ANNUAL PROGRESS REPORT

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

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FOREWORD

This report summarizes the progress of an investigation of the effects 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 from the start of the contract on April 1, 1964 to June 30, 1965.

The Project is under the general supervision of J. T. Meers. The graphite single crystal work has been carried out by R. Bacon, R. Sprague, D. E. Soule, C. W. Nezbeda, and G. Wagoner. The pyrolytic graphite work has been carried out by O. L. Blakslee, N. F. Graves, C. E. Lowell, D. G. Proctor, J. D. Ruggiero, E. J. Seldin, A. Silvaggi, G. B. Spence, G. Wagoner, and T. Weng. W. E. Biles, P. H. Higgs, and G. L. Rowe performed the compression annealing of pyrolytic graphite at the Advanced Materials Laboratory, Lawrenceburg, Tennessee. This report was prepared by E. J. Seldin with the assistance of the participants in the program.

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ABSTRACT

This report summarizes the results of fifteen months of work on the production, characterization, and measurement of the mechanical properties of unirradiated graphite single crystals, as-deposited pyrolytic graphites, and pyrolytic graphites which have been compression annealed to align the crystallite c-axes. Several methods of growing graphite single crystals and several combinations of compression annealing conditions were tried. Material characterization has included X-ray methods, optical and electron microscopy, interferometry, and an optical reflectivity technique. A tensile test and shear test for single crystals were devised, and values for shear strengths were obtained from the latter test for natural graphite crystals. Tension and compression stress-strain tests, using resistance strain gages, were made on both as-deposited and compression-annealed pyrolytic graphite. Static torsion tests were also made on both types of pyrolytic graphite. Shear strengths of compression-annealed pyrolytic graphite were obtained by compression-shear tests in addition to results obtained by using the torsion apparatus and the single crystal shear apparatus. Elastic constants were also obtained by the sonic resonance of long thin bars and compound oscillators consisting of graphite specimens with metal end pieces. For the resonant bar method, Timoshenko's equation for the flexural vibrations of a long thin bar was solved, and the solution was used to compute the value of one modulus from the measured resonant frequency and a known value of the other modulus. To make this computation economical for a large number of bars, a program was written for a digital computer. Ultrasonic tests were performed for the determination of two of the elastic constants and their stress dependence. A complete set of elastic compliance and stiffness constants was obtained for as-deposited unirradiated compression-annealed pyrolytic graphite. An analysis of the data was made to define the limits of accuracy in the data and to deduce a self-consistent set of elastic constants for compression-annealed pyrolytic graphite.

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 of the work for the first year has been the production and pre-irradiation evaluation of these materials.

The four preceding progress reports^(1,2,3,4) describe the production of materials, the development of individual tests compatible with the severe anisotropy of the test specimens, and the experimental results obtained in the period covered by each report. These four reports are condensed and summarized.

The tests on single crystals of graphite were confined to tensile and shear tests, which yielded only values of the shear strength of natural single crystals. Attempts to grow large single crystals were not successful.

Most of the mechanical testing was performed on highly ordered compression-annealed pyrolytic graphite. The technique of compression-annealing pyrolytic graphite has been described in the literature⁽⁵⁾; this technique permits the aligning of the c-axes of the crystallites of pyrolytic graphite within about one degree while the a-axes remain randomly oriented. Because the graphite crystal is transversely isotropic, the misalignment of the a-axes should cause little error in the measurement of the elastic constants and, significantly, of the shear strength between layer planes.

Considerable effort was devoted to characterizing the quality of the as-deposited and compression-annealed pyrolytic graphites and to adapting the technique of compression annealing for the production of large disks of compression-annealed pyrolytic graphite. Elastic constants were evaluated by means of static tension, compression and torsion tests, and also by means of sonic resonance and ultrasonic tests. A reasonably consistent set of elastic constants has been obtained for compression-annealed pyrolytic graphite; except possibly for the shear modulus, these constants are believed to be typical also of the single crystal.

2. SUMMARY

Very small graphite crystals of good quality have been produced by the thermal decomposition of aluminum carbide. In addition, very thin single crystals of graphite up to 6mm in diameter have been grown in a carbon supersaturated iron melt. The best crystals were formed by melting pure iron in a graphite boat at 2700°C: the melt becomes saturated with carbon, the iron then slowly evaporates, and the graphite crystals grow in the supersaturated melt. The best source of single crystal graphite for mechanical testing purposes, however, was the supply of natural graphite crystals found in calcite from Essex County, New York. Several dozen crystals were obtained by dissolving the calcite in acid, but only a few of these crystals are of adequate quality to be used for mechanical property determinations.

Various combinations of time, temperature, and pressure in the compression-annealing of pyrolytic graphite were tried with good success, but the fine grain, substrate nucleated material displayed a greater tendency to side-slip during annealing than did the coarse grain commercial quality pyrolytic graphite. The conclusion reached from the many compression-annealing tests which were made is that highly columnar, essentially soot-free pyrolytic graphite requires more refined annealing procedures than ordinary commercial pyrolytic graphite.

Optical, X-ray and electron microscope techniques have been used to evaluate the as-deposited and compression-annealed graphites. Optical and X-ray methods were used to determine the half-widths of the crystallite distribution at or near the surface of a sample. An interferometric method of studying the surface of pyrolytic graphite samples was also devised; the interference fringes form contour maps of the surface, indicating the effects of inclusions. An electron microscope study of cathodically etched, replicated c- and a-faces of both single crystals and pyrolytic graphite reveals multiple cracks in the a-surface and a continuum of etch pits on the c-surface. In some instances, a row of etch pits has been identified as the base line of a cleavage step on the crystal surface.

Attempts to measure the modulus $1/s_{11}$ of a single crystal in a static tensile test have thus far been unsuccessful. The shear strengths of several natural graphite crystals have been measured and the values found to be in good agreement with Gillin and Kelly's quoted value of 3.9 to 4.9×10^6 dynes/cm². Several specimens of compression-annealed pyrolytic graphite were tested in the single crystal shear apparatus; the values obtained were in good agreement with those found by using the torsion apparatus and the compression-shear wedges.

Static tensile tests of compression-annealed pyrolytic graphite have yielded values of $1/s_{11}$ ranging from 47 to 108×10^{11} dynes/cm², values of s_{12} in the range $-.0018 \pm .006 \times 10^{-11}$ cm²/dyne, and values of s_{13} in the range $-.0033 \pm .0008 \times 10^{-11}$ cm²/dyne. The tensile stress-strain curves for the better specimens tended to be linear and showed no hysteresis effects.

A single flexure test on a bar of compression-annealed pyrolytic graphite yielded a value of $1/s_{11}$ which was in good agreement with tensile tests on specimens cut from the same disk.

Static compression tests of compression-annealed pyrolytic graphite have yielded values of $1/s_{33}$ ranging from 3.3 to 4.4×10^{11} dynes/cm². The best value, $1/s_{33} = 3.65 \pm .07 \times 10^{11}$ dynes, was obtained for a specimen which exhibited a perfectly linear stress-strain curve with no hysteresis loop and behaved like a perfectly elastic material until failure.

Static torsion tests were performed on small disks of compression-annealed pyrolytic graphite. The shear modulus $1/s_{44}$ ranged from 0.018 to 0.031×10^{11} dynes/cm² with an average of 0.025×10^{11} dynes/cm². The stress-strain relation in torsion exhibits anelastic behavior; when the torque was cycled, narrow hysteresis loops formed and some residual strain was indicated.

The shear strength of pyrolytic graphite was measured by using compression-shear wedges. Shear strengths ranging from 120 to 350 lb/in² were obtained for compression-annealed pyrolytic graphite by extrapolating measured values to the limit of zero normal force. These values were in good agreement with those obtained with the torsion apparatus.

A resonant bar method was used for the determination of the elastic constants $1/s_{11}$ and $1/s_{44}$ for long thin bars of compression-annealed pyrolytic graphite. The longitudinal resonance yielded the $1/s_{11}$, and the shear modulus $1/s_{44}$ was calculated from Timoshenko's equation by using the appropriate flexural resonant frequency and c_{66} as measured ultrasonically. For the latter purpose, Timoshenko's equation for the flexural vibrations of a long thin bar was solved, and the applicability of the solution for isotropic and anisotropic materials was tested. It was shown that for near-isotropic bodies with a relatively high G/E (shear to Young's modulus) ratio, only Young's modulus can be determined accurately from flexural vibrations of a bar. However, for compression-annealed graphite with a very low shear modulus compared with Young's modulus, only the shear modulus $1/s_{44}$ can be calculated from the flexural vibrations of a bar.

The dependence of the Timoshenko constant, k , upon both the harmonic number and the cross-sectional shape was investigated for nearly isotropic materials, and two important conclusions were drawn. First, to within one per cent variation, the value of k is independent of harmonic number (at least up to $n = 3$) and of the length to diameter ratio. Second, as G/E increases from $1/3$ to $1/2$, the value of k decreases monotonically. The analysis of the vibrational frequencies of isotropic square bars gave a value of k which is significantly less than the theoretical value for a round bar with the same value of G/E . A value of $k = 0.85 \pm .05$ may be determined for rectangular bars of compression-annealed pyrolytic graphite by extrapolating the results for several materials; and this value of k should apply to all harmonics, to all reasonable values of the D/T and D/L ratios, and to varying amounts of anisotropy.

Exact frequency equations for the compound torsion oscillator (CTO) were derived, and the results were applied respectively to steel-aluminum-steel and steel-graphite-steel oscillators for both as-deposited and compression-annealed pyrolytic graphite. For aluminum, the compound torsion oscillator value was 3 per cent below that obtained by the resonant bar test; for graphite the values obtained by the CTO technique were consistently 2 to 5 per cent

lower than the values obtained by ultrasonic measurements. The program for the compound torsion oscillator was then modified so that computations could be made for the compound longitudinal oscillator (CLO); unfortunately, the values of $1/s_{33}$ obtained using the CLO method were consistently too low.

Measurements of the transit time of pulses in the ultrasonic frequency range yielded values of c_{44} and c_{66} for compression-annealed pyrolytic graphite. Our results indicate that the values of c_{44} obtained by ultrasonics, the compound torsion oscillator, and the first 5 to 10 flexural harmonics and the first torsional vibration of a resonant bar are all within about 15 per cent of one another and, sometimes, within about 5 per cent. It also appears that c_{44} may vary by 10 to 20 per cent for different layers from the same disk. However, values of c_{44} measured on specimens taken from different disks have varied by as much as a factor of 2, from roughly 0.017 to 0.034×10^{11} d/cm². In view of the expected tenfold increase in c_{44} after neutron irradiation, it appears that the accuracy of the measurements is satisfactory but that pre- and post-irradiation measurements will have to be made on the same specimen or, at least, on specimens from the same disk.

The change of the elastic stiffness constant c_{33} was measured ultrasonically as a function of c-axis compressive stress. The fractional change in c_{33} per unit stress σ is given by $\frac{1}{c_{33}} \frac{dc_{33}}{d\sigma} = \frac{d \ln c_{33}}{d\sigma}$. The calculated value of $\frac{d \ln c_{33}}{d\sigma}$ for one specimen was 9.1×10^{-11} cm²/dyne, a value which may be expressed as .63 per cent per 1000 lb/in².

A set of elastic constants for compression-annealed pyrolytic graphite was obtained by analyzing all the static, sonic resonant bar, and ultrasonic test results. The results are given below, where the c_{ij} and $1/s_{ij}$ are expressed in 10^{-11} cm²/dyne.

$c_{11} =$	106 ± 2	$1/s_{11} =$	101.5 ± 3
$c_{12} =$	18 ± 2	$s_{12} =$	$-.0015 \pm .0004$
$c_{13} =$	$2.72 (x 2^{\pm 1})$	$s_{13} =$	$-.0063 (x 2^{\pm 1})$
$c_{33} =$	$3.6 \pm .1$	$1/s_{33} =$	$3.48 \pm .2$
$c_{12}/c_{11} =$	$.17 \pm .01$		
$c_{44} = 1/s_{44} = .018 \text{ to } .035$			

3. MATERIALS PREPARATION

3.1. Production of Graphite Single Crystals

G. Wagoner

Graphite single crystals have, of course, been known from antiquity, for single crystals occur frequently in natural graphite deposits. Furthermore, for many years single crystals have been used in investigations reported in the scientific literature.⁽⁶⁾ The degree of perfection of the natural crystals, however, is a matter of concern in interpreting experimental results, and imperfections have in some cases resulted in widely divergent conclusions.⁽⁷⁾ The resulting uncertainty was the impetus for a search for a method of producing synthetic single crystals which are more nearly perfect than those occurring in nature.

Synthetic single crystals of graphite have been made by a number of methods. Almost a decade ago, D. E. Soule and H. S. Pattin of this Laboratory made graphite single crystals by direct crystallization from solution in molten iron. Foster, Long, and Stumpf⁽⁸⁾ produced graphite single crystals by thermal decomposition of aluminum carbide. Noda and Matusoka⁽⁹⁾ made some very small crystals by melting carbon at 100 atmosphere pressure and 4050°K and allowing it to cool. Others^(10, 11) have made graphite by precipitation from molten nickel, titanium boride, tungsten, zirconium carbide, chromium, rhenium, molybdenum, and undoubtedly, many other metals. However, the largest synthetic crystals produced thus far by any method have been a few millimeters in their greatest dimension.

Two methods were applied in the effort to produce graphite crystals: thermal decomposition of Al_4C_3 and precipitation from molten metal. When the method of Foster, Long, and Stumpf⁽⁸⁾ was employed, good flake graphite crystals were produced as large as 5mm in diameter and about 0.05mm thick. Such specimens appeared to be of very high perfection in that they were optically flat, but isolating a crystal from its neighbors without damage has been very difficult. Furthermore, X-ray examination showed most such crystals to be bicrystals or polycrystals with a random rotation about the c-axis occurring between some of the layer planes of the graphite structure.

