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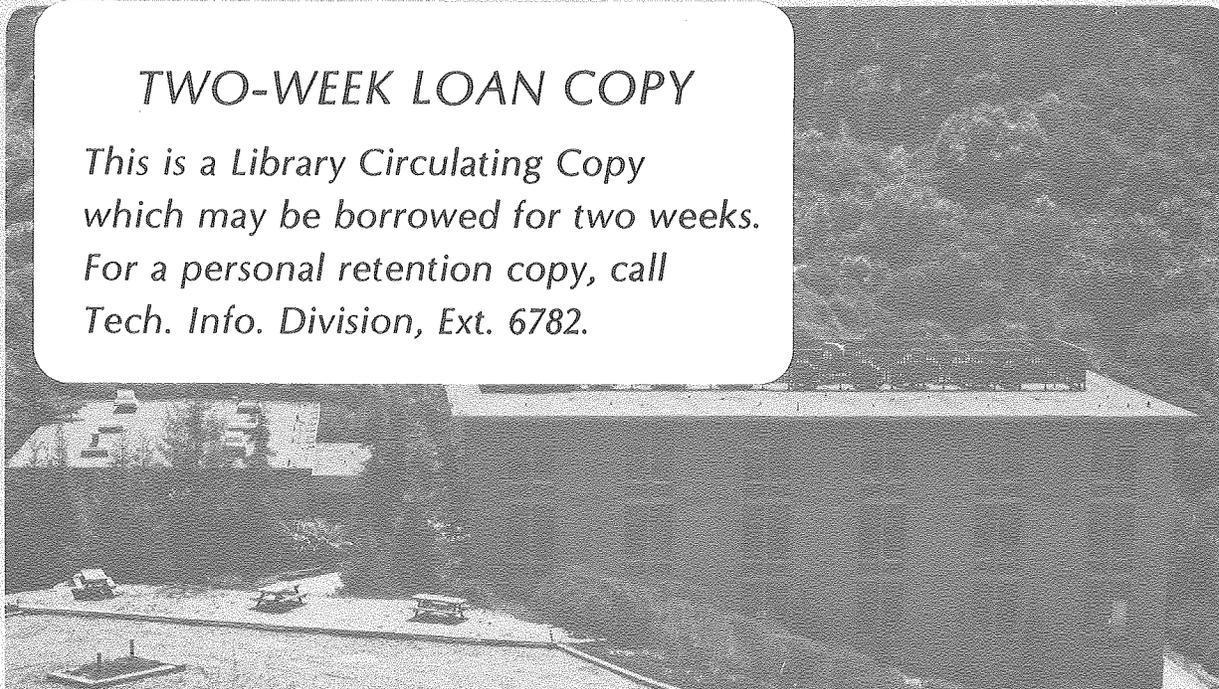
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EFFECT OF GRINDING ON THE STRUCTURE
OF GLASSY CARBON

by

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ABSTRACT

An earlier suggestion that various allotropic forms of carbon pre-exist as micron size crystallites in glassy carbon was investigated. Samples previously heated only to 1000°C and thinned by crushing (grinding) or by ion melting and observed using transmission electron diffraction and microscopy gave single crystal or spotty ring patterns for the former but only diffuse rings for the latter. Wide range X-ray diffraction, small angle X-ray scattering, density and surface area measurements of as received plate and ground material show that grinding flattens the internal pore structure of the material, decreasing the specific surface area by 25 percent and increasing the radius of gyration by about 8 percent. It is concluded that the spot patterns indicating crystalline forms result from strain relief during grinding.

