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EFFECTS OF NEUTRON DAMAGE ON THE MECHANICAL
PROPERTIES OF PYROLYTIC AND SINGLE-CRYSTAL GRAPHITE

MASTER

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SEMIANNUAL PROGRESS REPORT
JULY 1, 1965 TO DECEMBER 31, 1965

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

UNION CARBIDE CORPORATION
CARBON PRODUCTS DIVISION
PARMA TECHNICAL CENTER

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Principal Investigator
J. T. Meers

UNION CARBIDE CORPORATION
CARBON PRODUCTS DIVISION, TECHNICAL CENTER

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Parma, Ohio
44130

February 25, 1966

FOREWORD

This report summarizes the progress of an investigation of neutron damage on the mechanical properties of both graphite single crystals and pyrolytic graphite which has been compression-annealed. The work is jointly supported by the United States Atomic Energy Commission under Contract No. AT-(40-1)-3237 and Union Carbide Corporation, Carbon Products Division. The contract is administered by Dr. D. F. Cope, Director, Reactor Division, Oak Ridge Operations. The report covers the period July 1, 1965 to December 31, 1965.

The Project is under the general supervision of J. T. Meers. The graphite single crystal work has been carried out by D. E. Soule and C. W. Nezbeda. The pyrolytic graphite work has been carried out by O. L. Blakslee, N. F. Graves, D. G. Proctor, E. J. Seldin, G. B. Spence, and T. Weng. This report was prepared by J. T. Meers with the assistance of the participants in the program.

ABSTRACT

The problem of measuring the stress-strain curve for graphite single crystals subjected to basal plane shear has been investigated, and the behavior of single crystals under basal plane shear is described and compared with that of the compression-annealed pyrolytic graphite. Work has continued on the production and evaluation of compression-annealed pyrolytic graphite. A careful analysis has been made of the optical reflectivity method of measuring the c-axis misorientation of the pyrolytic graphite. Calculations have been made to determine the feasibility of measuring c_{13} on compression-annealed pyrolytic graphite; with present measuring techniques, a reliable value of c_{13} probably cannot be obtained directly from experiment.

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1. INTRODUCTION

The general objective of the program is to determine the effects of neutron irradiation upon the mechanical properties of graphite single crystals and of highly ordered pyrolytic graphite. The specific objective for the work during the first year was the production and pre-irradiation evaluation of these materials. This work has been completed and is described in the first annual summary report.⁽¹⁾

Work during this semiannual period has been directed toward the production and evaluation of irradiation test material and the exploration of the stress-strain relationship for in-plane shear of graphite single crystals.

2. SUMMARY

The optical reflectivity apparatus, which is used to measure the surface flatness of compression-annealed pyrolytic graphite, was subjected to a careful analysis in order to correct the measurements for the inherent broadening of the apparatus. The measured half-width at half-maximum, $\phi_{\frac{1}{2}}$, is related to the half-width which is a function of the graphite surface, $\theta_{\frac{1}{2}}$, and to the inherent half-width of the apparatus, $\psi_{\frac{1}{2}}$, by the expression:

$$\theta_{\frac{1}{2}} = \frac{1}{2} \sqrt{\phi_{\frac{1}{2}}^2 - \psi_{\frac{1}{2}}^2}.$$

This expression was used to correct the observed half-width of disk M304, the most highly oriented sample of compression-annealed pyrolytic graphite which has been produced thus far.

The apparatus used for measuring the shear strength, σ_4 of single crystal graphite, was modified to measure the shear modulus of very thin specimens. The reliability of the apparatus was proved by measuring specimens of compression-annealed pyrolytic graphite, the shear moduli of which had been measured previously by sonic means. The agreement between the sonic measurements and the static measurements was excellent.

The stress-strain relationships as measured in shear for single crystal graphite and for compression-annealed pyrolytic graphite are very different. The single crystal behavior is similar to the behavior of the hexagonal close-packed metals, zinc and cadmium. The single crystal displays the characteristic curve of the single glissile slip system contained in the a-b planes with little interaction between dislocation systems. This long glissile slide occurs at very low critical shear stress. The pyrolytic graphite has the somewhat brittle behavior of a more complex multiple slip mechanism with interacting slip systems. Strain hardening, caused by cyclic stressing at increasingly higher stresses, was observed for single crystals. Hardening occurred to a lesser extent for M304 pyrolytic graphite, but it was not observed for the less perfect M-311 pyrolytic graphite even after 10 cycles.

Static tensile tests were run on three disks of compression-annealed pyrolytic graphite. The modulus of each of these disks was relatively low, indicating that the quality of the material was not adequate for the irradiation program.

A new torsion apparatus has been constructed; it is similar in principle to the apparatus used in previous work, but it has been automated to make data collection more convenient.

Calculations to determine the feasibility of measuring the stiffness constant, c_{13} , for compression-annealed pyrolytic graphite by ultrasonic techniques show that there is little hope of determining it accurately from a measurement of the velocity of a quasi-transverse ultrasonic wave. Although the possibility exists of introducing the waves at the desired angle into the c-face of a specimen by a refraction technique, it is concluded that the effort required to develop this method can be more profitably expended in measuring the other four stiffness constants.