The paper of Foster, Long, and Stumpf implies that single crystals of Al_4C_3 are thermally convertible to single crystals of graphite by evaporation of the metal cation. It appeared that one might be able to produce large single crystals of Al_4C_3 and, subsequently, decompose them to produce large graphite single crystals. In practice, quite large Al_4C_3 single crystals were produced, but in no case was a single crystal of graphite derived by thermal decomposition. All the graphite derived from Al_4C_3 single crystals was highly polycrystalline. Apparently, the graphite single crystals which are produced by thermal decomposition of Al_4C_3 in a furnace are formed by crystallization from the carbonaceous vapor of the decomposing Al_4C_3 . The vapor deposition mechanism is also supported by the observation that many of the crystals are turbostratic, a common imperfection in pyrolytically deposited graphite.

The growth of graphite single crystals from Al_4C_3 is, thus, a tricky operation in that vapor deposition requires careful control to prevent multiple nucleation. One must adjust the temperature to produce slow thermal decomposition of aluminum carbide, and the container must be adjusted to prevent too rapid escape of the atmosphere. If the process is carried out too rapidly, multiple nucleation will produce a highly polycrystalline graphite; yet, if the temperature is not high enough, only Al_4C_3 crystals are produced. The method which seems to be most reliable has been to pack the starting materials in a tube furnace and then slowly increase the temperature through the crucial temperature range from 1700°C to approximately 2500°C . In this manner, at some point of the heating cycle, good conditions for the growth of graphite single crystals are attained; and, once formed, the graphite crystals are stable during further heating.

The mechanism of formation of the graphite crystals is not clear. It is believed that the explanation of Foster, Long, and Stumpf is not tenable and that a simple evaporation of aluminum from Al_4C_3 crystals with a subsequent rearrangement of the carbon atoms probably does not occur. It seems more likely that some carbonaceous species, such as Al_2C_2 , evaporate from the decomposing carbide. Then, perhaps in a manner analogous to the formation of pyrolytic graphite from methane, the carbon is deposited as a single crystal followed by evaporation of the aluminum.

Incidental to the formation of graphite crystals is the preparation of the aluminum carbide starting material. In a series of experiments conducted in an induction heater, methods of obtaining complete reaction of aluminum and carbon were worked out. Only by using a cryolite flux was oxidation of the aluminum reduced sufficiently to permit reasonably complete reaction. Considerable care was required to exclude oxygen during formation of the aluminum carbide to prevent formation of aluminum oxycarbide, a needle-like crystalline material the presence of which precludes the formation of large crystals of Al_4C_3 . The formation of large crystals of Al_4C_3 and the formation of large crystals of graphite seem to occur under similar conditions, except that the graphite crystals grow at somewhat higher temperature.

Several attempts to obtain crystallization of graphite upon a "cold finger" immersed in a solution of graphite in molten iron and in copper-nickel, copper-iron, and copper-cobalt alloys were carried out. In a number of instances, shiny layers of graphite several thousandths of an inch thick were formed. However, the process reached equilibrium after a short time, and an hour in solution produced no additional deposit on the "cold finger". A plausible explanation is that the low thermal conductivity of the graphite deposit may thermally insulate the "cold finger" from the molten metal bath and nullify the thermal gradient which is the driving force for crystallization. Progressive cooling of the "cold finger" might correct this difficulty.

A second problem with "pulling" crystals of graphite from molten metal is that surface nucleation occurs. Any graphite crystal which forms on the surface of the metal immediately cools more rapidly than the metal because of its greater emissivity, provided cooler surfaces are available to absorb the radiation. The only way to avoid such surface nucleation is to reverse the radiation flow and "drive" the graphite back into solution (or at least to nullify the radiation cooling at the surface). Although this surface nucleation of crystals interferes with crystal growth at the surface, it should not greatly alter the growth of crystals on the "cold finger" below the surface layer. It is believed that the generally poor results of the various "cold finger" tests are not related to surface nucleation but, rather, are due to improperly controlled thermal gradients or to impurities which prevented crystal growth.

The most successful method used to produce graphite single crystals was the crystallization of graphite from molten metal. This method appears to have the promise of producing very large crystals in that it is similar to the hydrothermal method in common use for sapphire and other oxides. The simplest variation of this method was to melt iron (or some other metal that dissolves carbon) in a graphite crucible. Heating was continued until the metal evaporated, leaving behind crystals which were produced as the solution became supersaturated. The main problem with this method was that too much nucleation always occurred, and a given crystal did not grow very large before being blocked by a neighbor.

The best crystals were produced by these conditions: pure iron in a graphite crucible was heated in a tube furnace to approximately 2700°C. The iron melt became saturated with the dissolving graphite; then, the iron slowly evaporated, leaving a supersaturated solution in which the graphite crystals grew. The temperature was then lowered to reduce the vapor pressure of iron over the melt and thus decrease the rate of crystal growth (and nucleation). The degree of supersaturation required to produce crystal growth was less than that required to nucleate new crystals; thus, lower evaporation rates produced larger crystals. Hold temperatures below approximately 2650°C, however, required impractically long furnace runs. Several runs at 2675°C produced small crystals of good quality; the occasional large crystals were invariably so thin that they were severely damaged by removal from the crucible. As a result, crystal growing was discontinued, and attention was directed toward obtaining naturally occurring single crystals of graphite.

3.2. Natural Graphite Crystals

D. E. Soule and C. W. Nezbeda

Essex County, New York, has been a particularly fruitful area for obtaining natural graphite crystals, and a screening evaluation of marble, quartz, calcite, and granites from Essex County was made in August of 1964. The graphite crystals found in calcite were of the best quality; and, when the decision was made to obtain natural graphite crystals, approximately 300 pounds

of Essex County calcite was obtained. The crystals were recovered by acid leaching. After the calcite was digested, the remaining sludge was washed, and the graphite crystals were removed with a wet camel hair brush. The crystals were then washed, dried, and purified in a stream of gaseous chlorine at 3000°C. Since this last step can be destructive if a furnace element breaks, only a few crystals were processed per run. A typical array of crystals from a fist-size piece of calcite is shown in Figure 1. Although a large number of crystals have been recovered, only a very few are of sufficient quality to be used for mechanical property determinations.

N-6271

FIGURE 1. Natural Graphite Crystals Obtained from Calcite.

3.3. Compression-Annealed Pyrolytic Graphite

Three methods of stress-annealing pyrolytic graphite have been reported in the literature. In the first method, ^(12,13) a tensile stress was applied parallel to the average basal plane while the material was heated to about 2750°C. Later, Blackman and Ubbelohde ⁽¹⁴⁾ reported stress-annealing small samples of pyrolytic graphite by heating the samples on a mandril suitably shaped to introduce thermal stresses. Still later, Ubbelohde, Young, and Moore ⁽⁵⁾ applied a compressive stress perpendicular to the average basal plane while the sample was heated to approximately 2800°C. Tensile stress-annealing has the inherent disadvantage that, before the crystallites have become completely aligned, the layer planes start to delaminate causing cracks to develop perpendicular to the planes. Neither the first nor second methods are easily adapted to the production of large quantities of material. On the other hand, Ubbelohde, Young, and Moore indicated that the compressive stress-annealing process could probably be scaled up to large sizes; they also reported that this method produced the highest quality material. For these reasons, the compressive stress-annealing process was chosen for the present work. Most of the development work on the compression-annealing process as well as production of material for the contract was done at the Advanced Materials Laboratory of the Carbon Products Division at Lawrenceburg, Tennessee. A small pressing furnace was constructed and used at the Carbon Products Research Laboratory.

Commercial quality pyrolytic graphite has a continuously renucleated or regenerative growth cone structure. The nucleation site is usually a small particle of nongraphitic carbon. The material is classified by grain size (the size of the growth cone structure, not the size of the graphite crystals). As the concentration of nucleation sites decreases, the structure of the material changes into what is called singularly or substrate nucleated material. Theoretically, a fine grain, substrate nucleated pyrolytic graphite should be the best starting material for the present purposes. In practice, this material tends to develop microcracks and even total delaminations during manufacture. A compromise has to be accepted between material which has good starting structure and that which will develop a minimum of microcracks.

For the initial work, a supply of commercial quality pyrolytic graphite was furnished free of charge for use on this contract by High Temperature Materials, Inc. (HTM), a subsidiary of Union Carbide Corporation. Three furnace loads of special fine grain substrate-nucleated materials were thereafter ordered from HTM.

Of the first two furnace loads, one was made from methane and the other propane. Each furnace produced 13 plates, each approximately 7 inches in diameter. The methane plates were approximately $1/2$ inch thick; the propane plates, approximately $3/8$ inch thick.

Prior to most of the compression anneals, the material was given a separate thermal anneal. During a thermal anneal, pyrolytic graphite expands in directions parallel to the basal plane and contracts in the direction perpendicular to the basal plane, thereby reducing the dimensional changes which must take place in the subsequent compression anneal. In the early work, compression anneals were made on plates from $3/4$ to $5 1/2$ inches in diameter, on both single plates and on stacks of several plates. As expected, more difficulty was experienced in producing good material as the diameter of single plates was increased and the number of plates in the stack was increased. One difficulty not anticipated was that the original surfaces of large plates were almost always slightly wedge shaped. Although plane parallel surfaces were ground on the plates before pressing, the inherent wedge shape of the layer planes provided a driving force which caused the material to flow laterally when the axial compressive stress was applied. This lateral flow was uneven and always produced wrinkles in the layer planes. Since the tendency to flow laterally also depends on the cone structure, it is difficult to predict whether or not a given set of annealing conditions will cause lateral flow, but it soon became evident that the special, fine-grain substrate-nucleated pyrolytic graphite would require much more careful control than had been necessary in the annealing of commercial pyrolytic graphite.

A series of experiments was performed to determine the best conditions of pressure and temperature for annealing the special propane and methane deposited graphite. The plate diameter was reduced to 1.5 inches for these tests, and experiments were carried out at temperatures and pressures which ranged from 2650°C to 3400°C and 1000 to 8000 lb/in², respectively. The best annealing conditions for propane deposited material were found to be 2800°C and 4000 lb/in². The propane base material side-slipped slightly under these conditions, but less severe conditions are not sufficient to straighten the layer planes. Several pieces were given an additional anneal at temperatures of 3350°C while under a pressure of 800 lb/in²; the additional heat treatment did not cause marked changes in the material.

After compression-annealing conditions were established for 1.5 inch diameter disks of pyrolytic graphite, the sample size was increased to 2.5 inches. These larger samples of propane material also showed a slight tendency to side-slip. A subsequent thermal anneal at 3350°C and 500 lb/in² did not produce any noticeable improvement. The optical reflectivity half-widths of the crystallite orientation distributions for the material thus annealed have been in the range 0.2 to 0.7 degree, except for poorer material near the surfaces of the disks. These favorable results led to the decision to scale up to 3.5 inches sample size.

After most of the graphite disks from the first two furnace loads were thermally and compression-annealed, a third furnace load of pyrolytic graphite was ordered. Before conditions and type of gas to be used in the preparation of the material for this order were specified, a basic question had to be resolved. It had been found by optical microscopy that the propane material had less soot but more internal delaminations than the methane material. The high misorientation around soot particles tends to lock the layer planes together; thus, when the amount of soot is reduced, delaminations become more frequent. The contract objective of producing pyrolytic graphite representative of the natural graphite single crystal requires the elimination of as much soot as possible. However, it was feared that the increased delaminations of the as-deposited soot-free material might so weaken the material after compression annealing that meaningful mechanical property measurements could not be made.

Samples from the previous methane and propane furnace runs were simultaneously compression-annealed by placing two or three disks in the load train with ZTA grade graphite spacers between the disks. This procedure eliminated the possibility of any differences in the final material being due to variations in pressing conditions. Next, the shear strength was measured on samples cut from the methane and propane disks; it was felt that the shear strength would be more critically affected by delaminations than any other property. From the results of these tests, no significant difference due to the starting material could be found between the methane and propane material. Consequently, it was decided to order fine-grain substrate nucleated pyrolytic graphite similar to the propane material. Engineers at High Temperature Materials, Inc. suggested that methane gas be used, but with different manufacturing conditions than those which had been used for the first furnace load made with methane. In view of the previous failure to attain high quality by compression-annealing 5-inch diameter plates, it was decided to place the order for 3 to 3.5-inch diameter plates.

Twenty-five plates approximately 3.5 inches in diameter and about $\frac{3}{8}$ inch in thickness were obtained. In accordance with our numbering system, these plates made from methane in the third furnace are designated M301 to M325. Plate M301 was used for the evaluation of the as-deposited material. Sixteen plates from this furnace load were compression annealed at the Advance Materials Laboratory in Lawrenceburg, Tennessee. The annealing conditions of 2800°C and 4000 lb/in² which were established for the propane material also proved to be suitable for this methane material. The as-deposited plates had excellent internal structure, but they were, unfortunately, slightly bowed, having convex curvature on the substrate side. The roughly conical substrate face of as-deposited plate M301, which is believed to be typical of the group, showed a misalignment of approximately 2 degrees from one side of center to the other. This geometrical defect in the as-deposited plates caused some difficulties in the compression annealing process.

Some of the as-deposited plates were machined flat on both surfaces; these plates showed evidence of side slipping during compression annealing, probably because the layer planes were slightly inclined to the surfaces of the plate. Best results were obtained by compression-annealing plates the surfaces of which retained their curvature, but which were of uniform thickness. Since there is a tendency for imperfections on the surfaces of either the specimen or mold to be propagated through the material during compression annealing, some plates were first compression-annealed at 1500 or 2000 lb/in² pressure to make them relatively flat, the surfaces were retouched by stripping or machining, and, finally, the plates were compression-annealed again at higher pressure and/or temperature. Pressure ranging from 1500 to 5000 lb/in² and temperatures of 2800°C and 2900°C have been used. Under the best processing conditions, these methane deposited pyrolytic graphite plates yielded good quality compression-annealed pyrolytic graphite. However, attempts will be made in future production of pyrolytic graphite to eliminate or reduce the curvature in the as-deposited plates.