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I. INTRODUCTION

Whittaker and Tooper have reported that many crystalline forms of carbon are observed in electron microscope investigations of glassy carbon, GC.^{1,2} These authors made observations on samples of GC obtained from two sources* covering heat treatments at 1800°C, 2000°C and 3000°C. Although diffuse rings associated with GC diffraction patterns were observed with the greatest frequency, about 10 percent of the regions they examined gave sharp, often spotty electron diffraction patterns, and sometimes superimposed patterns of more than one crystallite. The fragments that gave single crystal patterns were generally in the size range 0.1 to several μm , and they were able to index several patterns proving the presence of chaoite, carbon VI, lonsdalite and diamond in addition to graphite. Whittaker and Tooper proposed a model of GC in which the material consists of carbon in all its possible crystalline forms connected by a 3-dimensional random network of a variety of C-C bonds, probably mostly graphite-like, which comprises the greater part of the bulk of glassy carbon. They argued that the presence of these crystalline forms would cause broadening of the X-ray "graphite" lines, in addition to the crystallite size effect, because they have many reflections that lie near the graphite reflections. Therefore, the estimates of crystallite sizes less than 100 \AA obtained from X-ray diffraction line broadening would be too low since crystalline regions as large as 2 μm were observed.

* Beckwith Carbon Corp. Van Nuys, CA. (heated to 1800°C) and Lockheed Missiles and Space Company, Sunnyvale, CA. (heated to 2000°C for 2 h or 3000°C for 8 h, during processing).

Observations similar to those of Whittaker and Tooper have been reported by Hücke³ and Saxena.⁴ In fact Saxena obtained spot patterns in GC heated only to 1000°C. However, Saxena used two different methods of specimen preparation. When specimens were prepared for electron microscopy by crushing the sample prior to mounting on standard 200 mesh grids as was done by Whittaker and Tooper, spot or spotty ring patterns such as in Fig. 1(a) could often be observed to come from regions shown in Fig. 1(b). However, when specimens were prepared by ion milling only diffuse rings were observed [Fig. 1(c)], and no regions resembling isolated crystallites were found [Fig. 1(d)]. Saxena suggested that the spot patterns are therefore an artifact of the specimen preparation. The structure of GC is probably closer to the skin-like model of Ban and Hess⁵ than the over-simplified interwound lath-like model of Jenkins, et al.⁶ Thus the process of crushing GC material simply flattens previously highly deformed and strained skin-like regions in the first case but leaves them undisturbed during ion milling. Saxena also called attention to work which showed that when the GC precursor is loaded with a few percent of micron sized graphite in the early stages of processing the material graphitizes completely upon subsequent heating to 2600°C.⁷ Thus if micron sized crystallites do exist in bulk GC heated only to 1000°C, then after heat treating at 2800°C a complete conversion to graphite should have occurred, which was not observed.

Saxena did not obtain lattice image photographs of his GC as was done later by Bose, et al.,⁸ but even without this direct evidence his argument is believed to be correct. One additional argument against the preexistence of micron sized crystals in bulk GC is that none have

been observed in either optical micrographs or SEM micrographs. The failure to observe sharp X-ray diffraction lines is consistent with a small volume fraction of crystalline phases. However, if the skin flattening hypothesis is correct, then if GC is ground sufficiently one should observe a decrease of line widths, even in conventional wide range X-ray line profiles. In addition, the crushing, shearing action of grinding should also alter the pore-structure and density of GC. In this work the structure of ground GC is compared with that of as-received GC plate heated to 1000°C.

II. EXPERIMENTAL

Samples cut from GC plates* were heat treated at 1000°C for one hour in an Astro furnace in argon atmosphere. Some material was ground dry and some ground using 1, 1, 1-trichloroethane as a grinding aid in a vibratory ball mill.** Subsequently X-ray absorption and fluorescence measurements showed that about one weight percent of iron was picked up from the steel balls during the grinding, but the amount of iron in the as-received plate was negligible. Densities were obtained using water and kerosene in a pycnometer, and also by gas displacement using helium. Samples were prepared for X-ray measurements by (1) grinding the as-received plate material to transmit 36 percent of the incident $\text{CuK}\alpha$ X-ray beam (the optimum thickness $t = \frac{1}{\mu}$) and (2) placing the powder samples of optimum thickness in a holder with transparent backing so that the same sample could be used in transmission or reflection

* Polycarbon, Inc., North Hollywood, CA.