3. MATERIALS PREPARATION

All of the pyrolytic graphite materials used in the program have been compression-annealed at the Carbon Products Division, Advanced Materials Laboratory, Lawrenceburg, Tennessee. Prior to the deactivation of the Advanced Materials Laboratory in June 1965, ten annealed plates of pyrolytic graphite were prepared for the irradiation tests. These annealed plates were evaluated and were found to be of too poor quality for the irradiation test program.

A new furnace and the tooling required for compression annealing have been fabricated for use at the Parma Technical Center. Compression-annealing of as-deposited pyrolytic plates will be initiated in January 1966. The materials which will be prepared are intended for use in the irradiation test program.

4. MATERIAL CHARACTERIZATION

4.1. Criterion of Acceptable Quality

The modulus $1/s_{11}$, as determined from the static tensile test, has been found to vary over a considerable range. The better aligned compression-annealed pyrolytic graphites, which had average c-axis misorientations of only a few tenths of a degree, yielded linear stress-strain curves with moduli $1/s_{11}$ equal to or greater than 85×10^{11} dynes/cm² (123×10^6 lb/in²). This value of $1/s_{11}$ has been arbitrarily selected as an acceptable lower limit; only material having $1/s_{11}$ equal to or greater than 85×10^{11} dynes/cm² will be acceptable for use in the irradiation program.

4.2. Optical Reflectivity

E. J. Seldin

A need to improve the resolution of the optical reflectivity apparatus arose when some very flat compression-annealed pyrolytic graphite (M304) was produced, the half-width at half maximum of which, as measured with the apparatus, was comparable with that measured for a plane mirror. As a result, the apparatus was carefully aligned, and the experiment itself was analyzed. The resolution was greatly improved by careful adjustment of the

apparatus and by the introduction of a small aperture directly in front of the detector. In the analysis of the experiment, a formula was derived which relates the measured half-width at half maximum to a half-width which is a function of the surface and to an inherent half-width of the apparatus.

Apparatus

Figure 1 shows the optical reflectivity apparatus. An incandescent light bulb source illuminates the slit of a collimator, and the beam of light from the collimator is directed at an arbitrary fixed angle of incidence on the surface of the specimen, from which it is reflected into a telescope. At the focal point of the objective lens of the telescope is a silicon diode detector the electrical resistance of which decreases as the intensity of the light which falls on it increases. The telescope scans the reflected light beam at a constant rate of rotation while the intensity of the light beam, as detected by a simple circuit containing the diode, is recorded on a strip chart recorder. The half-width at half maximum of the recorder tracing of intensity vs. the angle of rotation is then taken as an index of the flatness of the reflecting surface.

Figure 1
Optical Reflectivity Apparatus

N-7353

The optical reflectivity apparatus is basically a spectrometer. The resolution of the apparatus was maximized by replacing the silicon diode with an eyepiece lens with cross-hairs. The standard adjustment techniques for aligning a spectrometer were employed to focus the collimator, and the central axis of the collimator was adjusted so that it was in the plane swept out by the central axis of the telescope during rotation. The silicon diode was then inserted in the end of the telescope, and the direct beam from the collimator was scanned. The position of the silicon diode and the width of the collimator slit were adjusted to give the narrowest output response curve on the recorder. A collimator slit width of 0.1 mm was close to the optimum size; a further reduction in slit width did not reduce the base width of the output response curve but led instead to a triple peak in the curve which is believed to be a diffraction effect. The half-width at half maximum intensity which was obtained after this procedure was 0.05 degree, a value which was a little lower than the lowest half-width previously obtained with the apparatus. The reflected beam from an optical flat was then scanned, and the same half-width was obtained.

A further improvement was made in the resolution of the apparatus by introducing a small aperture directly in front of the silicon diode detector. The diode has an effective light collecting area with a diameter of 1 mm. Since the image of the collimator slit is, in the case of reflection from an optical flat, approximately equal to the slit width, i.e., 0.1 mm, most of the width of the output response curve was due to the effect of scanning a narrow beam with a wide detector. Circular apertures with several different diameters were tried, and an aperture of 0.2 mm diameter was finally chosen: the half-width at half maximum was reduced to 0.015 degrees. This half-width is believed to be sufficiently small for the characterization of the surfaces of compression-annealed pyrolytic graphite. Further improvement in the resolution can be made by using a smaller aperture, but the intensity of the output signal is also reduced as the size of the aperture decreases. The aperture size which was chosen represents a compromise in that it allows an acceptably small instrument half-width and requires no major modifications in the light detection system.

Analysis of the Output Response

It is the purpose of the analysis to give a correction for instrument broadening and to indicate at what point further improvement in the resolution of the apparatus may be desirable. The experiment is illustrated schematically in Figure 2. The incident light beam is directed toward the reflecting surface at a fixed angle of incidence α and is reflected toward the telescope, which rotates and scans the reflected beam. The recorder plots the output response function $T(\phi)$, which represents the intensity of the light as a function of the angle of rotation ϕ . We shall assume $\phi = 0$ corresponds with the central maximum of $T(\phi)$.