3.4. Isostatic Pressure Annealing of Pyrolytic Graphite*

Several experiments were conducted in which pyrolytic graphite specimens were annealed under a hot-isostatic-pressing process. Bare and tantalum-clad pyrolytic graphite samples were isostatically pressed at 2650°C and 13000 lb/in² for one hour. The experimental results for two samples are given in Table 1.

TABLE 1

HOT-ISOSTATIC GAS-PRESSED PYROLYTIC GRAPHITE

Specimen No.	Average Diameter in.	Average Diameter Expansion, %	Average Thickness, in.	Average Thickness Contraction, %	Weight, gm	Weight Loss, %	Approximate Density, gm/cc	Density Increase, %
<u>Canned</u>								
IV Before	1.2442		0.4757		20.7626		2.18	
IV After	1.2458	0.129	0.4591	3.57	20.2411	2.51	2.22	1.83
<u>Uncanned</u>								
V Before	1.2446		0.4700		20.4302		2.14	
V After	1.2484	0.305	0.4600	2.13	20.1877	1.118	2.18	1.87

* At the suggestion of J. G. Conner, this work was performed at Battelle Memorial Institute by P. D. Ownby and D. C. Carmichael.

The plasticity of graphite is very low at 2650°C; hence, the changes effected by these conditions are small but measurable. The method appears promising. A very interesting material should be produced by isostatically pressing pyrolytic graphite at 2800-3000°C under pressures similar to those used in these experiments.

4. MATERIAL CHARACTERIZATION

Since the mechanical properties of both the single crystals and compression-annealed pyrolytic graphites may depend on the orientation and distribution of crystallites and on the presence of twins, kinks, and other imperfections, several methods have been used for the characterization of the structure of the materials. Most of the effort has been devoted to the characterization of the pyrolytic graphites in both the as-deposited and compression-annealed states. An X-ray test was used to obtain a crystallite orientation function which is a measure of the degree to which the graphitic structure of the material was enhanced by the compression-annealing process. An optical reflectivity method was devised to obtain a somewhat analogous measure of the degree of flatness of the surface of the material. Surfaces of the pyrolytic graphites were examined by optical microscopy after being polished by standard techniques and after cathodic etching. In addition, surface replicas were examined in the electron microscope, and the electron micrographs were compared with optical micrographs of the same surfaces. Some estimates of crystallite sizes were made in the electron microscope by traversing thin flakes of compression-annealed pyrolytic graphite while observing diffraction patterns. The densities of the compression-annealed pyrolytic graphites were also very carefully determined.

4.1. X-ray Techniques

C. E. Lowell

One measure of crystal perfection is based upon the probability that adjacent layer planes are in correct relative position, and this probability is related to the interplanar spacing. The spacing varies from approximately 3.44 Å in the case of completely randomly stacked layers to 3.354 Å in the case of the perfectly stacked layers of a graphite single crystal. In our experiments, the

interlayer spacings were determined by use of a Norelco 114.6mm Debye camera. The spacings were calculated from the position of the highest (001) order observed. Powder specimens were taken from several parts of each sample to give a representative value.

The measured c-spacing values of various samples of pyrolytic graphite are summarized in Table 2. These results confirm the observations by optical microscopy that the pyrolytic graphite as-deposited from propane has a greater preferred orientation than the methane material and that the region near the bottom (substrate) side of both the propane and methane material has a greater preferred orientation than the region near the top side.

For the characterization of the degree of alignment of the crystallites in compression-annealed pyrolytic graphite, an important quantity is the crystallite orientation function, $N(\theta)$, defined by

$N(\theta)$ = probability of finding a crystallite with its c-axis within a cone of unit solid angle making an angle θ with the normal to the average basal plane.

The normalization condition is

$$\int_{\theta=0}^{\pi/2} \int_{\phi=0}^{2\pi} N(\theta) \sin \theta \, d\theta \, d\phi = 1.$$

For pyrolytic graphite, this distribution is symmetric and is peaked about $\theta = 0^\circ$. For convenience, the distribution will be characterized by its half-width at half height, $\theta_{\frac{1}{2}}$ (some authors use the full width at half height in reporting their work).

TABLE 2

X-RAY CHARACTERIZATION OF SPACING OF PYROLYTIC GRAPHITE

Specimen No.	Position in Plate	Interlayer Spacing	
		Line Measured	c-spacing (A)
<u>Commercial</u>			
As-deposited		(004)	3.425 ± .005
Thermal Anneal		(008)	3.359 ± .001
C4 (Compression Annealed)		(008)	3.355 ± .001
C5 (Compression Annealed)		(008)	3.356 ± .001
<u>Methane</u>			
M108-15	Top	(004)	3.422 ± .005
(As-deposited)	Bottom	(004)	3.424 ± .005
M103-1 (Compression Annealed)		(008)	3.362 ± .001
M112-1 (Compression Annealed)		(008)	3.355 ± .001
		(008)	3.359 ± .001
<u>Propane</u>			
P208-101, 105	Top	(004)	3.419 ± .005
(As-deposited)	Bottom	(004)	3.417 ± .005
P208-113	Middle	(008)	3.356 ± .001
(Compression Annealed)			

The Norelco diffractometer was used in the evaluation of the degree of preferred crystallite orientation; the X-ray apparatus and sample arrangement which evolved after trials with different sample shapes are shown schematically in Figure 2. The sample shown is a 0.125-inch diameter rod, one inch long; in the test, it was rotated about its central longitudinal axis. As-deposited pyrolytic graphite samples were cut with the rod axis parallel to the plane of deposition. Fabrication problems made necessary the use of square cross-section samples in the case of the compression-annealed pyrolytic graphite; evaluation of corrections for this geometry showed the effect to be negligible over the small angular range of the crystallite distribution in these samples. When the apparatus was aligned, the angle between the incident beam and the reflected beam corresponded with the (002) layer plane reflection. In the absence of horizontal divergence, which is minimized by the two parallel slit assemblies, only crystallite planes the normals of which are perpendicular

to the sample axis and parallel to the plane formed by the incident and reflected beam can reflect into the counter. The measured intensity is then proportional to the mass of those crystallites within the irradiated region the c-axes of which are in the required position for reflection. The intensity was recorded on a strip chart as a function of the angle of sample rotation, θ . If θ is measured from the position of maximum intensity, the resulting curve is assumed to be the unnormalized crystallite orientation distribution function.

N-6147

FIGURE 2. Method for Measuring Surface Orientation by X-rays

Tests were conducted on an MgO single crystal sample and on two samples of compression-annealed pyrolytic graphite. The results are shown in Table 3. There is one note of caution to be observed: the calculated depth at which the reflected intensity of the diffracted X-ray beam within the graphite falls to one per cent of the surface layer is 0.031 inch, indicating that this value is essentially a surface measurement. Further evidence that the measurement is surface is shown by the difference in the peak half-width at half maximum of the 002 line for the two sides of the sample and also by the fact that the peak positions are not 180° apart. The X-ray method of measuring preferred orientation appears to be plagued by instrument broadening, and experiments with disk-shaped samples indicate that the broadening is very dependent on sample geometry. For a single crystal of MgO in the shape of a disk 0.025 inch thick, $\theta_{\frac{1}{2}}$ was thirty times that given in Table 3. No corrections for instrument broadening were determined for the rod-shaped samples.

TABLE 3
ORIENTATION OF MgO AND PYROLYTIC GRAPHITE
AS MEASURED BY X-RAYS

Material	$\theta_{\frac{1}{2}}^*$		Maximum Position	
	Side 1	Side 2	Side 1	Side 2
MgO	0.05°	0.05°	0.00°	180.00°
Compression-Annealed Commercial	0.56°	0.60°	0.00°	181.15°
Compression-Annealed Methane Base	1.68°	1.95°	0.00°	183.94°

* Precision is estimated to be $\pm 0.015^\circ$.

4.2. Optical Reflectivity Evaluation of Pyrolytic Graphite Surfaces

G. Wagoner and O. L. Blakslee

A simple method of determining the flatness of a cleaved surface of compression-annealed pyrolytic graphite has been developed. The method consists simply of shining a pencil of light onto the surface and observing the reflected intensity. The intensity of the reflected beam will be given by $I_o r f(\theta)$, where

I_0 is the incident light intensity, r is the (specular) reflectivity, and $f(\theta)$ is the fraction of the surface lying at the appropriate angle θ to reflect light into the detector. To obtain $f(\theta)$ one can either rotate the sample about a line lying in its surface with a fixed light source and detector or hold the light source and sample fixed and rotate the detector (there is a factor of two involved in the angular spread). Maximum resolution may be obtained if entrance and exit slits and lenses are used to assure that the light rays are parallel as they strike the surface. By using a photometer to make quantitative observations of the intensity of the reflected beam as a function of the angle of the pyrolytic graphite slab with respect to the beam, one can obtain directly a plot of the fraction of the surface that lies at a given angle, θ , with respect to the average normal of the surface of the slab. The limit of resolution of the optical system used here was evaluated with a plane mirror; adjustment of the apparatus gave a half-width at half height as low as 0.1. degree.

Figure 3 shows the results of an evaluation of a cleaved surface of compression-annealed specimen number C101. If one makes the assumption that the angle of the cleaved surface is characteristic of the crystallite orientation in the material below the surface, the plot in Figure 3 directly indicates the crystallite orientation distribution function. By this optical reflectivity method, the measured half-width at half height of this specimen is about 0.6° ; it is less than this value if instrumental broadening is accounted for. Microscopic observation of the surface of the specimen showed that, in addition to the predominant area which yielded the above result, there were microscopic bosses which probably gave diffuse reflection.

N-5934

FIGURE 3. Intensity of Reflected Light as a Function of the Angle Between the Average Pyrolytic Graphite Surface Normal and the Crystallites Oriented to Reflect into the Detector

Table 4 gives the results of the optical reflectivity measurements made on a large number of specimens of compression-annealed pyrolytic graphite. The minimum and maximum half-width values $\theta_{\frac{1}{2}}$ are given for all of the specimens, and a weighted average is given for those specimens the measurements for which were sufficient in number and scope to be representative of the block.

There have been indications that the crystallite orientation distribution varies significantly with position in the block, especially that the material near the ram faces during annealing is more disordered than that in the middle. Optical reflectivity surveys were, therefore, made along the c and a-axes of several blocks. Figure 4 shows $\theta_{\frac{1}{2}}$ as a function of position along the c-axis for four representative blocks. Figure 5 is a similar plot of $\theta_{\frac{1}{2}}$ as a function of position along the diameter of disk M304.

TABLE 4
CRYSTALLITE ORIENTATION OF COMPRESSION-
ANNEALED PYROLYTIC GRAPHITE

Sample	No. of Measurements	Min.	$\theta_{1/2}$ Max.	Avg.*	Sample	No. of Measurements	Min.	$\theta_{1/2}$ Max.	Avg.*
C5	32	0.15°	1.32°	0.37°	P207-1	4	0.19°	0.32°	
C103-1	5	.37	.83		P207-3	4	.25	.32	
C103-2	2	.40	.97		P207-4	4	.26	.38	
M101-1	9	.55	1.01		P207-9	1	.26		
M103	16	.32	.88	.64	P207-10	2	.29	.48	
M106	18	.40	1.34	.52	P207-11	2	.30	.40	
M107-1	6	.20	.63		P207-12	6	.16	.20	
M107-2	7	.30	4.4		P207-13	7	.20	.37	
M107-3	8	.25	3.0		P207-15	4	.16	.21	
M107-4	10	.32	2.5		P207-17	7	.29	1.4	
M107-6	2	.29	.49		P210-3	10	.17	.23	.21
M107-7	2	.22	.27		P210-4	9	.21	.65	.51
M108-22	2	.32	1.44		P210-5	2	.17	.27	
M108-23	2	.62	1.11		P211-1	1	.29		
M108-25	2	.28	.75		P211-2	2	.35	.43	
M108-27	2	.66	.67		P211-3	10	.64	.91	.79
M108-28	6	.32	.50		P213-2	11	.68	2.3	1.8
M109-1	4	.55	.65		M304	27	.08	.78	.13
M110-2	19	.16	.88	.47	M305	4	.31	1.15	.46
M110-3	61	.13	2.7	.60	M307	72	.11	.75	.21
M110-4	7	.31	.57		M308	27	.09	.70	.19
M110-5	2	.39	.49		M309	7	.33	1.18	.54
M111	4	.51	.52		M311	29	.22	1.12	.38
M112-14	4	.73	.91		M312	13	.15	.28	.19
P202-1	11	.30	1.9	.62	M313	4	.20	.28	
P205-2	2	.59	1.8		M314	6	.33	1.04	
P205-3	2	.61	2.3		M315	6	.20	.38	

* Measurements made on the surfaces grossly misoriented by the ram faces are excluded from the average.

N-7231

FIGURE 4. Half-Width $\theta_{1/2}$ vs. Position Along C-Axis as Determined by Optical Reflectivity

N-7230

FIGURE 5. Half-Width $\theta_{1/2}$ vs. Position Along A-Axis as Determined by Optical Reflectivity (M304)

4.3. Comparison of Optical Reflectivity and X-ray Methods

O. L. Blakslee and C. E. Lowell

The X-ray and optical reflectivity methods of measuring the crystallite orientation distribution of the compression-annealed material were compared by measuring several samples by both methods. The X-ray and optical values of $\theta_{\frac{1}{2}}$ and the ratio of these values are given in Table 5. The X-ray value was usually about twice the optical value, but the ratio varied from 1.1 to 2.9. There are several reasons why the X-ray and optical results could differ. The instrumental broadening in the X-ray method may be greater for graphite than the 0.05 degree estimated from measurements on an MgO crystal; or, alternatively, the X-ray distribution may actually be different from the optical distribution because of the difference in wave lengths (smaller crystallites contribute to the X-ray beam) and because the X-ray beam penetrates approximately 0.03 inch and measures a volume rather than a surface distribution. Soot particles seem to broaden the optical distribution, presumably by diffraction effects. It is felt that this diffraction broadening is not important in the propane-deposited material but is present in the upper half of the first load of methane-deposited material and in most commercial-quality material. On well-annealed material, either method can be used to compare the relative degree of crystallite alignment of different samples.