** Courtesy of Dr. D. L. Kantro, Portland Cement Association Research Laboratory, Skokie, IL.

measurements. A GE XRD-5 diffractometer was used for wide range diffraction measurements, and also adapted for small angle scattering SAXS measurements with a modified slit system.⁹ Surface areas were obtained using both SAXS data as described in Ref. 9, and by single point B.E.T. nitrogen gas adsorption measurements. An AMR scanning electron microscope was used to estimate particle sizes of the ground materials. The radius of gyration, R_g , was obtained from Guinier plots (\ln Intensity vs h^2 , $h = 4\pi\sin\theta/\lambda$) of the SAXS data near $h = 0$.

III. RESULTS

X-ray diffraction. As shown in Fig. 2 the wide range X-ray diffraction patterns of the materials ground dry or wet were essentially identical. They were also closely similar to the pattern of the GC plate, so that it would be difficult without detailed analyses to find any evidence in the wide range diffraction patterns for grinding induced structural changes. It is possible that grinding in the vibratory ball mill was so severe that the expected flattened had occurred, and a subsequent size reduction had also occurred before grinding was discontinued. However, the effect of grinding for different times was not studied. More convincing evidence for structural change was found in the SAXS measurements. As shown in Fig. 3, the SAXS patterns of the ground material are also identical, but in this case clearly different from that of the plate. The onset of the limiting -4.0 slope in the Porod plots (\ln intensity vs $\ln h$ plot) occurs at a smaller angle in the ground material indicating a decrease in surface area. Guinier plots

of the data are shown (Fig. 4) where it is seen that the radius of gyration has been increased about 8 percent by the grinding.

Results of the other measurements given in Table 1 also indicate that grinding has produced structural changes. The specific surface area S/V derived from SAXS has decreased by about 25 percent, and although the densities in water and kerosene are unaffected, the helium density approaches that of pyrolytic graphite. The porosity changes as stated are deceptive: The values for ground material represent the internal pores as well as interstices between loosely packed ground particles.

IV. DISCUSSION

From the lattice image micrographs it is clear that no simple model of the structure of GC can be drawn, but that of Ban and Hess is convenient. It is known that the pores in GC have sharp edges,⁹ and are therefore slit-like. If we grossly simplify the model to that of oblate ellipsoids of revolution of semi-minor axis b and semi-major axis a connected by small diameter pores, then the effect of grinding is to decrease the axial ratio b/a of the ellipsoids. Small angle X-ray scattering theory¹⁰ defines the radius of gyration of a particle as

$$R_g^2 = \frac{\int_V \bar{r}^2 \rho(\bar{r}) dV}{\int_V \rho(\bar{r}) dV}$$

where r is radius from the origin defined as $\int \bar{r} \rho(\bar{r}) dV = 0$, $\rho(\bar{r}) =$ electron density at \bar{r} , and V is the volume of the particle. If the "particles" are pores which have negligible interaction this definition is still applicable for a porous body. Obviously, if the "pores" are

oblate ellipsoids then decreasing b/a adds more weight to the larger values of \bar{r} above and hence increases R_g . Similarly S is decreased while V is unchanged (the density in water and kerosene was unchanged). Thus S/V is decreased.

Some indication of the size of the pores can be obtained from the fact that whereas the water and kerosene densities are not changed by the grinding, it has opened small pores enough to admit helium. Thus one can conclude that the pores in as-received plate material are narrower than $2.5\text{-}3.0 \text{ \AA}$,¹¹ the diameter of a helium atom, and while they are opened enough to admit helium when ground, are still too narrow to admit N_2 molecules, $\sim 6 \text{ \AA}$,¹² or water, $4\text{-}6 \text{ \AA}$,¹³ or kerosene.