Figure 2

Schematic of Optical Reflectivity Test

N-8686

We assume in this analysis that the inherent broadening of the apparatus is due to the fact that all of the rays in the incident beam of light are not parallel, and we assume that the angular distribution of the intensity of the incident beam is given by some function $S(\psi)$. In the absence of a reflecting surface, the telescope scanning the incident beam would then observe the function $T(\phi) = S(\phi)$; in fact, $S(\psi)$ is obtained in just this manner. We shall assume that $\psi = 0$ at the maximum of $S(\psi)$.

The degree of flatness of the reflecting surface can be described by the function $I(\theta)$, the distribution of surface normals per unit area, where θ is the angle of deviation from the axis of rotational symmetry of the specimen. We assume that $I(\theta)$ is a symmetrical function with its central maximum at $\theta = 0$ and that it is the same for all planes passing through the axis of rotational symmetry of the specimen. For the case where the reflecting surface is an optical flat, $I(\theta)$ is a delta function, being equal to unity at $\theta = 0$ and equal to zero for all other θ .

The output function $T(\phi)$ can be related to the incident beam function $S(\psi)$ and the specimen surface distribution function $I(\theta)$ by the following reasoning. Consider, in Figure 2, a ray of light incident at some arbitrary angle $\alpha + \psi$. With the telescope set to observe only those rays incident at some angle $\alpha + \phi$, the ray incident at angle $\alpha + \psi$ will be observed only if the surface normal is at an angle θ such that $\theta = (\psi - \phi)/2$.

[Proof: The total angle between the incident and reflected ray is $2\alpha + \psi + \phi$. Half of this angle is $\alpha + (\psi + \phi)/2$. From Figure 2 and the definition of θ , we obtain

$$\theta = (\alpha + \psi) - [\alpha + (\psi + \phi)/2] = (\psi - \phi)/2.$$

Note that θ is independent of the angle of incidence α . Note also that if the positive direction of either ψ or ϕ in Figure 2 is reversed, the sign of θ is changed but the magnitude remains constant; thus, the results of this analysis are not changed.]

The intensity of the light reflected at ϕ is obtained by using the product of the intensity of the incident beam $S(\psi)$ and the surface distribution function $I(\theta)$ evaluated at $\theta = (\psi - \phi)/2$ and summing over all values of ψ . This step

yields

$$T(\phi) = \sum_{\text{all } \psi} S(\psi) I\left(\frac{\psi - \phi}{2}\right), \quad (1a)$$

which also can be expressed in integral form as

$$T(\phi) = \int_{-\infty}^{\infty} S(\psi) I\left(\frac{\psi - \phi}{2}\right) d\psi. \quad (1b)$$

Two special cases are of interest:

(1) For an optical flat, $I(\theta)$, is a delta function, i. e., $I(0) = 1$ and $I(\theta) = 0$ for $\theta \neq 0$. The above equations then yield $T(\phi) = S(\phi)$, the condition which is actually observed.

(2) For a perfectly collimated incident beam of light, $S(0) = 1$ and $S(\psi) = 0$ for $\psi \neq 0$. The above equations then yield $T(\phi) = I(-\phi/2) = I(\phi/2)$. In other words, when there is no instrument broadening, the observed response $T(\phi)$ gives $I(\theta)$ directly, except that now $\theta = \phi/2$.

In the integral equation (1b), $I(\theta)$ can be considered in a mathematical sense to be an operator function which operates on the function $S(\psi)$ to produce the function $T(\phi)$. The equation then gives us a means of obtaining $I(\theta)$ from the observed $T(\phi)$ and $S(\psi)$. In practice, one can tabulate the observed input function $S(\psi)$ and the measured function $T(\phi)$ and use a standard computer program for a set of linear equations to calculate and plot the function $I(\theta)$.

Since we are not particularly interested in obtaining the exact function $I(\theta)$ but rather, are interested in using the half-width at half maximum intensity as an index of the surface, we may use a simpler method of analyzing the data. One may assume that the input and response functions are both Gaussian; computations based on the assumption offer a fairly good approximation to the actual shapes of the input and response curves and allow us to solve the integral equation (1b) analytically for $I(\theta)$. The solution is easy to obtain because $I(\theta)$ must also be Gaussian.