TABLE 5
CRYSTALLITE ORIENTATION DISTRIBUTION
HALF-WIDTH AT HALF-HEIGHT

Sample	Method		Ratio X-ray/Optical
	Optical	X-ray	
M110-2	0.18	0.52	2.9
M110-3	.38	.78	2.1
P210-3	.20	.38	1.9
M110-4A	.57	.83	1.5
M110-4B	.32	.64	2.0
P210-4A	.65	.71	1.1
P210-4B	.21	.34	1.6
M110-5	.42	.76	1.8
P210-5	.27	.61	2.3
P210-6	.22	.43	1.9
M111-1	.51	.72	1.4
P211-1	.29	.53	1.8

Values of $\theta_{\frac{1}{2}}$ were also obtained by the X-ray method on several specimens of as-deposited pyrolytic graphite. The half-widths ranged from 20 to 25 degrees and were lower on the substrate side than on the top side of the as-deposited pieces. On as-deposited plate M301, $\theta_{\frac{1}{2}}$ was 22° on the substrate side and 24° on the top side; the distribution function obtained by the optical method on the unmachined top surface of this plate gave $\theta_{\frac{1}{2}}$ equal to 7.1° , and no value was obtained from the much duller substrate side. There is an obvious discrepancy between the two results which is probably due to causes other than instrument broadening. One may speculate that the difference in the two results arises from the fact that X-rays will detect smaller crystallites, and the smaller crystallites are probably more misoriented.

4.4. Interferometric Method of Evaluating Cleaved Graphite Surfaces

G. Wagoner

Highly oriented graphites, such as single crystals and compression-annealed pyrolytic graphites, are very easy to cleave. Visual examination of the resulting surfaces often indicates the degree of preferred orientation, the presence of twins, growth cones, and other structural characteristics; however, it is desirable to substantiate the qualitative impression one gets by such visual or microscopic examination with more quantitative evidence. Presented here are some observations of interference patterns with the specimen forming one mirror of an interferometer.

The 5461 A line from a mercury lamp was used to set up the interference pattern between the sample and an optically flat mirror. The interference pattern could be magnified with a microscope and either scanned visually or photographed to obtain a topographical map of the surface. The vertical displacement between fringes is one-half wave length (2730 Å). Thus, by counting the number of fringes per unit length of the sample surface, one may measure the angle between the optical flat and that part of the sample surface. The smoothness of the surface is also indicated by the character of the fringes, a smooth surface giving dark continuous fringes and a rough one showing discontinuous crooked fringes. Figures 6 and 7 show the patterns of two compression-annealed pyrolytic graphite samples which appeared quite similar

to the unaided eye. The pattern of Figure 6 was produced by a sample of compression-annealed pyrolytic graphite made from commercial quality material, whereas the pattern of Figure 7 was produced by a sample of pyrolytic graphite made from propane and compression annealed at 3600°C. The pattern of Figure 7 shows smooth contours, indicating no appreciable roughness greater than approximately one-quarter wave length in height. The angle between the "top of the hill" and the steepest slope is 0.9°.

Figure 6, when contrasted with Figure 7, shows a much less well defined set of fringes. Undulations of the surface produce the fringe waviness. Most of the bumps are between 1500 Å and 3000 Å in height, as shown by a change from light to dark in the interference pattern. The distance across the bumps is about 0.01mm. Thus, the bumps are about 100 times as wide as they are high.

Evidently, the interference technique of evaluating pyrolytic graphite surfaces is highly useful. Surface waviness, the variations in angle of the surface, cleavage steps, and other surface imperfections are clearly visible and quantitatively measurable. The resolution of height variations is a few thousand angstroms, a value which is somewhat better than the best resolution obtained by using a good optical microscope.

N-6766

FIGURE 6 Surface Undulations of Compression-Annealed Pyrolytic Graphite Containing Lampblack Inclusions

N-6767

FIGURE 7. Surface Smoothness of a Compression-Annealed Pyrolytic Graphite Deposited from Propane

4.5. Optical Microscopy

J. D. Ruggiero and N. F. Graves

Optical microscopy was used to study the structure of both as-deposited and compression-annealed pyrolytic graphite. The detection of structural detail was accomplished by the use of normal incident light, polarized light, and cathodic etching by ion bombardment. Typical cone structure, deformation slip, and other orientational effects were revealed by polarized light due to the inherent birefringency of graphite.

Representative specimens were cut and mounted in accordance with standard metallographic procedures. Specimens too small or too fragile to withstand mounting press pressures were set up in liquid epoxy. Surface preparation was done on motorized laps in the following sequence:

1. rough surfacing - using silicon carbide disks, through 600 grit,
2. intermediate polishing - using 0.3 micron alumina or nylon covered wheel, and
3. final polishing - using an automatic manipulator, chromic oxide polishing compound, and bonded nap cloth wheel covering.

The entire operation, exclusive of mounting, was done in approximately one hour. The majority of this time was used for the final polishing operation, which produced a metallic mirror-like finish on the specimen surface. For the compression-annealed material, cleavage produces a c-face suitable for direct observation; polishing is not desirable.

Cathodic etching was accomplished by applying a potential between the specimen cathode and cell anode in a chamber with a partial pressure of argon. In this manner, an ion beam was formed. Ions, accelerated towards the specimen surface, eject graphite atoms in a preferential manner at structural defects.

Figure 8 shows the cone structure typical of commercial quality, as-deposited pyrolytic graphite. This particular micrograph shows a coarse grain band in a medium grain size material. Figure 9 shows this same band, but not exactly this same region, after cathodic etching. In order to show the microcracks which appear after cathodic etching on the reproduced figure, the magnification has been increased to 500 X.

A thermal anneal of as-deposited pyrolytic graphite at 3000°C for 30 minutes produces improvements in layer spacing and crystallite preferred orientation which can be detected by X-rays, but the material is far from being perfectly aligned. Figure 10 shows that no major change in appearance has been produced by this thermal anneal in the same material shown in the two previous figures. The effect of compression-annealing this material is shown in Figure 11. The cone structure has been eliminated except in the coarse grain band. A higher annealing pressure would have caused some improvement but would not have "ironed out" the material in the coarse grain band. Thus, one may assume that, in order to obtain the highest quality compression-annealed material, one must start with well-ordered as-deposited pyrolytic graphite.

Optical microscopy of the as-deposited propane base plates shows that this material has a uniform fine grain, substrate nucleated structure with almost no optically visible difference from the bottom to the top of the plates. Figure 12 shows the structure of as-deposited propane plate number P208. A similar investigation of the first order of methane base pyrolytic graphite showed that this material was not homogeneous. Near the substrate surface, this methane material has a fine grain, substrate nucleated structure (Figure 13, showing as-deposited methane plate number M108.) The middle of the plates contain a medium grain size cone structure of much higher concentration. The concentration of medium grain size cones decreases toward the top of the plates. This latter structure is shown in Figure 14. The third furnace order, consisting also of methane base pyrolytic graphite, was much improved and comparable in quality to the propane base plates. Figure 15 shows the

structure of plate M301, typical of the structure observed throughout the plate. The material has a uniform fine grain, substrate nucleated structure from the bottom to the top of the plate, a structure very similar to that of the propane-deposited material. This plate has one large delamination just above the area shown in Figure 15 but exhibits very few of the small microcracks found in the propane material. The average cone size is slightly smaller than that of the previous materials, and the density (2.16 g/cm^3) and crystallite distribution are similar to the properties of the previous materials.

N-5963

FIGURE 8. Cone Structure of a Regeneratively Nucleated Commercial Quality Pyrolytic Graphite Showing a Coarse Grain Band in a Medium Grain Size Region. Magnification 75X.

N-5964

FIGURE 9. Region Near that of Figure 8. Sample has Been Cathodically Etched to Reveal Fine Microcracks. Magnification 500X.

N-5965

FIGURE 10. Region Near That of Figures 8 and 9. Specimen Has Been Thermally Annealed with No Major Change in Cone Structure. Unetched. Magnification 75X.

N-5966

FIGURE 11. Region Near That of Previous Three Figures. Specimen Compression-Annealed. Note Elimination of Structure Except In Coarse Grain Band. Magnification 75X.

N-5967

FIGURE 12. Fine Grain, Substrate Nucleated Structure of As-Deposited Propane Plate P208. Magnification 75X.

N-5968

FIGURE 13 - Fine Grain, Substrate Nucleated Structure Near the Bottom of As-Deposited Methane Plate M108. Magnification 75 X.

N-5969

FIGURE 14 - Medium-Grain Structure Near the Top of As-Deposited Methane Plate M108. Magnification 75 X.

FIGURE 15. Fine Grain, Substrate Nucleated Structure of As-Deposited Methane Disk M301. Magnification 75X.

Examination of the a-face of compression-annealed specimens which had been cathodically etched by ion bombardment revealed the presence of what appear to be fine microcracks which are not visible on the polished but unetched surfaces. Figure 16 shows the structure revealed by etching the a-face of compression-annealed specimen C4. The interpretation of this structure is not clear. Cracks as short as a fraction of a millimeter can occasionally be seen on polished but unetched a-faces, but their frequency of occurrence is far less than that shown in Figure 16. It seems strange that a crack structure which is easily visible at 50 X magnification on an etched surface is totally invisible even at 500 X magnification on the unetched surface.

The technique of cathodic etching was applied to the c-face of both as-deposited and compression-annealed pyrolytic graphite. Nothing new was revealed on the as-deposited material, but a totally new structure was revealed by cathodically etching the c-face of the compression-annealed material. The structure varies somewhat from specimen to specimen; one example is given in Figure 17.

N-5961

FIGURE 16. Structure, Presumably Microcracks, Revealed by Cathodic Etching on the a-face of Compression-Annealed Specimen C4. Magnification 100 X.

The structure is not completely understood, but the many junctions of three lines at approximately 120 degrees strongly suggest that some of the lines are true grain boundaries between crystals. Some lines are identifiable cleavage steps. Micrographs of several etched specimens all indicated that the average basal plane dimension of the graphite crystals in compression-annealed material is in the range of 10 to 50 microns. These crystals are about 100 times larger than those reported for material thermally annealed at similar temperatures. Electron microscopy work, discussed in Section 4.6, has confirmed the crystallite L_a dimension of tens of microns.

N-5962

FIGURE 17. - Structure Revealed by Cathodic Etching on the c-face of Compression-Annealed Specimen C4. Magnification 1000 X, Oblique Lighting.

Compression-annealed pyrolytic graphite also contains deformed areas which resemble the mechanical lenticular twins or kink bands formed by shear stresses in some metals. Bowed or S-shaped marks are visible without etching on cleaved c-surfaces where they reflect light in a completely different direction from that reflected over the general area. The deformations are not so easily identified at the a-face and require etching. The marks may occur singly, but often several are aligned to form a distinctive pattern. Sizes range from microscopic to those large enough to be seen without optical aid. One was observed, by successive cleavages, to extend at least $\frac{1}{4}$ inch through the lamellar planes.

In Figure 18, the outline of the deformation mark on the c-surface indicates that it is mechanically introduced as a result of stress. The direction of deformation appears to follow that resulting from a stress pattern rather than from a crystallographic direction. However, at the a-surface, as shown in Figure 19, the basal slip lines of the band intersect those on either side at approximately the $20^{\circ} 48'$ angle expected of graphite twins. As shown in Figure 20, the same type of deformity has been observed in pyrolytic graphite that has only been thermally annealed; without compressive forces, the deformation was limited to comparatively thin lamellae, as evidenced at the cleavage fracture in the foreground.

N-8002

FIGURE 18. A Mechanical Lenticular Twin in Compression-Annealed, Propane Deposited Pyrolytic Graphite, c-Surface.

N-8003

FIGURE 19. A Mechanical Lenticular Twin in Compression-Annealed Propane Deposited Pyrolytic Graphite, a-Surface.

N-8004

FIGURE 20. Mechanical Twins or Kink Bands in Thermally Annealed, Propane Deposited Pyrolytic Graphite, c-Surface.

4.6. Electron Microscopy

R. Bacon, A. Silvaggi, and R. Sprague

Specimens of compression-annealed pyrolytic graphite produced from commercial and propane base material were observed by transmission electron microscopy. Standard cleaving procedures were used in thinning the graphite specimens for electron transmission, and the specimens were mounted for microscopy on standard copper support grids of 85 micron mesh opening. For this experiment, we define a crystallite as the area over which there occurs substantially zero rotation of the layer planes about the c-axis. Selected area electron diffraction was obtained by using a beam of about one micron diameter; the specimen was traversed until a rotation of the diffraction pattern was noticed. Usually two-thirds of a grid opening could be traversed before rotation occurred. The observations made by this procedure indicate an average crystallite size, after preparation, of about 50 microns. It must be kept in mind that, due to as yet unavoidable stresses induced during specimen preparation, 50 microns is a minimum size and, as such, might be more truly representative of the preparation procedure than of the manufacturing method. On the other hand, only a few grains observed by optical microscopy of cathodically etched specimens were as large as 50 microns.

Surface replicas suitable for electron microscopy were obtained from both a-faces and c-faces of unetched and cathodically etched compression-annealed pyrolytic and single crystal graphite. Initially, a cellulose acetate replica was made using the Faxfilm technique. This replica was then shadowed at 45° with a platinum-carbon pellet, and carbon was evaporated onto the replica to make a carbon film replica containing the platinum "shadows." The last step was to dissolve the cellulose acetate.

The a-face of a compression-annealed unetched pyrolytic graphite sample is shown in Figure 21. No detail of the structure is detectable; the line is a scratch on the sample surface.