It is unfortunate that direct electron microscope observations of the ground material are difficult to perform, and hence a direct test of the skin-flattening hypothesis is not demonstrated in this work. Lattice image micrographs have been obtained in this laboratory for a series of samples heated in the range 1000° to 2700°C .¹⁴ However, despite numerous attempts it has proved to be impossible to obtain lattice fringes for material heated to temperatures less than 2100°C . These samples were all thinned by ion milling. Since fringes are readily observable if the crystallite size is of the order of one micron, it is clear that none are initially present in material heated only to 1000°C , or if so are present in a highly strained condition. On the other hand it is clearly established that when materials heated only to 1000°C are prepared by crushing spotty patterns are observed. The evidence presented herein strongly favors the explanation originally

proposed by Saxena: The spotty patterns are the result of stress relief during specimen preparation.

ACKNOWLEDGMENT

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FIGURE CAPTIONS

Figure 1. (a) Selected area electron diffraction pattern corresponding to the area (b) in the sample thinned by grinding/crushing, (c) selected area electron diffraction pattern corresponding to the area (d) in the specimen thinned by ion milling.

Figure 2. Wide angle X-ray diffraction line profiles.

Figure 3. Porod plots of small angle X-ray scattering data.

Figure 4. Guinier plots of small angle X-ray scattering data.