Let us assume that $S(\psi) = e^{-a^2\psi^2}$ and $I(\theta) = e^{-b^2\theta^2}$. The appropriate half-widths for these functions are:

$$\psi_{\frac{1}{2}} = \frac{0.834}{a} \quad \text{and} \quad \theta_{\frac{1}{2}} = \frac{0.834}{b} \quad (2)$$

From the integral equation (1b), we obtain

$$T(\phi) = \int_{-\infty}^{\infty} e^{-a^2\psi^2} e^{-b^2\left(\frac{\psi - \phi}{2}\right)^2} d\psi \quad (3)$$

which can be written, by removing all terms which do not contain ψ outside of the integral, as

$$T(\phi) = e^{-a^2b^2/(4a^2 + b^2)} \int_{-\infty}^{\infty} e^{-(a^2 + b^2/4)\left[\psi - b^2\phi/(4a^2 + b^2)\right]^2} d\psi. \quad (4)$$

The integral in the above equation is a constant. Therefore, we can write

$$T(\phi) = \text{constant} \cdot e^{-c^2\phi^2}, \quad (5)$$

where

$$c^2 = a^2b^2/(4a^2 + b^2). \quad (6)$$

Since $\phi_{\frac{1}{2}} = \frac{0.834}{c}$, equations (2) and (6) can be combined to yield

$$\theta_{\frac{1}{2}} = \frac{1}{2} \sqrt{\phi_{\frac{1}{2}}^2 - \psi_{\frac{1}{2}}^2}. \quad (7)$$

Equation (7) is a simple expression for obtaining the half-width $\theta_{\frac{1}{2}}$ of the surface distribution function from the observed half-width $\phi_{\frac{1}{2}}$ and the instrument half-width $\psi_{\frac{1}{2}}$.

Results

With the 2 mm aperture in front of the silicon diode, the instrument half-width $\psi_{\frac{1}{2}}$, as measured by scanning the direct beam from the collimator and also by scanning the reflection from an optical flat, was 0.015 degree.

A specimen of compression-annealed pyrolytic graphite from disk M304 was used as the reflecting surface, and a half-width $\phi_{\frac{1}{2}}$ of 0.10 degree was measured from the output response curve on the recorder. [Note that in previous reports this value would correspond to $\theta_{\frac{1}{2}} = 0.05$ degree.] Using the correction formula, Equation (7), we obtain $\theta_{\frac{1}{2}} = 0.049$ degree. This measurement represents the lowest half-width which has thus far been obtained for compression-annealed pyrolytic graphite.

Past data, taken at times when the instrument half-width was not accurately known, still give reliable qualitative characterizations of the materials tested. The analysis presented here indicates that the correction for instrument broadening becomes greater as the half-width $\theta_{\frac{1}{2}}$ of the surface distribution function approaches the instrument half-width $\psi_{\frac{1}{2}}$. The half-width $\phi_{\frac{1}{2}}$ of the output response function, which is the measured half-width, will always be equal to or greater than the instrument half-width. The resolution of the apparatus is now sufficiently high to determine accurately the half-widths for the best materials we have made. If some of the graphite surfaces to be tested in the future are appreciably more nearly flat than the best material made thus far, it may be desirable to reduce the instrument half-width still further.

5. STATIC SHEAR TESTS ON SINGLE CRYSTALS AND COMPRESSION-ANNEALED PYROLYTIC GRAPHITE

5.1. Apparatus Modification

D. E. Soule, C. W. Nezbeda, and D. G. Proctor

The apparatus which was used for measuring the shear strength of single crystal graphite⁽¹⁾ was modified to measure the shear modulus of very thin graphite specimens. Initially, four changes were made:

1. The force couple was shifted directly to the shear heads to reduce the effective compliance and torque on the overall apparatus.
2. The transducer coil was shifted directly to one shear head to reduce error in strain actually measured.
3. Since bowing of the aluminum base plate was detected when the load was applied, the pulleys were shifted to a separate plate below the original.
4. A Daytronic type 6 transducer exciter-demodulator was used in place of the Daytronic 201 AH to improve the sensitivity.

With these modifications, shear modulus measurements were made accurately on compression-annealed pyrolytic samples, but less successfully on single crystals.

For the measurement of the shear modulus of a single crystal, the transverse shear carriage still had too much compliance. Therefore, a new carriage with extremely low compliance was designed, which utilized a 1" diameter, 60-case hardened shaft riding in special adjustable split-ball bushing mounts. For a 10 kilogram load, the displacement of the stationary shear head was calculated to be approximately 2×10^{-5} cm. For the same load, the displacement of the moving or longitudinal shear head was calculated to be 1×10^{-6} cm. These displacements are smaller than those produced in a typical single crystal graphite sample by factors of 200 and 4000, respectively. In one additional modification of the apparatus, a new 3" diameter micrometer head replaced the old one so that the transducer circuit could be calibrated directly in divisions to 0.0001". The revised apparatus is shown in Figure 3.

5.2. Shear Modulus for Pyrolytic and Single Crystal Graphite

D. E. Soule, C. W. Nezbeda

Testing the Shear Apparatus

Two cylindrical samples, designated as F and G, were cut from a block of M-311 (D & E) compression-annealed pyrolytic graphite in a region previously measured nondestructively by sonic methods. Each sample was cycled a number of times by loading and unloading to progressively higher loads. The first sample, F, was cycled seven times by adding and removing a set of weights. Measurements on the second sample, G, were made by using a continuous stream of water as the load in seven tests and weights as the load in four tests. The results are given in Table I. There is excellent agreement between the static and sonic measurements; furthermore, there was no systematic change in shear modulus with the repetitive loading for either sample F or G.