N-6768

FIGURE 21. A-Face of Compression-Annealed Unetched Pyrolytic Graphite.

The a-face of a compression-annealed etched pyrolytic graphite sample is shown in Figure 22. The etch has revealed a series of parallel lines upon which occasional etch pits are located. It is not possible to determine whether these lines are cracks or represent disordered planes which etch preferentially.

The replicated a-face of an unpurified single crystal which was cathodically etched is shown in Figure 23. Although this crystal was of good quality, the cathodic etch brings out a structure which appears to be microcracks over the entire sample. There are many circular etch pits located in or along the cracks: the average etch pit diameter is about 800 Å, and the minimum distance between cracks is about 400 Å, which is even closer than that found in compression-annealed pyrolytic graphite.

N-6769

FIGURE 22. A-Face of Compression-Annealed Cathodically Etched Pyrolytic Graphite, Electron Micrograph 5200X.

N-6770

FIGURE 23. A-Face of an Unpurified Cathodically Etched Single Crystal Graphite, Electron Micrograph 7300 X.

The c-face of compression-annealed pyrolytic graphite sample C-4 as determined by an electron micrograph is shown in Figure 24. It should be compared with the optical micrograph of the same sample (Figure 17). The heavy lines seen in the optical micrograph appear in the electron micrograph as well-defined rows of etch pits. The heavier rows appear to cross over or dominate the lighter rows, but no consistent pattern can be observed. The entire background is covered with etch pits, some apparently random, others showing short-range order. Figure 25 shows the c-face of another and similar sample of compression-annealed pyrolytic graphite.

N-6771

FIGURE 24. C-Face of Compression-Annealed Cathodically Etched Pyrolytic Graphite Sample No. C-4, Electron Micrograph 5200 X.

N-6772

FIGURE 25. C-Face of Compression-Annealed Cathodically Etched Pyrolytic Graphite Sample No. C-5, Electron Micrograph 7300 X.

Figure 26 is the c-face of an unpurified single crystal. The appearance of this etched surface is very similar to that of the pyrolytic graphite c-faces. Inspection of the crystal by optical microscopy permitted the identification of some large cleavage steps and well-defined rows of etch pits frequently occurring at the base of such steps (marked "AA" in Figure 26). Since it is expected that many smaller cleavage steps, essentially unobservable by normal microscopy methods, must occur in all samples, it is a good assumption that many of the etch pit rows are caused by cleavage steps. However, it is difficult to interpret the complicated patterns of intersecting and crossing lines entirely on this basis.

N-6773

FIGURE 26. C-Face of an Unpurified Cathodically Etched Single Crystal Graphite, Electron Micrograph 5200 X.

4.7. Density by Hydrostatic Weighing

O. L. Blakslee

A hydrostatic weighing technique was used for determining the density of compression-annealed pyrolytic graphite. Carbon tetrachloride was chosen as the working fluid because: (1) it wets graphite, (2) it does not absorb contaminants from its environment, (3) its density dependence on temperature is well known, and (4) it has a relatively high density. The experimental procedure was to weigh the sample in air and then weigh it immersed in carbon tetrachloride, noting both the initial weight and the steady state weight. (The weight changes as the carbon tetrachloride soaks into surface cracks. This operation may take 20 to 30 minutes.) The temperature of the carbon tetrachloride is recorded.

The density is calculated from the following equation:

$$\rho_g = \frac{M\rho_f}{M-M'} - \frac{M'\rho_a}{M-M'}$$

where

ρ_g = density of graphite,

ρ_f = density of fluid,

ρ_a = density of air,

M = weight mass necessary to balance graphite in air,

and M' = weight mass necessary to balance graphite in fluid.

The term $\frac{M'\rho_a}{M-M'}$ corrects for air buoyancy and is approximately

.0005 g/cc.

The term $M-M'$ is calculated by subtracting the combined weight of the sample and the holding basket in the fluid from the total of the basket in the fluid plus the weight of the sample in air.

The fluid density (ρ_f) at a temperature T ($^{\circ}\text{C}$) is equal to $1.6326 - 1.911 T \times 10^{-3} - 0.690 T^2 \times 10^{-6}$.⁽¹⁵⁾

Table 6 shows the density of several samples determined by this technique.

TABLE 6

DENSITIES OF COMPRESSION-ANNEALED PYROLYTIC GRAPHITES

Sample	ρ^*	ρ^{**}
M106-12	2.2457 g/cc	2.2573 g/cc
M110-5	2.2600	2.2600
M111-1	2.2609	2.2616
P202-1C	2.2561	2.2567
P210-5	2.2578	2.2579
P210-6	2.2614	2.2614
P211-1	2.2522	2.2530
P211-2	2.2516	2.2526
P213-2-RB	2.2553	2.2567
M302-2	2.2596	2.2613
M304-C	2.2602	2.2603
M305-US	2.2601	2.2608
M308-C	2.2605	2.2609

* From initial weight in fluid.

** From steady state weight in fluid.

5. STATIC TESTS OF SINGLE CRYSTALS

Because of the small size and shape of graphite single crystals, only a limited number of mechanical tests can be made on them. The two tests which seemed most feasible are (1) a tensile test with the stress parallel to the basal plane which will give the stress-strain curve and tensile strength and (2) a shear test in which the top crystal plane is sheared with respect to the bottom plane.

5.1. Tensile Tests of Graphite Single Crystals

R. Bacon and R. Sprague

Specimen Preparation

In the preparation of a tensile specimen from a graphite crystal, the crystal was first mounted in a thermoplastic "dop stick", and one side of the

crystal was cleaved, using scotch tape, until a monoreflectant, unstepped surface was obtained. A drop of polyvinyl alcohol (PVA) was then applied to the prepared surface. After the PVA solidified, a piece of scotch tape was placed over the PVA; the tape was then used to strip the PVA and a thin (5 to 20 μ) crystal from the part of the crystal which remained on the dop stick. The tape was then dissolved with acetone, and the PVA and thin crystal were placed in a steel mask which was in the dog bone shape desired for a tensile specimen. The mask held the crystal rigidly while the unprotected crystal area was sand-blasted away by an airbrasive machine.

The dog bone shaped crystal and PVA mount were handled with tweezers and transferred to filter paper in a covered petrie dish. The filter paper was wetted with water, but not so much that the crystal floated. Complete dissolution of the water soluble PVA required a day or more; but when this operation was completed, the filter paper was air dried, leaving the crystal free on its surface. The crystal was then carefully transferred by means of the hairs of a fine brush to the tensile mount.

The tensile mount consisted of two surface ground steel bars held in a jig. One end of the tensile specimen was cemented to the upper support bar with a thin layer of DuPont conductive silver paint. This operation was accomplished by positioning the crystal and flowing a drop of acetone into the interface between the crystal and the previously applied paint. The jig was used to transfer the support bars and crystal to the tensile machine, where they were clamped rigidly in place. The jig was then removed, leaving the crystal supports in the desired alignment. The lower end of the specimen was then cemented to the lower bar in the same manner as described above for the upper end.

Tensile Test Apparatus

A line drawing of the apparatus for stress-strain tensile testing of single crystals of graphite is given in Figure 27; its basic components consist of:

- a. A tension load cell of the resistance strain gage type,
- b. An upper specimen grip attached rigidly to the tension element of the upper load cell,
- c. A lower grip attached rigidly to the crosshead,
- d. A crosshead (motion guided vertically), and
- e. A displacement transducer of the LVDT-type (linear variable differential transformer) to measure directly the motion of the crosshead.

The tension load cell was calibrated with standard weights, and the displacement transducer was calibrated by a micrometer, using a 50:1 displacement lever. The output from the load cell, measuring the tension in the specimen, was entered on the Y-axis of an X-Y recorder. The output from the displacement transducer was entered on the X-axis. This output (measuring the crosshead displacement) represents the specimen elongation and the machine compliance.

Perfect alignment of the machine was assured by mounting the load cell so that it could be translated and rotated (about any horizontal axis) until the flat surface-ground faces of the two specimen grips were in perfect alignment. Mounting of the specimen onto the two sample grips was effected by removing the grips from the testing machine to the laboratory bench and fixing them in proper relative position in the special jig according to the procedure described above.

Because the rigidity or stability of the upper grip assembly is limited by a quarter-inch threaded connection into the load cell, there is a possibility of some unavoidable bending of the upper grip assembly relative to the lower grip during removal of the specimen mounting jig. Since the slightest motion would damage the specimen, provision was made for the upper grip assembly to be held in place by a keeper which could slide up and down on the crosshead ways. The keeper was moved down, free of the upper grip assembly, just prior to testing so that only the specimen itself could exert a force on the load cell.

FIGURE 27. Tensile Test Apparatus for Single Crystal Graphite

N-6396

System Proving

The compliance of the microtensile machine, defined as all the compliance other than that attributed directly to the specimen, was measured. In one experiment, a solid steel bar was substituted for the specimen and supports, so that only the compliance of the machine was measured. In a second experiment, the machine compliance was measured with the specimen supports in place and a steel bar cemented to and connecting the supports; the cemented area was equivalent to the normal crystal grip area. Hence, the machine compliance and the compliance of the cement were measured. The compliance of the machine was measured with several cements: Duco cement, Courtright cement, Eastman 910 epoxy cement, and DuPont conductive silver paint. The silver paint gave the lowest compliance and was also the easiest to use with this specimen.

Many tests were made with metal foils of known elastic modulus to check the accuracy of the tester. Foils of titanium, aluminum, and tungsten were mounted by using silver paint, and the modulus was measured in the microtensile machine. Aluminum appeared to be so compliant that the yield point was reached in an indeterminate part of the stress-strain curve. This result was confirmed by testing on a larger Instron machine.

Titanium foil of about $1/4$ mil thickness was air-abrasive machined in the steel mask to the same size and shape as that used for graphite specimens and subsequently tensile tested. The modulus obtained with the microtensile machine was about 10×10^6 lb/in², whereas that indicated by the manufacturer is about 5×10^6 lb/in². This same specimen was then removed from the supports, and the area of the grip was trimmed in successive stages to determine whether the measured compliance was a function of grip area. The grip area was reduced from about five times that of the gage area to an area nearly equal to that of the gage area with no change in sample compliance.

Modulus values obtained with the microtensile machine using a tungsten ribbon as test specimen have ranged between 43.7×10^6 lb/in² and 57.7×10^6 lb/in². The handbook value is 51.5×10^6 lb/in². Much of the scatter in the values of these preliminary experiments with tungsten can be attributed to irregularities in the thickness of the specimen.

Results with Graphite Crystals

Preliminary results using cleaved compression-annealed pyrolytic graphite crystals instead of natural single crystals gave moduli very much lower than those obtained in the static, sonic, and ultrasonic tests on larger specimens. After the preliminary experiments were completed, several changes were made in the microtensile machine, and the machine tests described above were conducted. Further experiments are necessary to establish reproducibility of results and to determine the effect of gage length on the measured modulus. The great scatter in the results of past experiments on compression-annealed pyrolytic graphite occurred with specimens having gage lengths 6mm and lower. Most experiments on natural graphite crystals must be made with gage lengths below 3mm, due to the small size of available crystals.

5.2. Shear Tests of Graphite Single Crystals

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

An apparatus, designed to measure shear strength in both single crystal and pyrolytic types of graphite, is shown schematically in Figure 28. The main shearing carriage consists primarily of a $1\frac{1}{2}$ inch, 60-case hardened rod traveling in special adjustable split ball bushings with a tolerance of less than .005 inch. This rod is kept from rotating by a $1\frac{1}{4}$ inch outrigger arm traveling in a resiliently mounted ball bushing. The static friction of this entire carriage arrangement is on the order of 17 grams.

Perpendicular to the shearing carriage movement is mounted a normal displacement carriage containing four ball bushings riding on two $1\frac{1}{4}$ inch, 60-case hardened rods. This movement can also be actuated by a pulley arrangement and the shear studied as a function of normal force.

The detachable shearing heads, shown in the inset, vary in diameter from 2 to 8mm, thus accommodating a wide range in sample areas.

Because of the exceedingly low shear strengths of the small single crystals measured, the shearing force on the sample is provided by the weight of water flowing into a container which is connected to the shearing carriage. In this manner, the shear force can be continuously increased at almost any desired rate from a lower limit of about $1\frac{1}{2}$ gram per second.

N-6839

FIGURE 28. Single Crystal Shear Apparatus

For future modulus measurements, a differential transformer core of the Schaevitz shielded type has been attached to the shearing carriage and will be used in conjunction with a Daytronic 201 AH transducer-exciter-demodulator and a Mosely 2D X-Y recorder with time drive.

Figure 29 shows an overall view of the entire apparatus, and Figure 30 shows a closeup view of the shearing and displacement carriages with a sample in position for shearing. The natural single crystals were attached to the shearing heads with Eastman 910 epoxy cement. For maximum adherence, the crystals were first lightly etched with a gentle sand blast. Alignment of the crystals on the shear heads was carefully controlled, the cementing carried out in situ, and the cemented sample left in place for the actual shear.

N-7307

FIGURE 29. Overall View of Single Crystal Shear Apparatus

N-6924

FIGURE 30. Closeup View of Shearing and Displacement Carriages

The compression-annealed pyrolytic samples were cut from specific locations in the original compression-annealed block, cleaved, and then machined to the desired diameter on a lathe. These samples were also lightly etched by sand blasting to obtain sufficient adherence to the shear heads.

Typical results of the measurements on single crystal and pyrolytic samples are shown in Figure 31.

N-7233

FIGURE 31. Typical Shear Strength Results for Pyrolytic and Single Crystal Graphite

For single crystals, a generally expected initial increase in shear strength was common to all of the crystals measured. This condition is undoubtedly due to the occurrence of initial structural weak points, such as edge imperfections or partial internal delamination.