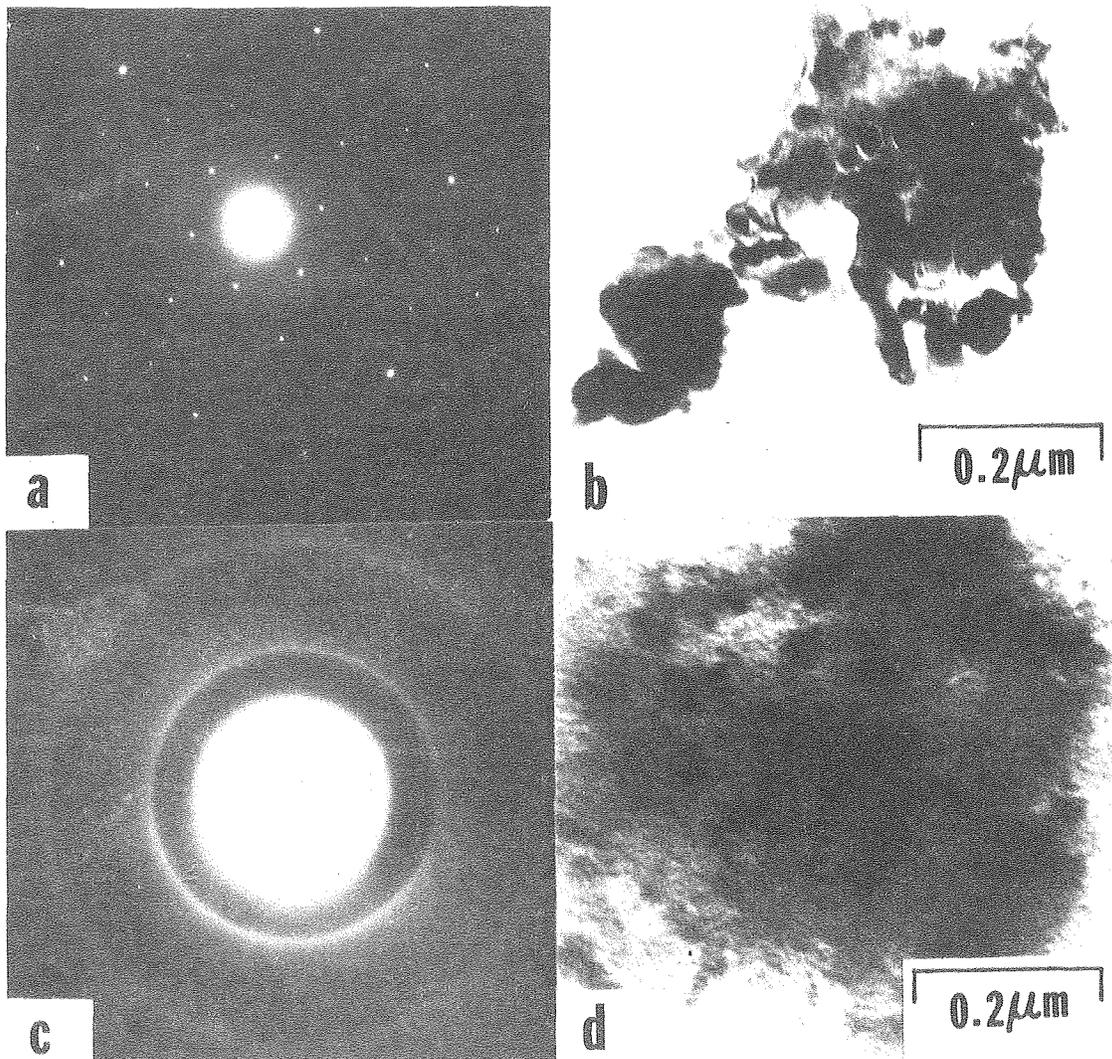
Table 1

	<u>GC Plate</u>	<u>GC Ground</u>
S/V (m^2/cm^3) from SAXS	1325	991
S/V (m^2/cm^3) from N_2 Absorption	<10	<10
Radius of gyration R_g (\AA)	7.9	8.6
DENSITY (Helium) (g/cm^3)	1.50	1.96
DENSITY (Water) (g/cm^3)	1.50	1.50
DENSITY (kerosene) (g/cm^3)	1.50	1.50
Particle Size (μm)	-	0.3-12.0
c, Pore Volume Fraction	0.321	0.744