Figure 3

Overall View of Modified Shear Apparatus

N-8307

TABLE I

Comparison of Static and Sonic Measurements of Shear Modulus $1/s_{44}$

Method of Measurement	Sample	$G(1/s_{44})$ (10^{11} dynes/cm ²)	Remarks
<u>Sonic</u>	M-311 D & E	0.0323	
<u>Pure Shear</u> (Static)	M-311 (D & E) F	0.0327 ± 0.0012	Ave. of 7 meas.
	M-311 (D & E) G	0.0323 ± 0.0018	Ave. of 11 meas.

Dependence of Shear Modulus on Thickness

When the accuracy of the shear technique with large pyrolytic samples was established, the task of establishing the validity of measurements made on much thinner samples, notably single crystals, was attempted. One factor, apart from a dependence on thickness itself, was the quantitative effect of light sand blasting of the sample surfaces. A sample H was cut from an area adjoining G (6 mm diameter) in the M-311 (D & E) slab and cleaved to thinner pieces (3 mm diameter) as shown by the "sample location scheme" in Figure 4. These samples were prepared for shear measurements in the same way that the single crystals were prepared. The relative sizes of the thickest 6 mm diameter sample and one of the thin 3 mm diameter samples are shown in Figure 5. Shear measurements were then made for the thickness range from 2.35 mm to 0.103 mm, a thickness below that usually encountered with single crystals. The results are shown in Figure 6, where it will be seen that within the ~10 per cent scatter of the data, the measured modulus is effectively independent of thickness.

The depth of the surface roughness produced by the light sandblasting was also checked under a microscope and found to average $\sim 4\mu$. This value represents approximately an 8 per cent uncertainty in thickness for the 0.103 mm case. Consequently, such a surface treatment probably does not produce a very extensive deformed region below the observed geometrical surface. This result is expected because of the resilience of graphite in

the c-direction and the virtual absence of dislocation propagation in that direction. It is believed, then, that these tests establish the validity of the single crystal shear modulus measurements.

Stress-Strain Curves on Single Crystals and Pyrolytic Graphite

Stress-strain curves have been obtained not only for pyrolytic samples but also for single crystals. A comparison of typical stress-strain curves measured in shear on the compression-annealed pyrolytic graphite sample M-311-K and the single crystal EPC-3 are shown in Figure 7. The dramatic difference in the character of the curves from these two graphites can be seen immediately. The single crystal curve is strongly reminiscent of the behavior of the hexagonal close-packed metals, zinc and cadmium.⁽²⁾ The single crystal displays the characteristic curve of a single glissile slip system contained in single planes with little interaction between dislocation systems. This long glissile slide occurs at a very low critical shear stress, characteristic of relatively few pinning points, allowing a long unimpeded movement in the basal plane. The pyrolytic graphite, on the other hand, has the somewhat brittle behavior of a more complex multiple slip mechanism with interacting slip systems. There is an almost negligible macroscopic slide occurring at a much higher stress. This condition is characteristic of a much higher density of pinning points due to crystallite boundaries, twins, kinks, and other lattice imperfections.

Figure 4

Sample Location Scheme

PYROLYTIC GRAPHITE M-311

Figure 5

Pyrolytic Samples Used for the Thickness Dependence Measurements

N-8230

Figure 6

Shear Modulus versus Thickness for Pyrolytic Graphite

N-8460

Figure 7

Comparison of Single Crystal and Pyrolytic Stress-Strain Curves

N-8462

A quantitative indicator of this difference is the ratio σ_s/ϵ (shear strength to strain) at fracture. For eleven single crystals observed to date, this ratio ranges from 0.002 to 1×10^8 dyne/cm² with $\epsilon = 22$ to 0.017; for the pyrolytic samples M-311 and M-304, the ratio ranges from 20 to 30×10^8 dyne/cm², with $\epsilon = 0.005$ to 0.002.

The initial linear elastic portion of the single crystal stress-strain curve exists only over a very limited region of strain ≤ 0.0005 . This strain corresponds to a shift of a carbon atom by only 0.0017 Å, a value representing 0.12 per cent of the distance to its nearest neighbor (1.42 Å), if it were assumed that the strain is taken up uniformly by the entire intrinsic lattice. The values for the shear modulus $G = 1/s_{44}$ measured on three single crystals (EP-85, EP-86, and EPC-3) are given in chronological order in Table II. The first two values are very preliminary and do not fairly represent the accuracy that was obtained with EPC-3, a thicker sample measured with an improved technique. It is believed that the best value for virgin crystals lies near 0.013×10^{11} dyne/cm². This value is to be compared with the approximate average value obtained from the indirect cantilever beam measurements of Baker and Kelly⁽³⁾ of 0.01×10^{11} dyne/cm². It is interesting to note that this value for EPC-3 is within a factor of approximately two of the shear moduli obtained with compression-annealed pyrolytic graphite; originally, we expected that the single crystal shear modulus might be smaller by as much as a factor of 10.

