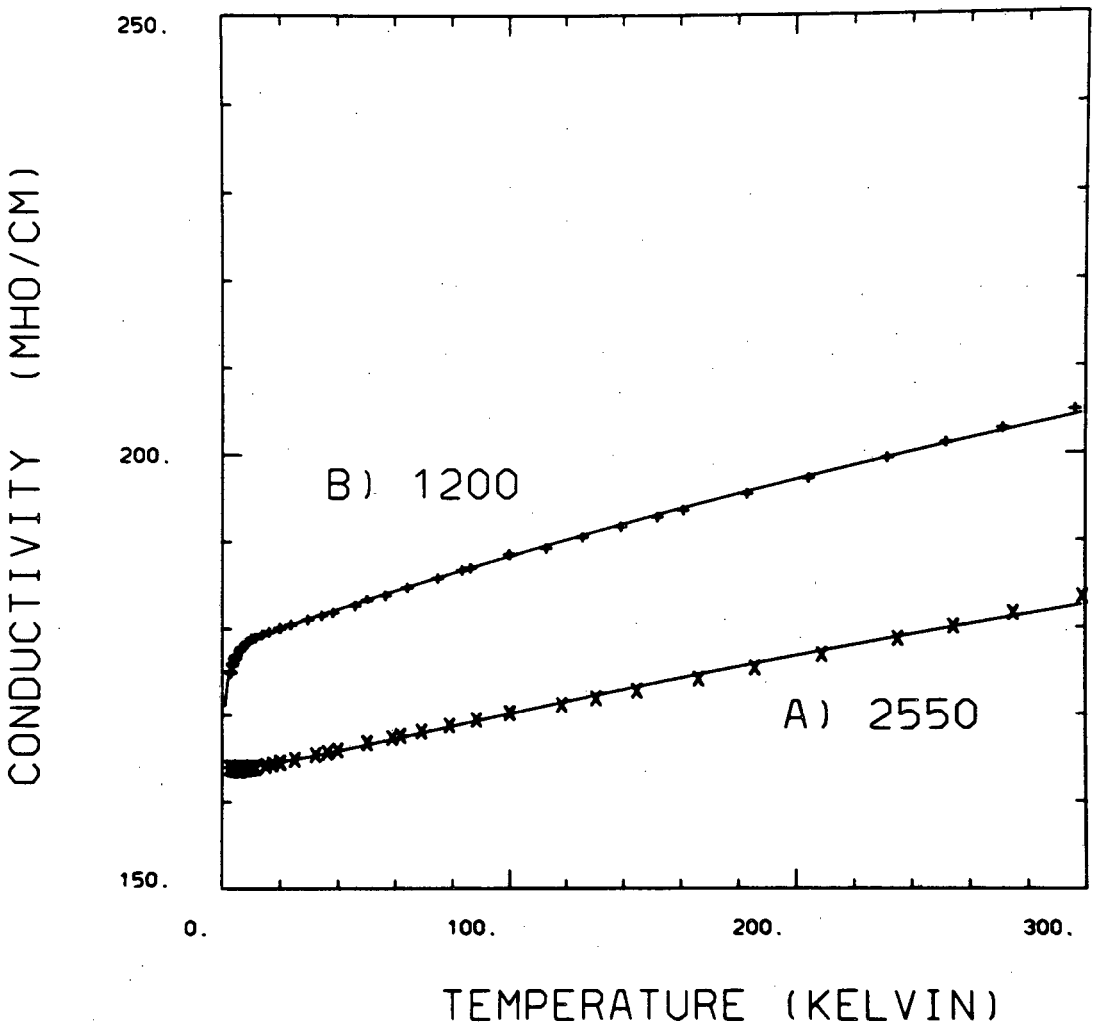

Fig. 1

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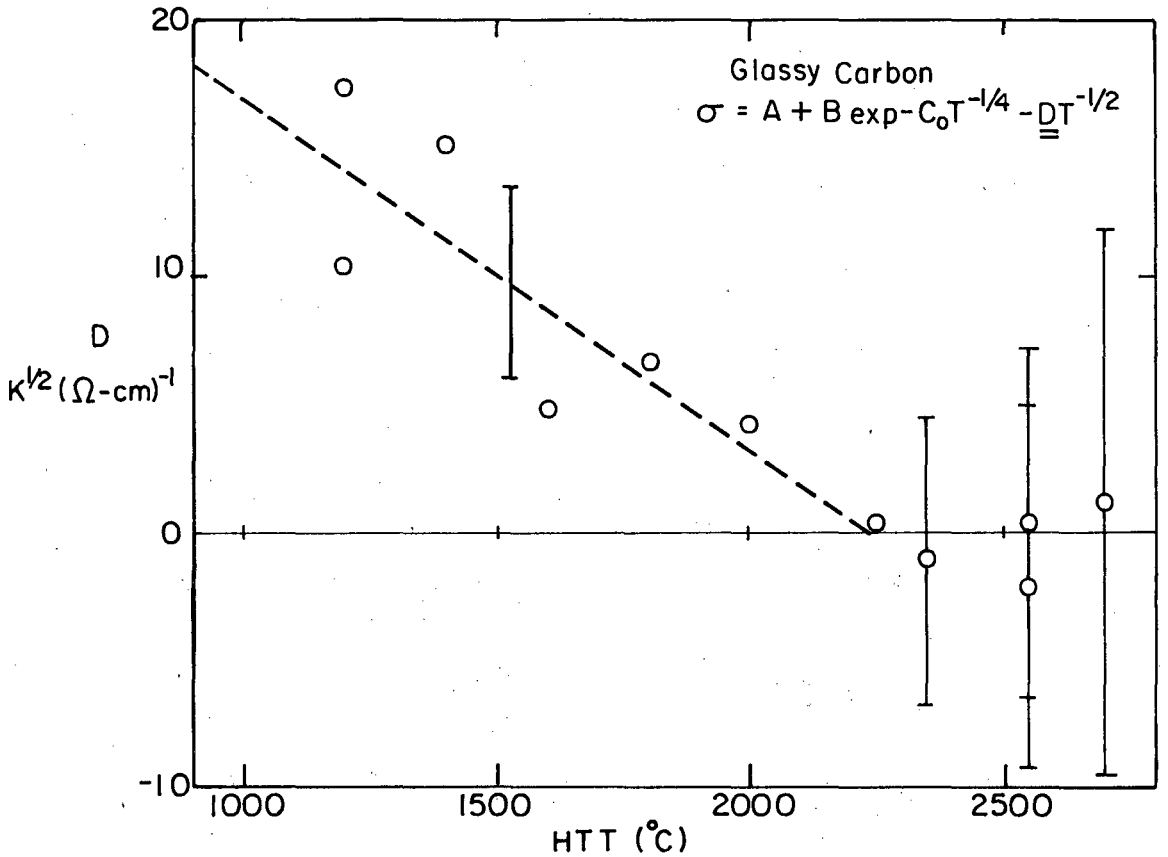