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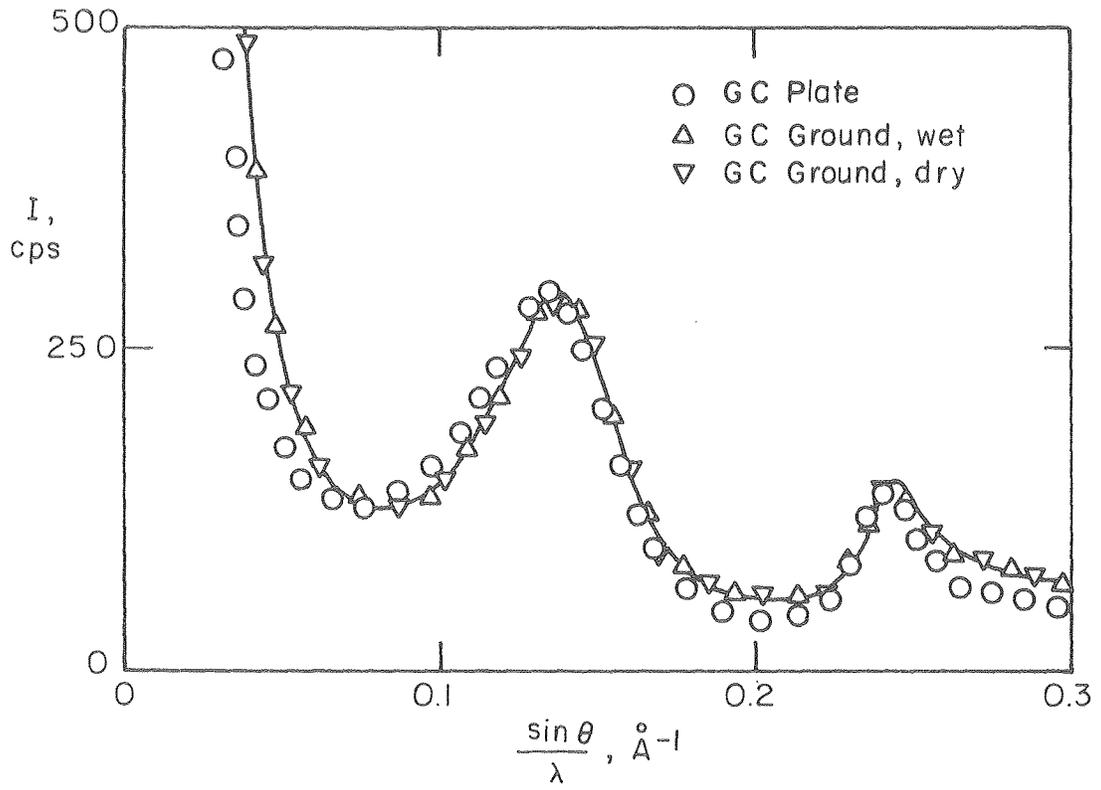
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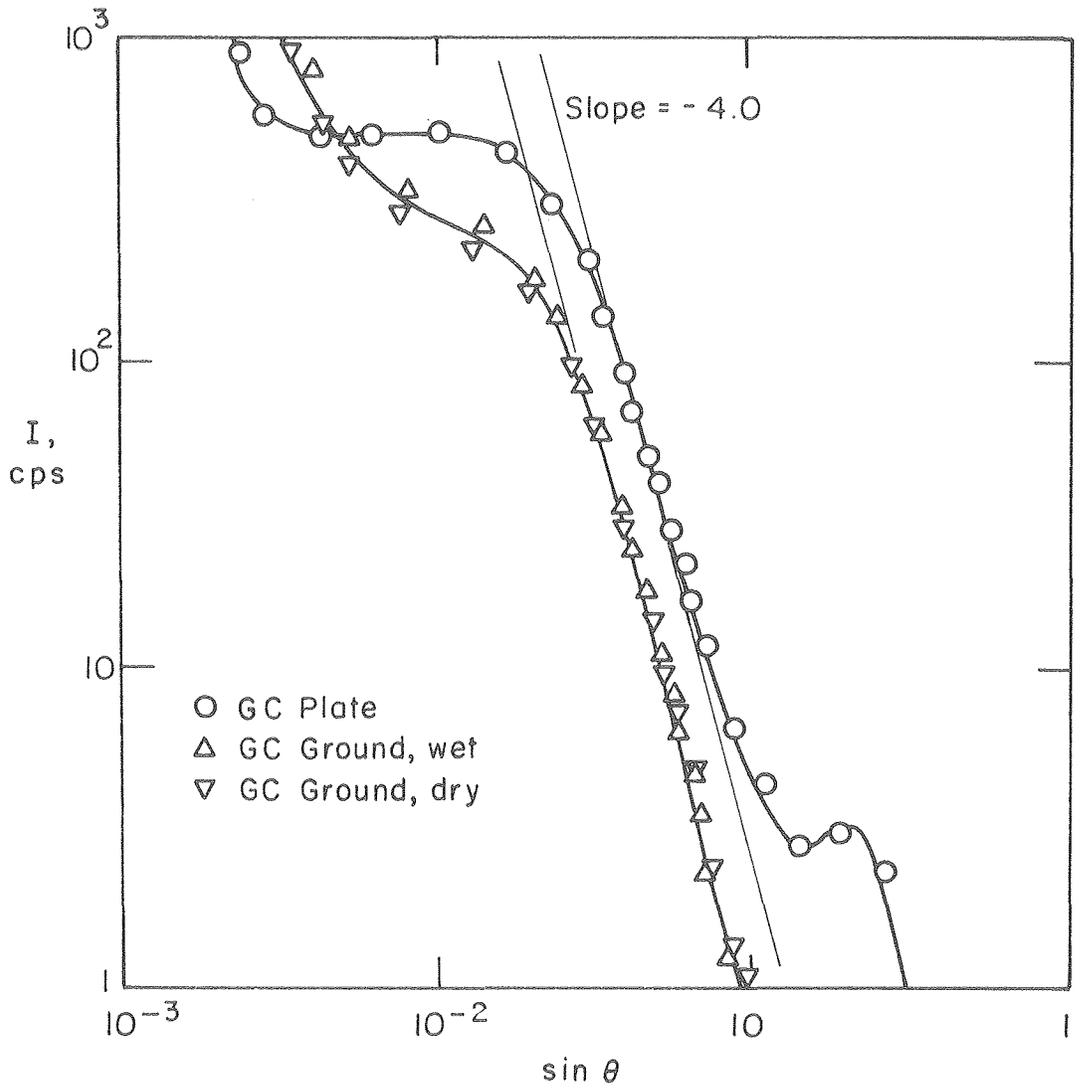
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Fig. 1