The compression-annealed pyrolytic graphite sample M-304-C2 was cut directly from the center of a bar previously measured with the resonant bar technique. As shown in Table II, a value of $1/s_{44}$ equal to 0.0246×10^{11} dyne/cm² was obtained by the resonant bar technique and 0.0242×10^{11} dyne/cm² by the ultrasonic method on a piece cut from an adjacent portion of the slab. Again, as with M-311, the agreement between the values of $1/s_{44}$ obtained by different experimental techniques is excellent on this virgin material. The shape of the stress-strain curve for M-304-C2 was also very similar to that of M-311; the stress-strain behavior is shown in Figure 8.

TABLE II
Basal-plane Shear Results

<u>Single Crystal Graphite</u>				
Sample	Area(cm ²)	Thickness(mm)	G _o (10 ¹¹ d/cm ²)	σ _s [*] (10 ⁶ d/cm ²)
EP-85	0.203	0.070	0.011	4.2±0.8
EP-86	0.160	0.263	0.026	
EPC-3	0.200	0.381	(I) 0.0132±0.0020 (II) 0.0176±0.0025	
Baker and Kelly ⁽³⁾ (Cantilever Beam)			(0.01)	
<u>Compression-annealed Pyrolytic Graphite</u>				
C-5			---	8.3±1.5
M-305			---	12.4±2.6
M-311-F			0.0327	12.2±1.2
-G			0.0323	
Blakslee (ultrasonic)			(0.0323)	
M-304-C2			0.0244	9.2±2.6
Blakslee (resonant bar)			(0.0246)	
" (ultrasonic)			(0.0242)	

Figure 8

Strain Hardening in Pyrolytic Graphite

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Strain Hardening by Cyclic Stressing

Experiments were carried out to investigate the effect of cyclic stressing single crystals at increasingly higher stresses. In the case of the single crystal EPC-3, the first cycle, I, was carried to a stress of 1.22×10^6 dyne/cm²; at that point, the stress-strain curve begins to bend over into the plastic region (see Figure 9). Cycle II (which is the curve shown in Figure 7) was carried higher to failure at $\sigma_s = 1.95 \times 10^6$ dyne/cm². Two results occurred: G increased and the curve reached a higher critical shear stress before bending over. These effects are attributed to the increased pinning of the dislocations. A similar effect, shown in Figure 8, occurred for M-304 pyrolytic graphite, although the phenomenon is not so pronounced. Such strain hardening was not seen in M-311 pyrolytic graphite even after ten cycles; this material has evidently reached a saturation in pinning density. This progression from a single crystal to a good pyrolytic graphite, M-304, to a moderately good pyrolytic graphite, M-311, can be shown quantitatively by the fractional increase in $1/s_{44}$ produced by the highest previously applied stress, $\sigma_{\max}$. The ratio $\frac{\Delta G}{G_o \sigma_{\max}}$ where G_o is the original shear modulus as determined in the first test, is an index of strain hardening and is shown in Table III.

The correlation between $G=1/s_{44}$ and σ_s can be seen by examining the ratios G/σ (shown in Table IV) for these graphites in the virgin, or as-received, and the saturated conditions. The two pyrolytic graphites, although quite different in their individual moduli, have an identical ratio equal to $265 \pm (\sim 70)$. The ratio G/σ is somewhat higher for the single crystal, due primarily to its very low initial shear strength σ_s . After a certain amount of strain hardening (the stresses being unequal for the three samples), these ratios tend to converge. In fact, EPC-3 and M-304 asymptotically approach each other, the former decreasing and the latter increasing. The fact that these values are as close as they are is quite remarkable. It is believed that this result indicates a strong correlation between the shear modulus and shear strength. They both must represent true macroscopic averages of the internal conditions.

Figure 9

Strain Hardening in a Single Crystal Graphite

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TABLE III
Strain Hardening Index of Different Graphites

Material	$\Delta G/G_o \sigma_{\max} (10^{-7} \text{ cm}^2/\text{dyne})$
Single crystal	
EPC-3	2.73
Pyrolytic	
M-304	0.61
M-311	~0

TABLE IV
Correlation Between Shear Modulus and Strength

Material	Initial G_o/σ_{s_o}	After Straining G^*/σ_s^*
Single Crystal		
EPC-3	677	419
Pyrolytic		
M-304	265	350
M-311	265	265

6. STATIC TESTS ON PYROLYTIC GRAPHITE

E. J. Seldin

6.1. Tensile Tests on Compression-Annealed Pyrolytic Graphite

Tensile tests were run on specimens from three disks of compression-annealed pyrolytic graphite in order to evaluate the material. The disks were prepared at the Advanced Materials Laboratory in Lawrenceburg.

The test results are summarized in Table V. The longitudinal modulus $1/s_{11}$ was measured for each specimen. Disk M306 was not perfectly flat, but the specimen was thick enough to allow the determination of the compliance s_{13} as well as s_{12} . Unfortunately, the transverse stress-strain curve for s_{13} was somewhat erratic; thus, there is considerable uncertainty in the value of this compliance. Because disk M310 was badly warped, no transverse compliances were measured. Disk M313 was relatively thin (0.2 inch) and had been repressed at high temperature after some outer layers had been removed. The resulting disk was very flat on the macroscopic scale, but the outer surfaces were observed under the optical microscope to be badly wrinkled. The degree of wrinkling decreased progressively from the outer layers toward the center layers. Specimen M313-2-1 contained one face which was badly wrinkled (outer face of disk) and one face which was much less wrinkled (interior of disk). Specimen M313-2-2, taken from the interior of the disk, had faces which were only moderately wrinkled.