This assumption of initial imperfections is strengthened by the fact that the shear strength values saturate, becoming asymptotic to a value most representative of the true shear strength of the entire sample. Accordingly, an average taken (omitting the first shear) from a total of 20 shears on 9 crystals gives a shear strength of $4.2 \pm 0.8 \times 10^6$ dynes/cm². This value is corroborated by the value of 4.3×10^6 dynes/cm² as obtained from the shear of a highly annealed and uniform crystal ECP-1, shown in Figure 32.

N-6998

FIGURE 32. Uniform and Extended Shear of Single Crystal ECP-1

When this crystal was sheared, an extreme and rather unique example of plastic slip was obtained. At the moment the crystal began to shear, no further increase of stress was applied. The crystal, however, continued to slip until the shearing carriage hit the stop, a distance of 5.5mm, whereas the diameter of the crystal was only 4mm. The crystal had still not fractured at this point, and the two halves had to be separated manually. The slip steps (see Figure 32) form a quite clear "deck of cards" effect. This crystal was evidently very homogeneous, since over 125 uniformly spaced slip steps can be seen. In other cases, crystals did show partial individual slips, but these were pinned before the actual fracture point was reached.

The average value for the shear strength in single crystal graphite is also in good agreement with the value of 3.9 to 4.9×10^6 dynes/cm² quoted by Gillin and Kelly⁽¹⁶⁾ obtained by extrapolation to zero normal force from compression-shear measurements.

In the case of compression-annealed pyrolytic graphite, the results are considerably more dependent upon the initial fabrication conditions of the particular sample measured. Results of measurements on pyrolytic sample 3-M304-E indicate the somewhat erratic behavior of successive shear values. This characteristic was present in all of the pyrolytic samples measured.

The magnitudes of the pyrolytic graphite shear strengths are also much higher than those of the single crystals (see Table 7). The higher shear strengths of the pyrolytic samples were to be expected, since pyrolytic graphite is polycrystalline and the grain boundaries undoubtedly act as pinning points for dislocation movement along the basal planes of individual crystallites. In addition, the degree of preferred orientation of compression-annealed pyrolytic graphite, although good and less than one degree, is not perfect; thus, additional bonding forces are operative.

TABLE 7

INDIVIDUAL SHEAR STRENGTHS OF SINGLE CRYSTAL
AND PYROLYTIC GRAPHITE SAMPLES IN UNITS OF 10^6 DYNES/CM²

<u>THERMALLY ANNEALED SINGLE CRYSTALS</u>				
Sample	Area (mm ²)	Shear Strength	Gillin & Kelly	
EC-3*	13.4	4.8, 4.2		
EP-74	5.74	4.6, 4.1		
ECP-1	12.6	4.3		
ECP-2	12.6	4.6		
EP-84	12.8	2.8	~4.-5	
ECPA-6	7.74	6.8		
ECPA-5	6.52	3.7		
<u>COMPRESSION-ANNEALED PYROLYTIC</u>				
			Seldin (Extrapolated from compression- shear data to zero normal force)	Half- Width $\theta_{\frac{1}{2}}$
C-5	71.1	8.3 ± 1.4	8.9 ± 1.1	0.45°
2-M305-PS	50.2	12.4 ± 2.6	15.7 ± 5.4	0.19°
3-M304-E	33.1	9.2 ± 2.6		

* For single crystals, type and order of preparation methods are indicated by the prefix letters, i. e., E, Essex County; C, cut; P, purified and annealed at 3000°C; and A, additional anneal at 3100°C.

6. STATIC TESTS ON PYROLYTIC GRAPHITE

The objective of the static tests on pyrolytic graphite was to obtain stress-strain curves to fracture in tension, compression, and torsion and to measure shear strengths. The tension and compression testing was performed on an Instron machine, using the load cell on the Instron to detect the stress and pairs of strain gages on the specimen to detect the longitudinal and transverse strains. The stress-strain curves were recorded during the test on X-Y recorders. In addition, one flexure test was performed on a bar of compression-annealed pyrolytic graphite to check the tension test results.

The shear strength tests were also performed on the Instron by compressing the graphite specimens between wedge-shaped fixtures. The torsion tests were run on a separate apparatus. Although the major part of the work was devoted to the testing of compression-annealed pyrolytic graphite, the elastic constants of as-deposited pyrolytic graphite were also determined.

Notation for Elastic Constants

For a linear material, the results of static tests can be expressed easily either in terms of the elastic compliance constants s_{ij} or in terms of engineering constants. The elastic compliance constants, for materials such as single-crystal and pyrolytic graphite which have hexagonal symmetry, are defined by the following equations relating strain ϵ_i to stress τ_i :

$$\begin{aligned} \epsilon_1 &= s_{11} \tau_1 + s_{12} \tau_2 + s_{13} \tau_3, & \epsilon_4 &= s_{44} \tau_4, \\ \epsilon_2 &= s_{12} \tau_1 + s_{11} \tau_2 + s_{13} \tau_3, & \epsilon_5 &= s_{44} \tau_5, \\ \epsilon_3 &= s_{13} \tau_1 + s_{13} \tau_2 + s_{33} \tau_3, & \epsilon_6 &= 2 (s_{11} - s_{12}) \tau_6. \end{aligned}$$

Since there is no commonly agreed upon notation for the engineering constants of anisotropic materials, these constants are denoted by the combination of elastic compliance constants to which they are equal. That is, the Young's moduli parallel and perpendicular to the symmetry axis are $1/s_{33}$ and $1/s_{11}$; the Poisson's ratio associated with τ_3 is $-s_{13}/s_{33}$, and the Poisson ratios associated with τ_1 are $-s_{12}/s_{11}$ and $-s_{13}/s_{11}$; and the torsion or shear modulus is $1/s_{44}$.

6.1. Tensile Tests on Pyrolytic Graphite

E. J. Seldin and T. Weng

In the tensile test, the stress τ_1 was applied parallel to the layer planes. The strain gages which detected the longitudinal strain ϵ_1 allowed the determination of the compliance s_{11} (or the Young's modulus $1/s_{11}$), whereas the gages which detected the transverse strains allowed the determination of the compliances s_{12} and s_{13} .

Several specimen designs and methods of gripping the compression-annealed pyrolytic graphite specimen were tried before a standard design and testing method was selected. The first tensile specimens were rectangular slabs which were gripped at each end by clamps; the specimens proved to be too fragile and they also slipped out of the clamps at stresses well below the fracture strength. A technique of potting the ends of the specimen (after the specimen had been formed in a dog bone shape with rounded shoulders) in epoxy resin was also tried. This method worked well for the as-deposited pyrolytic graphite specimens, but tests on the compression-annealed pyrolytic graphite specimens revealed that the strains detected on the c-faces were much greater than those detected on the a-faces. It was hypothesized that there was a nonuniform stress distribution in the gage section along the c-axis, with the outer layers of the specimen on which the gages were mounted being subjected to greater strain than the inner layers. Several tests were performed in which the size of the epoxy end pieces at the shoulders of the specimen was reduced and the force of attachment of the c-faces of the specimen to the epoxy was reduced, all of which tended to reduce the observed c-face strains and thereby confirm the hypothesis.

The tensile specimen design and the method of gripping the specimen which were finally chosen are shown in Figure 33. The specimen has straight shoulders and is mounted in metal end pieces. The specimen and end pieces were aligned in a special fixture, while epoxy cement was used to fill in the gaps between the ends of the specimen and the end pieces and also along the edges of the specimen as a fillet material between the specimen and the metal. The epoxy maintained the alignment of the specimen in the end pieces and also reduced the tendency for the layer planes to delaminate and fold back along the metal during the tensile test. With this design, the strains detected on the c-faces of the specimen were no longer consistently greater than those detected on the a-faces.

The stress-strain curves for both the longitudinal and transverse strains all tended to be linear in the tensile test. However, the experimental values of the Young's modulus $1/s_{11}$, as determined by the static tensile tests, were found to vary over a wide range. The tests conducted on specimens of the type shown

in Figure 33 gave $1/s_{11}$ in the range 47 to 108×10^{11} dynes/cm². The variation found in $1/s_{11}$ may be due to nonuniform stress distributions in specimens which are not perfectly flat and also to imperfections in the material. There is no good correlation, however, between the value of $1/s_{11}$ and the quality of the material as given by the half-width of the optical reflectivity measurement.

6.2. Flexural Test on Pyrolytic Graphite

T. Weng

A flexure test using 4-point loading was made on one bar of compression-annealed pyrolytic graphite.⁽³⁾ The load was applied perpendicular to the c-direction, and strain gages were applied to the two a-faces in the center of the bar to measure the tensile and compressive strains. The value of $1/s_{11}$ determined from both of the strain measurements was 80.5×10^{11} dynes/cm². The values of $1/s_{11}$ obtained in tensile tests on specimens from the same original block ranged from 59 to 108×10^{11} dynes/cm². The graphite which was tested was commercial-quality material, and the flexural test gave a modulus which was close to the average value obtained for the same material in the tensile tests.

6.3. Compression Tests on Pyrolytic Graphite

E. J. Seldin

Specimens of as-deposited pyrolytic graphite in the shape of rectangular parallelepipeds were tested in compression on the Instron machine. The specimens stood on the self-aligning table on top of the compression load cell. With the applied stress τ_3 perpendicular to the deposition surface, the stress-longitudinal strain curves tended to be nonlinear with increasing slope. When the applied stress τ_1 was parallel to the deposition surface, the variation of the slope of the stress-longitudinal strain curve with increasing stress was less consistent, and the results were somewhat different depending on whether the longitudinal strain gages were on the a-faces or c-faces. The moduli were determined from the slopes of the curves at high stress. For both pressing directions, the plots of transverse strain versus longitudinal strain were fairly linear so that the Poisson ratios in compression were essentially independent of stress.

For compression-annealed pyrolytic graphite, the applied stress τ_3 in the compression test was only along the c-axis. The strain gages, which detected the longitudinal strain ϵ_3 , allowed the determination of the compliance s_{33} (or the Young's modulus $1/s_{33}$). The compliance s_{13} could not be determined for compression-annealed pyrolytic graphite in the compression test because the Poisson ratio- s_{13}/s_{33} is so low that the measurement of the transverse strain ϵ_1 for this material was obscured by the transverse sensitivity of the strain gages.⁽⁴⁾

The compression-annealed pyrolytic graphite compression specimens were machined in the form of cylinders, with the maximum height of each cylinder being limited by the thickness of the pressed pyrolytic graphite disk (maximum thickness ≈ 0.3 inch). Characteristically, the stress-strain curves of short cylinders, whether of graphite or steel, were nonlinear. Tests on cylinders of steel and compression-annealed graphite showed that the quality of the stress-strain curves improved as the length-to-diameter ratio of the cylinders increased. A specimen diameter of $1/4$ inch was chosen as a standard; with this diameter, the specimen had a sufficiently high length-to-diameter ratio and sufficient surface area for the application of strain gages. However, with this size specimen, the stress-strain curve became overly sensitive to the position of the specimen on the self-aligning table.

The difficulty with the self-aligning table was resolved by placing the specimen in a compression cage with plane-parallel opposing faces. Excellent results were obtained with the specimen in the compression cage, but only when the specimen had perfectly flat, plane-parallel end faces. When the end faces of the specimen were not perfectly flat and plane-parallel, the linearity of the stress-strain curve could be improved by cementing the specimen between two steel cylinders with carefully ground plane-parallel end faces while the assembly was being aligned in a V-block; the objective of this method was to fill in the surface irregularities of the graphite with cement.

One well-aligned $1/4$ inch diameter cylindrical specimen of compression-annealed pyrolytic graphite with naturally plane-parallel end faces, which was tested in the compression cage without end pieces, yielded a perfectly linear

stress-strain curve and until failure, behaved, under a cyclic stress, like a perfectly elastic material; the average modulus for several tests was $1/s_{33} = 3.65 \pm .07 \times 10^{11}$ dynes/cm². For most of the specimens which were tested, the modulus was determined from the linear regions of the stress-strain curves at high stress. Values of $1/s_{33}$ ranging from 3.3 to 4.4×10^{11} dynes/cm² were obtained.

The maximum stress at failure varied between 36,000 and 59,000 lb/in². Failure always occurred by shear along layer planes; sometimes a specimen sheared along only one plane, but there were several cases in which a thin layer of material sheared out of position. The maximum compressive stress at failure is believed to be highly dependent on the degree of alignment of the layers in the material.

6.4. Torsion Tests on Pyrolytic Graphite

E. J. Seldin

In the torsion test, a solid cylinder of radius R and length L , with its longitudinal axis parallel to the c -axis, was subjected to a torque T . The modulus of rigidity $G = 1/s_{44}$, assuming the material to be linearly elastic, is given by

$$(1) \quad G = 2TL/\pi R^4 \theta,$$

where θ is the angle of rotation. The shear stress τ_4 within the cylinder varies linearly with the radius r according to the relationship

$$(2) \quad \tau_4 = 2Tr/\pi R^4.$$

The maximum shear stress at failure $\tau_{\max}$ due to a maximum torque $T_{\max}$ occurs at the periphery of the cylinder and is given by

$$(3) \quad \tau_{\max} = 2T_{\max}/\pi R^3.$$

The torsion test specimens were solid $1/2$ inch diameter disks which varied in length from .03 to .38 inch. The torsion apparatus is shown in Figure 34. The specimen was cemented between steel rods, and the torque was applied through a torsion shaft by dead weight loads. The rotation of one rod relative to the other was detected by means of a linear variable differential transformer (LVDT) which followed the motion of a 5-inch long lever arm attached

N-7287

FIGURE 33. Tensile Specimen Mounted in Metal End Pieces

to the movable rod. The curve of torque-vs.-angular deformation was linear near the origin, but it became nonlinear as the torque was increased and showed residual strain and hysteresis loops when the torque was cycled. The shear modulus $1/s_{44}$ was determined from the initial slope of the torque-vs.-angular deformation curve after correcting for the compliance of the apparatus. Because the true stress-strain curve for shear is not linear, Equations (2) and (3) do not hold exactly. Nadai⁽¹⁷⁾ has given geometrical transformation formulae for obtaining the curve of stress-vs.-angular deformation from the curve of torque-vs.-angular deformation. Nadai's correction, when applied to the torsion data for compression-annealed pyrolytic graphite, causes the true maximum shear stress at failure to be approximately 15 per cent lower than that given by Equation (3).