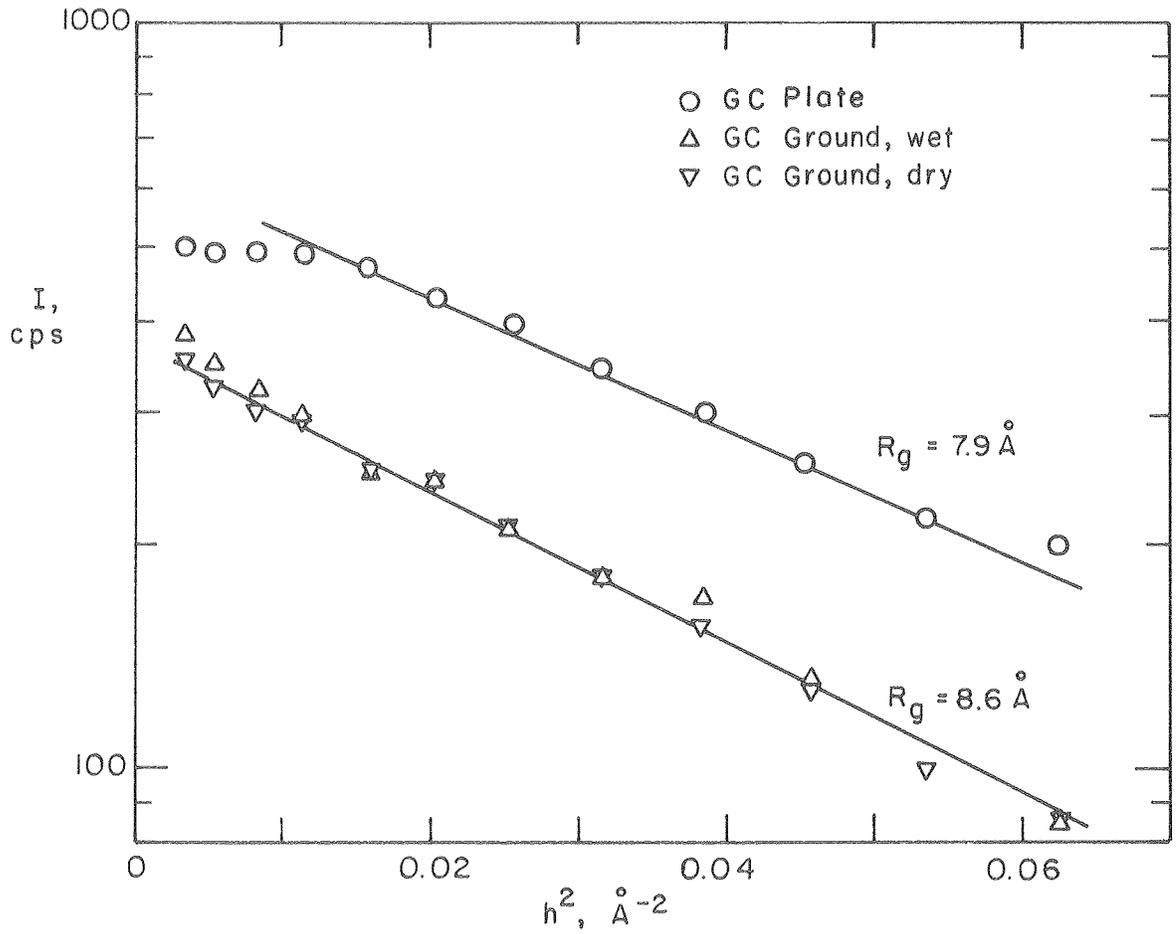
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Fig. 2



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Fig. 3



XBL803-4802

Fig. 4