The modulus $1/s_{11}$ for each specimen was relatively low, indicating that the quality of the material was not so good as some of the other materials which have been tested. It is felt that better material should be used for the irradiation program.

6.2. Torsion Test Apparatus

A new torsion apparatus, shown in Figure 10, has been constructed. It is similar, in principle, to the apparatus described in previous reports, but has been automated to make collection of data more convenient. The specimen which can be $1/4$, $3/8$, or $1/2$ inch in diameter, is cemented with Eastman 910

cement between steel specimen holders. The upper specimen holder is fixed to the frame of the apparatus by a set screw, and the lower specimen holder fits on top of the rotating torsion shaft. The lower end of the torsion shaft is connected through a clutch to a gear box, which is connected to a variable speed, reversible motor. In the center of the torsion shaft is a torque transducer; with associated electronic equipment, the torque transducer produces a voltage proportional to the torque over the range ± 200 oz. in. Calibration of the torque transducer is achieved by fixing the upper end of the torsion shaft, disengaging the clutch, and applying dead weight loads through strings and pulleys to the 2-inch diameter wheel below the torque transducer. The rotation of the lower specimen holder is communicated to the core of a linear variable differential transformer (LVDT) by a bar attached to a ring around the lower specimen holder. The distance between the center of the specimen and the axis of the LVDT core is 4 inches. Since the rotation of the specimen is usually extremely small, the linear motion of the LVDT core is directly proportional to the angular twist of the specimen. The LVDT is calibrated by means of a micrometer screw. Two microswitches mounted at the rear of the apparatus act as safety devices; when activated by the bar which rotates with the lower specimen holder, the microswitch turns off the motor which drives the torsion shaft.

In a torsion test, the outputs of the LVDT and torque transducer are applied to the X and Y axes, respectively, of an X-Y recorder, and the curve of torque-vs.-angle of twist is recorded as the test is performed. Cyclic tests in which the torque is reversed are easy to perform. The compliance of the apparatus has been determined: it is a small, easily applied, correction factor.

TABLE V
Results of Static Tensile Tests on Compression-Annealed
Pyrolytic Graphite

Specimen	Modulus $1/\epsilon_{11}$		$-\epsilon_{12}$		Poisson Ratios $-\epsilon_{12}/\epsilon_{11}$	
	10^4 lb/in ²	10^{11} dynes/cm ²	10^{-11} cm ² /dyne	10^{-11} cm ² /dyne	$-\epsilon_{12}/\epsilon_{11}$	$-\epsilon_{12}/\epsilon_{11}$
M 306-T1	122.5	84.5	.0021	.0030 $\pm .0008$	.18	.25
M 310-T1	114	78.6				
M 313-2-1	97.5	67.1				
M 313-2-2	122	84.0	.0017		.14	

Figure 10
Automated Torsion Apparatus

N-8599

7. ULTRASONIC TESTS ON PYROLYTIC GRAPHITE

O. L. Blakslée

Determination of c_{13} of Compression-Annealed Pyrolytic Graphite

The accuracy of the value for stiffness c_{13} of compression-annealed pyrolytic graphite is less than that of any of the other elastic constants and it has not yet been directly measured experimentally. We discuss here the feasibility of an experimental determination of c_{13} by ultrasonics. Garland and Silverman⁽⁴⁾ have shown that acoustical wave velocities for propagation at an angle θ to the c-axis are given by:

$$\rho U_t^2 = c_{66} \sin^2 \theta + c_{44} \cos^2 \theta, \text{ and} \quad (1)$$

$$\rho U^2 = c_{11} \sin^2 \theta + c_{33} \cos^2 \theta + c_{44} \quad (2)$$

$$\pm \{ (c_{11} - c_{44})^2 \sin^4 \theta + (c_{33} - c_{44})^2 \cos^4 \theta + 2 \sin^2 \theta \cos^2 \theta [(c_{11} - c_{44})(c_{44} - c_{33}) + 2(c_{13} + c_{44})^2] \}^{\frac{1}{2}} .$$

The velocity of a pure transverse wave polarized perpendicular to the c-axis is denoted by U_t . The other two waves are of mixed character; the plus sign in Equation (2) gives a quasi-longitudinal wave velocity, U_{ql} , and the minus sign gives a quasi-transverse velocity, U_{qt} . Since Equation (2) contains c_{13} , calculations were made to determine the feasibility of determining c_{13} by measuring the velocity of a wave propagating at some angle θ to the c-axis with $\theta \neq 0$ or 90° .

Figure 11 shows the per cent error in c_{13} per degree of error in θ as a function of θ for both the quasi-transverse and quasi-longitudinal waves. The plots were obtained by solving Equation (2) for c_{13} , differentiating with respect to θ , and calculating the derivative as a function of θ . It is impractical to use the quasi-longitudinal wave near $\theta = 0$, where the error is zero, because the wave is almost longitudinal. However, Figure 11 indicates that the quasi-transverse wave at $\theta = 13^\circ$ may possibly be used.