N-6759

FIGURE 34. Static Torsion Apparatus

Figure 35 is a representative plot of torque-vs.-angular deformation per unit length for a specimen of compression-annealed pyrolytic graphite tested in torsion to failure. A series of tests was usually run on a given specimen by using the successively smaller pieces which remained after each test; the value of the shear modulus generally fluctuated slightly in a random manner with successive tests, whereas the shear strength tended, in general, to increase with successive tests. The values of $1/s_{44}$ for compression-annealed pyrolytic graphite fell within the range of 0.018 to 0.031×10^{11} dynes/cm².

One specimen of as-deposited pyrolytic graphite was tested in a static torsion test. The shear modulus $1/s_{44}$ was determined from the initial slope of the curve of torque-vs.-angular deformation to be 0.13×10^{11} dynes/cm².

6.5. Static Shear Tests on Pyrolytic Graphite

E. J. Seldin

Shear strengths were obtained by compressing thin slabs of compression-annealed pyrolytic graphite between wedge-shaped compression-shear fixtures of the type shown in Figure 36. Several sets of shear fixtures were made; the area of the shear face was varied and four different angles of inclination of the shear faces were employed ($\theta = 15, 30, 45$ and 60 degrees). The force at shear failure was measured, and the normal and shear stresses were calculated from the shear force, the area of the shear face, and the angle of inclination. Plots were made of the shear stress vs. the normal stress, and the data were extrapolated linearly to find the shear stress in the limit of zero normal stress.

The values of shear strength in the limit of zero stress were found to range between 120 and 350 lb/in². For any particular specimen, the experimental values of shear strength varied 10 to 30 per cent about an average value. Tests with the same material in different size fixtures indicated that the shear strength was independent of the size of the fixture. The shear strengths obtained with the compression-shear fixtures also were in good agreement with those obtained for the same material in the torsion test and in the pure shear test, when such tests were performed. In general, the better quality graphite showed lower shear strength; in this sense, the shear strength is an indication of material quality.

N-6961

FIGURE 35. Torque vs. Angular Twist per Unit Length for Compression-Annealed Pyrolytic Graphite Specimen.

N-6370

FIGURE 36. Typical Stainless Steel Shear Fixtures.

6.6. Results of Static Tests on Pyrolytic Graphite

Table 8 summarizes the results of the static tests on the as-deposited and compression-annealed pyrolytic graphites. The table gives average experimental values for the Young's moduli, the shear modulus, the compliances s_{12} and s_{13} , and the Poisson ratios. The spread in values of $1/s_{11}$ for compression-annealed pyrolytic graphite given in Table 8 does not include the extreme values quoted in Section 6.1. Most of those extreme values were excluded because they could be attributed to obvious defects in the specimen; for example, a strain gage over a kink showed an abnormally high strain when the stress was applied, whereas a gage adjacent to a kink showed an abnormally low strain. In a similar manner, some of the extreme values for the modulus $1/s_{33}$ quoted in Section 6.3 have also been excluded. A range of values is given for both the shear strength and the c-axis compressive strength. The value for the a-axis tensile strength is the highest thus far observed; the true strength along the planes has not been obtained in our tensile tests because failure was always influenced by the presence of defects and imperfections in the specimen.

TABLE 8
RESULTS OF STATIC TESTS ON PYROLYTIC GRAPHITE

		Compression-Annealed Pyrolytic Graphite	As-Deposited Pyrolytic Graphite
Moduli (10^{11} dynes/cm ²)	$1/S_{11}$	88 ± 11	4.2 ± 1.2
	$1/S_{33}$	$3.7 \pm .5$	$1.9 \pm .3$
	$1/S_{44}$	$.025 \pm .007$	0.13
Compliances (10^{-11} cm ² /dyne)	S_{12}	$-.0018 \pm .0006$	$.48 \pm .09$
	S_{13}	$-.0033 \pm .0008$	-3.3 ± 1.3
Strength (lb/in ²)	a-axis Tensile	$\sim 15,000$	
	c-axis Compressive	$36,000 - 59,000$	
	Shear	$120 - 350$	
Poisson Ratios	$-S_{12}/S_{11}$	$.16 \pm .03$	$-.12 \pm .03$
	$-S_{13}/S_{11}$	$.30 \pm .07$	$.97 \pm .05$
	$-S_{13}/S_{33}$	$\sim .01$	$.35 \pm .07$

7. ULTRASONIC AND RESONANT BAR TESTS OF PYROLYTIC GRAPHITE

O. L. Blakslee, D. G. Proctor, and G. B. Spence

The objective of the ultrasonic and resonant bar tests was to measure most, but not all, of the elastic constants. This work supplements the static testing by providing more accurate values in the limit of near zero stress than can be obtained by static tests.

Analysis of the various resonant frequencies of vibrating bars cut in different orientations yields values of the elastic compliance constants s_{ij} . On the other hand, analysis of the velocities of ultrasonic pulses of longitudinal or transverse waves traveling in different directions yields values of the elastic stiffness constants c_{ij} . Since there are algebraic equations relating the s_{ij} and the c_{ij} , there is a redundancy in measuring both sets of constants. For the present program on compression-annealed pyrolytic graphite, this redundancy is a major advantage in that it provides a cross check on the accuracy of the experimental methods when applied to a material far more anisotropic than any previously studied. In addition, if it is not possible to measure all five c_{ij} and all five s_{ij} , it may be possible to calculate the unmeasured constants from combinations of measured s_{ij} and c_{ij} .

The extreme anisotropy, weak shear strength between layers, and high internal friction of compression-annealed pyrolytic graphite present new problems not encountered in ultrasonic and resonant bar testing of ordinary materials. Much of the work was directed towards solving these problems. As in the static testing, it has been helpful to test as-deposited pyrolytic graphite to gain experience on a material of intermediate difficulty.

Notation for and Relations Between Elastic Constants

The elastic stiffness constants for materials with hexagonal symmetry are defined by the equations:

$$\begin{aligned} \tau_1 &= c_{11}\epsilon_1 + c_{12}\epsilon_2 + c_{13}\epsilon_3, & \tau_4 &= c_{44}\epsilon_4, \\ \tau_2 &= c_{12}\epsilon_1 + c_{11}\epsilon_2 + c_{13}\epsilon_3, & \tau_5 &= c_{44}\epsilon_5, \\ \text{and } \tau_3 &= c_{13}\epsilon_1 + c_{13}\epsilon_2 + c_{33}\epsilon_3, & \tau_6 &= c_{66}\epsilon_6 = \frac{1}{2} (c_{11} - c_{12})\epsilon_6. \end{aligned}$$

For hexagonal symmetry, the elastic compliance constants are related to the elastic stiffness constants by the equations:

$$s_{11} + s_{12} = c_{33}/c,$$

$$s_{13} = -c_{13}/c,$$

$$s_{11} - s_{12} = 1/(c_{11} - c_{12}),$$

$$s_{44} = 1/c_{44},$$

$$s_{33} = (c_{11} + c_{12})/c,$$

$$\text{in which } c = c_{33} (c_{11} + c_{12}) - 2c_{13}^2.$$

7.1. Resonant Bar Tests

A. Apparatus and Techniques

In the resonant bar test, the bar is set into vibration by a stereophonograph cartridge excited by an audio oscillator. The vibrations are detected by a second stereophonograph cartridge the output of which, after preamplification, is displayed on a cathode ray oscilloscope. The resonant frequency for maximum amplitude of vibration is measured on a Beckman Universal EPUT and Timer Model 7350. The separation of vertical and horizontal motion by the stereo cartridges greatly facilitates the identification of the mode of vibration.

The resonant bar testing of stress-annealed pyrolytic graphite presents two problems. First, because pyrolytic graphite is made only in relatively thin pieces, it is not possible to cut a bar oriented perpendicular to the basal plane which is long enough (about 2 inches) for measurement. Those measurements would give the important constants s_{33} and s_{44} . One attempt to obtain longer specimens has been made by gluing several short pieces together. Several adhesives were tried: thermoplastic cement, epoxies, pitch, waterglass, and Duco cement. Waterglass and, perhaps, pitch have the advantage of resistance to neutron irradiation. With the compression-annealed material presently available, it was necessary to use about 10 glue joints to build up a bar 2 inches long; and the bar was very weak due to the low shear strength between layer planes. The probability of making one bad joint in 10 is large enough that this method is not very effective, although it might become so with thicker, undelaminated samples.

The second problem concerns the theoretical analysis of the flexural vibrations of a bar oriented with its axis parallel to the basal planes. Baker and Kelly⁽¹⁸⁾ have shown from studies of a graphite single crystal vibrating as a cantilever beam that, if the plane of vibration is perpendicular to the basal plane, the resonant frequency is determined primarily by the shear modulus $1/s_{44}$; however, if the plane of vibration is parallel to the basal plane, the resonant frequency is determined primarily by the Young's modulus $1/s_{11}$. Baker and Kelly used Timoshenko's equation to analyze their data. Since this equation is based on certain approximations, a literature search was undertaken to see (1) if a more exact solution of the flexural vibration problem had been made recently, (2) if there was any estimate of the possible error resulting from the application of Timoshenko's equation to the case where shear is more important than bending, and (3) if there is any plate mode of vibration which might give the shear constant $1/s_{44}$ more accurately. The answer to all three questions was no.

The necessity of working with small samples in this program has led to the design and construction of a new sample holder for the resonant bar apparatus. An inexpensive Atlas lathe bed was adapted to hold the small samples and the cartridge arms. Three carriages are mounted on the bed. The carriage tool post slide is mounted vertically on the middle carriage and used for sample height adjustment. A special rack was made to hold the sample while it was positioned on nodal point supports and to permit the sample to be raised or lowered so that the cartridges may clear the sample during the nodal point search procedure. The other two carriages hold Rek-O-Cut stereo cartridge arms which are adapted for the resonant bar work. The lathe bed and carriages are a convenient method of obtaining precisely controlled motion in two perpendicular directions. This apparatus facilitates measurements of small samples which are otherwise quite difficult to hold in position.

Figure 37 shows the entire apparatus, and Figure 38 shows the details of the rack which holds the sample. The rack has three supports. The two side supports slide in a track and are attached to a pair of arms that act as

proportional dividers. The positions of the nodal points* are symmetric about the center of the bar, and the distance between a given pair of nodal points for any particular resonance is proportional to the length of the bar. When the pins on the divider arms are placed at the ends of a bar, the supports are automatically set for the fundamental flexural or the second torsional-second longitudinal nodal points, depending upon where along the arms the pins are set. A tee-square slide is used to assure correct positioning of the sample on the supports. For all odd harmonics (fundamental = 1) of the longitudinal and torsional resonances and all even flexural resonances, there is a nodal point at the center. When one of these modes is measured, a knob on the left is turned which raises the center support above those on either side by means of a cam.

The transducers (Weathers stereo cartridges C-501 wired for either vertical or horizontal drive and receive) are mounted so that they can be quickly positioned for either transverse or longitudinal vibrations without affecting the balance of the tone arms. Either of the tone arms or both can be raised from the sample by foot-switch-operated electromagnets, leaving the operator's hands free to manipulate the sample or transducers.

One of the features of this apparatus is the versatility and precision of adjustment. The three carriages can be roughly positioned by the hand traverse, and the two pickup arms can be precisely moved horizontally by the crossfeed in one direction and the compound rest in the other. The sample can be positioned horizontally by the crossfeed and vertically by the compound rest.

* It is important to suspend a resonant bar at its nodal points so that the resonant frequency is not affected by the support.

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FIGURE 37. Sonic Modulus Resonant Bar Apparatus

N-6775

FIGURE 38. Details of Sample Holder for Sonic Measurements

B. Resonant Bar Theory: Timoshenko's Equation

The flexural vibrations of a long thin bar are described rather accurately by a differential equation proposed by Timoshenko.⁽¹⁹⁾ Timoshenko's contribution was to include, in an approximate way, the deformation of the bar due to the shear of one cross-section with respect to its neighbor. The solution of Timoshenko's equation for appropriate boundary conditions at the ends of the bar yields a transcendental equation involving: the resonant frequency, f ; the Young's modulus parallel to the axis of the bar, E ; the shear modulus, G , for the shear of one cross-section over another; and quantities related to the dimensions of the bar. The transcendental equations for the various end conditions have been extensively studied from the point of view of predicting the resonant frequency if the dimensions and elastic moduli are known. For the present purpose, the problem is reversed: we wish to compute the value of one modulus from the measured resonant frequency and a known value of the other modulus. So that this computation might be made economically for a large number of bars, a program was written for a digital computer. Details of the computer program were given in an earlier report.⁽³⁾

In his equation, Timoshenko introduced a constant k , of the order of unity; with the introduction of this constant, the true distribution of shear stress over the cross-section of the bar is replaced by a single average value. For a specified bar in a particular mode of vibration, it is possible to find a value of k such that the solution of Timoshenko's equation is exact.

The flexural vibrations were analyzed, using an iterative method of calculation: initially, a guess was made for the input values of the moduli and k for the computer program; then, moduli were calculated from the resonant frequencies and the input data. On the basis of this calculation, the input values of the moduli and k were adjusted; and the process was repeated until the moduli calculated from the different harmonics agreed, on the average, with the input values. It was found that a small error in the input value of E (or G) would cause a large error in the computed values of G for the first few harmonics (or of E for the higher harmonics.) For isotropic materials, this process determines unique values of E , G , and k . For materials of

hexagonal symmetry and bars cut parallel to the basal plane, this process must be supplemented by an independent measurement of one of the four quantities c_{44} , c_{66} , and the two k values associated with these moduli.