Fig. 2

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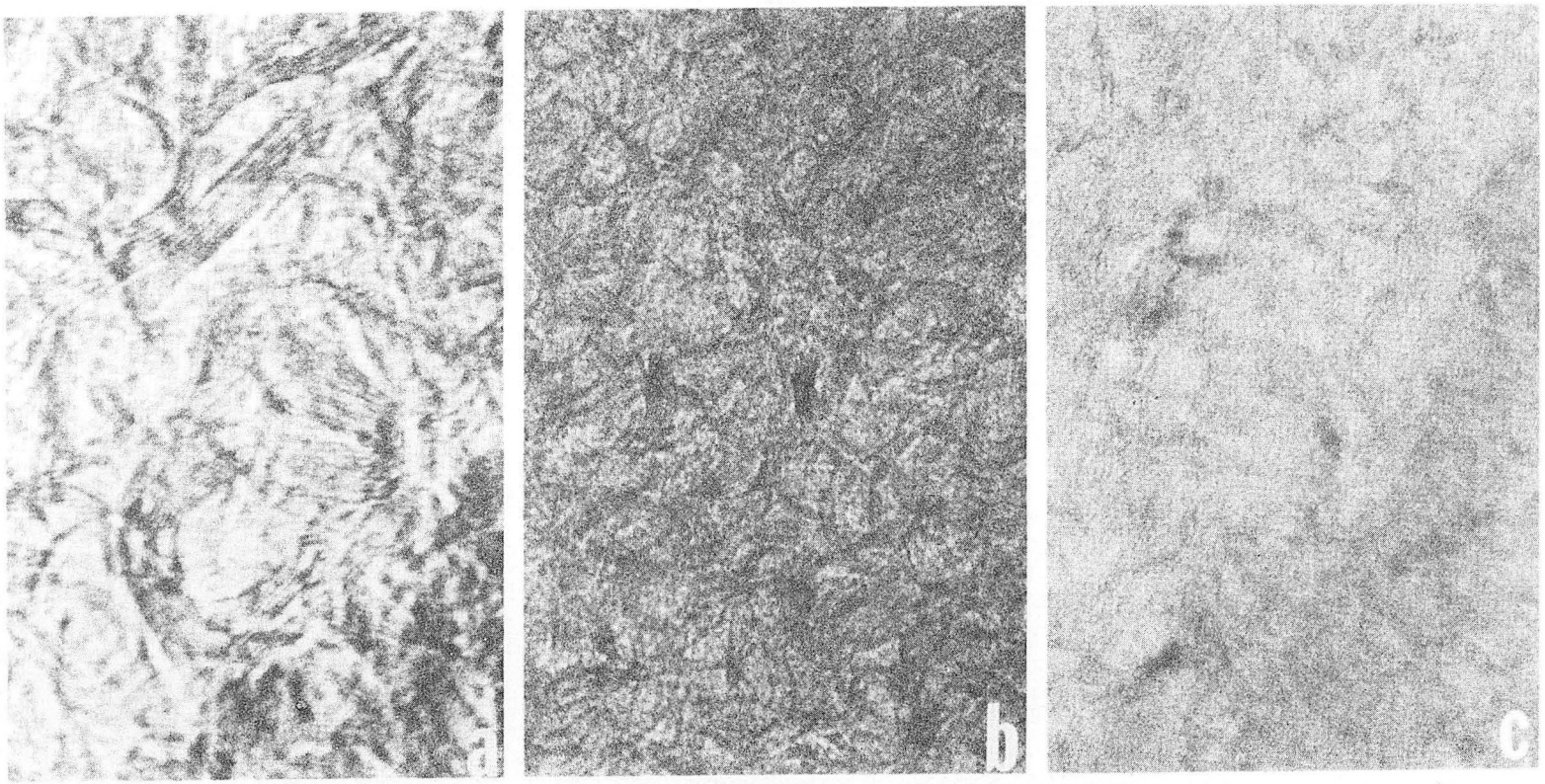

Fig. 3

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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