Calculations were performed to evaluate the error introduced in the determination of c_{13} from the velocity of the quasi-transverse wave at $\theta = 13^\circ$ by errors in each of the independent variables: c_{11} , c_{33} , c_{44} , θ , and $2\rho U_{qt}^2$. In these calculations, the following elastic constants were used:

$$c_{11} = 106 \pm 1 \times 10^{11} \text{ dynes/cm}^2,$$

$$c_{33} = 3.6 \pm 0.1,$$

$$c_{44} = 0.025 \pm .005, \text{ and}$$

$$c_{13} = 2.72 \times 2^{\pm 1}.$$

The average and extreme values were used, and it was determined that a one per cent error in c_{44} causes negligible error in the calculated c_{13} , that a one per cent error in θ causes -0.7 to -2.5 per cent error in the calculated c_{13} , and that a one per cent error in c_{11} causes 1.0 to 1.3 per cent error in the calculated c_{13} .

The calculated value of c_{13} is much more sensitive to errors in c_{33} and $2 \rho U_{qt}^2$, and the magnitude of the possible error in c_{13} strongly depends on the actual value of c_{13} (see Figure 12). Figure 12 indicates that if c_{13} is less than approximately 2×10^{11} dynes/cm², there is little hope of determining it accurately from a measurement of the velocity of a quasi-transverse ultrasonic wave.

One additional complication is presented by the fact that the laminar structure and very weak interplanar bonds of compression-annealed pyrolytic graphite make the machining of a 13° face extremely difficult. Although the possibility exists of introducing the waves at the desired angle into the c-face of a specimen by means of a refraction technique, it is concluded that the effort required to develop this method can be more profitably expended in measuring the other stiffness constants. We conclude that no attempt should be made to determine c_{13} directly from experiment at the present time.

Figure 11

Per Cent Error in c_{13} Per Degree Error in θ vs. θ

N-8721

Figure 12

Per Cent Error in c_{13} Due to a One Per Cent
Error in Either ρU_{qt}^2 Or c_{33}

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8. IRRADIATION TEST PROGRAM

The research program was reviewed in August, 1965, at the United States Atomic Energy Headquarters, Germantown, Maryland. The suggested irradiation schedule contained in the Research Proposal was amended and reduced to the schedule given in Table VI. Suggested dates for completion are given.

TABLE VI
CPD Irradiation Program

A. Low Temperature

Irradiation Facility: Hanford Production Reactor, Cold Snout Facility
Irradiation Temperature: 40 to 60°C $\pm$ 5°C
Nominal Exposures: 2, 5, 20, 50 MWD/AT
Number of Capsules: 4 plus 2 for experiment checkout
Dimensions of Capsule: Inside 2-3/4" diameter x 14-1/2" long
Start Irradiation: April 1966
Complete Irradiation: May 1966

B. Intermediate Temperature

Irradiation Facility: Hanford Production Reactor, Hot Test Hole
Irradiation Temperature: Nominal 650°C
Nominal Exposures: 300, 650, and 1000 MWD/AT
Number of Capsules: 3
Dimensions of Capsule: Inside 4" x 4" x 24"
Start of Irradiation: As soon as samples are ready
Complete Irradiation: -

C. High Temperature

Irradiation Facility: ETR or GETR
Irradiation Temperature: 1000°C $\pm$ 50°C (approx.)
Nominal Exposures: 800 (1/2 cycle), 1600-3200 (1-2 cycles) MWD/AT
Number of Capsules: 2
Dimensions of Capsules: Inside 3/4" diameter x 4" long per module;
4 to 5 modules
Start Irradiation: When samples are available
Complete Irradiation: 3 months later

Each capsule will contain a number of test specimens. The details are given in Table VII.

TABLE VII
Samples for Each Irradiation Capsule

<u>Sample Use</u>	<u>No. Per Capsule</u>	<u>Maximum Sample Dimensions, in.</u>
Sonic Resonant Bar Test	3	1/4 x 1/4 x 2-5/8
Ultrasonic, Sonic (CTO) Test	5	1/2 diam. x 5/16
Tensile Test	4	5/16 x 5/8 x 2-1/4
Compression Test	3	1/4 diam. x 5/16
Torsion (Static) Test	4	1/2 diam. x 5/16
Shear 60° (Static) Test	1	1/4 x 1/4 x 1/4
Shear 45° (Static) Test	1	1/4 x 1/4 x 1/4
Shear 30° (Static) Test	1	1/4 x 1/4 x 1/4
Shear 15° (Static) Test	1	1/4 x 1/4 x 1/4
Single Crystals	1	3/4 diam. x 1
X-ray Specimens	1	1/8 x 1/8 x 1

The irradiations will be performed by members of the Battelle Northwest Laboratories under the direction of Dr. H. H. Yoshikawa, Manager, Graphite Research and Development. Irradiations will begin as soon as test specimens are available.

njr

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