For the compression-annealed pyrolytic graphite bars, $1/s_{11}$ was calculated from the c_{66} measured by ultrasonics and the fundamental flexural resonance parallel to the basal plane (FFT). The $1/s_{44}$ was found by two methods: (1) the flexural resonances perpendicular to the basal plane (FFD) and the $1/s_{11}$ calculated by FFT, and (2) the fundamental torsional resonance and the c_{66} measured ultrasonically. The Timoshenko shear equivalence constant k used in the flexural calculations was 0.85.

In calculating $1/s_{44}$ from the flexural resonant frequencies, we found that the results for thick (c-axis dimension) specimens and high harmonics were less affected by changes of assumed $1/s_{11}$ than were those results for thin specimens and low harmonics.* Slight errors in the thickness or width dimensions caused approximately the same per cent error in the calculated modulus, and in the same direction. Errors in the length of the bar caused two or three times as much error in the calculated modulus, but in the opposite direction. Only the fundamental torsional resonant frequency was used in the calculation of $1/s_{44}$; for reasons which are not yet understood, the higher harmonics of the torsional vibration led to exceptionally high values of $1/s_{44}$ which were not in agreement with any other determinations of this modulus.

7.2. Compound Oscillator

The resonant bar tests discussed in the previous section were made on bars several inches in length along the a-axis. Resonant bar tests could not be made on free-standing bars having their long dimensions along the c-axis because the maximum possible length of such bars would be approximately 0.3 inch and the resonant frequencies would be too high to measure. However, resonant bar measurements are possible on very short specimens if the ends of the short pieces of graphite are weighted; this weighting results in a compound

* Increasing the input $1/s_{11}$ decreases the calculated $1/s_{44}$. If one calculates $1/s_{11}$, decreasing the input $1/s_{44}$ increases the calculated $1/s_{11}$; but the low harmonics are then affected less than the high.

oscillator with resonant frequencies in a measurable range. The compound oscillator most commonly used in this work was a short cylinder of graphite approximately $1/4$ inch by $1/2$ inch diameter, weighted on both ends by pieces (inertia masses) of $3/4$ inch long steel drill rod of the same diameter.

Thermoplastic cement and salol (phenyl salicylate) were both used successfully as bonding agents between the graphite and steel. Each has one drawback; the former gives a thick joint and the latter a joint which is very fragile and sensitive to shock.

The moduli of the specimen were calculated from the resonant frequencies, and the densities, dimensions, and known moduli of the inertia masses by means of a pair of transcendental equations; the solutions of these equations were programmed for a digital computer. The equations are:

For odd harmonics

$$X \tan X = \frac{M}{2M'} \cdot \frac{Y}{\tan Y},$$

and for even harmonics

$$\frac{X}{\tan X} = \frac{-M}{2M'} \cdot \frac{Y}{\tan Y},$$

where

- $X = \pi f l \sqrt{\rho/E}$
- $Y = 2\pi f l' \sqrt{\rho'/E'}$
- $f =$ resonant frequency
- $l =$ specimen length
- $l' =$ length of individual inertia mass
- $\rho =$ specimen density
- $\rho' =$ density of inertia masses
- $E =$ specimen modulus
- $E' =$ modulus of inertia masses
- $M =$ mass of specimen, and
- $M' =$ mass of individual inertia mass.

The inertia masses are assumed to be identical.

These equations were applied to the case of the compound torsion oscillator (CTO), where the resonance was in torsion, and to the compound longitudinal oscillator (CLO), where the oscillator vibrated in a longitudinal mode. The equations could be used with specimens and inertia masses having cross-sections of different shape and area; but it should be emphasized that the equations are rigorously correct only for round compound torsion oscillators in which the specimens and inertia masses are of the same diameter.

Compound oscillators were constructed with pyrolytic graphite centers and steel and also with different combinations of metals. Best results were obtained with the torsional resonance. For aluminum between steel end pieces, the calculated modulus of rigidity was 3 per cent low. For compression-annealed pyrolytic graphite between steel end pieces, the values of $1/s_{44}$ were consistently 2 to 5 per cent lower than the value obtained by ultrasonics on the same specimen. The ultrasonic technique has been carefully checked and is regarded as accurate; even so, it is not completely clear that the CTO determination is in error, because the ultrasonic wave averages the elasticity values of the material through which it is propagated in one way, whereas the compound oscillator averages elasticity values in a different way. It is possible, however, that the discrepancy is an error resulting from the quality of the glue joints; the analysis assumes perfect junctions.

The moduli determined with the compound longitudinal oscillator (CLO), whether made of graphite and steel or combinations of different metals, were always too low. The calculated modulus tended to approach more closely to the true value as the length of the specimen increased and as the modulus and density of the inertial masses increased. However, moduli can be determined more easily and more accurately by means other than the CLO.

7.3. Ultrasonic Tests

The velocity v of a wave traveling through a material of elastic modulus E and density ρ is given by $v = \sqrt{E/\rho}$. The objective of the ultrasonic test is to determine the modulus from a measurement of the velocity of a wave. In practice, the measurement which is actually made is the transit time for a pulse through a specimen of known length or the time for a pulse to travel through the specimen and be reflected back to the transmitter. The modulus which is

determined depends on the direction and mode of propagation of the wave in the material. For compression-annealed pyrolytic graphite, a wave propagated along the a-axis will yield the modulus c_{11} or c_{66} , depending on whether the mode of vibration of the wave is longitudinal or transverse. For a wave propagated along the c-axis, the modulus which is determined will be either c_{33} or c_{44} , depending on whether the mode of vibration is longitudinal or transverse.

The ultrasonic testing was done by the pulse technique using an Arenberg Pulsed Oscillator Model PG-650C and a Tektronix Dual-Beam Oscilloscope Type 555. Initial measurements on compression-annealed pyrolytic graphite showed that the ultrasonic attenuation was very high. Even at a frequency as low as 1 mc, the attenuation coefficient, in db/cm, associated with the measurement of c_{44} was a factor of 10 to 100 times higher than that for polycrystalline graphite and 100 to 1000 times higher than that for metals. With such high attenuation, pulse-echo methods in their simplest form are not satisfactory; more elaborate procedures had to be used. Because of the high attenuation, an Arenberg Model PA 620 narrow-band preamplifier was included in the receiver transducer circuit to improve the signal-to-noise ratio.

The choice of a couplant to attach the transducer to the sample presented somewhat of a problem. Thermoplastic cements cannot be used because the heating necessary to attach the transducer will also cause some annealing of the room-temperature radiation damage. It was found that stopcock greases, such as Nonaq, will not effectively couple shear waves at the low frequencies which had to be used to avoid high attenuation. The best couplant tried was salol (phenyl salicylate). The salol was applied as a super-cooled liquid at room temperature. After the transducer was positioned, the salol was crystallized by seeding the excess at the edge of the transducer. The transducer could be removed by heating (for nonirradiated samples) or by soaking in acetone for about 2 hours.

Ultrasonic measurements on compression-annealed pyrolytic graphite were made by the buffer rod technique illustrated in Figure 39. For the measurement of c_{11} and c_{66} , some echoes were received; thus, two methods could be used. First, only one crystal was used for both transmitting and

receiving, in which case the buffer rod was necessary so that the electronics might recover from the initial large electrical driving pulse before the echoes returned. This method has the advantages of cleaner pulses and of requiring only one joint next to the sample. In the second method, the echoes were received by attaching a second transducer to the opposite side of the sample. This method has the advantage of better electrical isolation between the transmitting and receiving circuits.

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FIGURE 39. Ultrasonic Buffer Rod Method: XT = Crystal Transmitter, B = Aluminum Buffer Rod, S = Sample, and XR = Crystal Receiver.

Values for c_{33} and c_{44} were determined by measuring the transit time of a single pulse traveling in one direction through the sample, because no good echoes were received. This transit time was obtained from the difference between the total transit time of the pulse traveling through the buffer rod plus sample and the transit time of the pulse traveling through just the buffer rod. Using this technique, one need not know the time delay between the start of the driving electrical signal and the start of the mechanical vibrations in the transducer. The ultrasonic attenuation was found from the transmission coefficients and the decrease in receiver signal voltage between the buffer rod and the sample positions.

Although quartz crystals are preferred because of their durability and stability, PZT-5 transducers were used for transmitting because of their higher electromechanical efficiency. The receiver transducer is used nonresonantly (for example, a 5 mc transducer for a 1 mc pulse), in order to avoid modifying the shape of the acoustic wave train.

Some tests were made to check the influence of the specimen size on the value of the modulus which was determined.⁽⁴⁾ The velocity of a longitudinal wave along the a-axis was determined first for a bar of compression-annealed pyrolytic graphite and then for the two pieces into which it was cleaved. Slightly lower velocities (0.1 and 0.6 per cent lower) were determined for the two smaller bars, indicating a possible wave guiding effect; however, the effect is negligible for our purposes. One other phenomenon which has been observed in the compression-annealed pyrolytic graphite may be due to wave guiding: it was found impossible to propagate 1 mc longitudinal waves along the c-axis of $1/2$ inch diameter disks without complete distortion of the wave form. No difficulty was encountered in propagating the same longitudinal waves through the same specimens when they were 1-inch disks. On the other hand, shear waves at 1 mc were easily propagated through the same specimens both before and after they had been machined to $1/2$ inch diameter. The c_{44} measured were the same in both cases.

In another series of tests,⁽³⁾ measurements of the transit time of a shear wave along the c-axis of a specimen and then along the three parts into which it was cleaved led to consistent results: the sum of the transit times through the parts was equal, within the limits of experimental error, to the transit time through the original piece. However, there was some variation in the shear modulus c_{44} through the material.

7.4. Stress Derivative of c_{33} and c_{44}

The change of c_{33} and c_{44} with c-axis compressive stress was investigated.⁽⁴⁾ The moduli were determined by the ultrasonic test method while the specimen was compressed, using the apparatus shown in Figure 40. Pressure was applied to the specimen by squeezing the entire assembly shown in Figure 40 in a hydraulic press. The change in transit time of the pulse was measured as a function of pressure.

The stress derivative of c_{33} , given by $\frac{1}{c_{33}} \frac{dc_{33}}{d\sigma}$, was evaluated using 5 mc longitudinal waves for two specimens of compression-annealed pyrolytic graphite: the values obtained were 9.1 and 12.6×10^{-11} cm²/dyne. Expressed

in another set of units, the values of the stress derivative are 0.63 and 0.87 per cent per 1000 lb/in². In the first approximation, the stress derivative of c_{33} is constant; closer examination of the data reveals that this value may increase slightly with increasing compressive stress.

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FIGURE 40. Apparatus for Compressional Stress Derivative Measurements

An attempt was also made to find the stress derivative of c_{44} , but attenuation of the 5 mc waves forced the use of 1 mc waves, further reducing the precision by a factor of five. In addition, coupling of the shear wave proved difficult. No definite values of the stress derivative of c_{44} were found, but it was determined qualitatively that this derivative is very close to zero or slightly negative.

7.5. Results of Ultrasonic and Resonant Bar Tests

A summary of the experimental results of the ultrasonic and resonant bar tests is presented in Table 9, which includes values for the elastic constants of as-deposited and compression-annealed pyrolytic graphite.

For the as-deposited pyrolytic graphite, the tests were run on two materials of different quality.⁽¹⁾ The values for the elastic constants given in Table 9 are averages for the two materials. The resonant bar test gave $1/s_{11}$ and the ultrasonic test yielded directly four stiffnesses. The four measured stiffness constants and the one measured compliance constant form five independent constants. From these constants, the remaining five constants can be computed from the transformation equations given on Page 72. The calculated value of c_{12} is given in Table 9. The four missing compliances were calculated from the equations for each of the two materials, and the values which were obtained were in good agreement with those obtained directly in static tests. It was interesting to note that the combined ultrasonic and resonant bar data confirmed both the positive sign and the magnitude of the static values of s_{12} .

For the compression-annealed pyrolytic graphite, the values of the elastic constants in Table 9 are, in all but one case, average values which are midway between the maximum and minimum values which were obtained for large numbers of specimens. The numbers in Table 9 are meant to show, mainly, the range of values which were obtained. A more selective choice of data on high quality materials leads to slightly different "average" values than those given in Table 9; an analysis of the data is given in Section 8 in which more selective average values were used.

The resonant bar results in Table 9 show considerable variation in the values of $1/s_{11}$. The results on individual specimens⁽⁴⁾ lead us to conclude that the value of $1/s_{11}$ determined by the resonant bar test is extremely dependent on the quality of the material; the better quality compression-annealed pyrolytic graphite gave values of $1/s_{11}$ from 89 to 99 x 10¹¹ dynes/cm². The values of $1/s_{44}$ obtained from the resonant bar tests were in good agreement with the values of c_{44} obtained for the same material in the ultrasonic test.

The compound torsion oscillator (CTO) test gave excellent values for c_{44} , values which compared favorably with the ultrasonic test results on the same specimens.⁽²⁾ One should not compare, for this purpose, the average values of c_{44} for the CTO and ultrasonic tests given in Table 9: the average ultrasonic test value is based on tests on a much larger number of specimens. The c_{44} obtained by ultrasonic tests on the same group of specimens used in the CTO tests was $0.019 \pm .002 \times 10^{11}$ dynes/cm².

The compound longitudinal oscillator (CLO) test was used on only one specimen. The value of $1/s_{11}$ which was obtained is relatively low. However, CLO tests on various combinations of metal rods gave consistently low values for the modulus in every case. We conclude that the test is not reliable.

The ultrasonic tests yield four of the five stiffness constants, and the data contain greater consistency and less scatter than the data from any of the other tests. The values obtained for the stiffness c_{11} showed the smallest amount of variation from one material to another, and the values obtained for c_{66} also showed relatively small scatter as compared to the values obtained for the other constants. Values for these two stiffnesses were selected from only the highest quality material; a best value of c_{12}/c_{11} of $0.17 \pm .01$ was thus obtained. In a similar manner, the average value of c_{33} for the better quality graphite was approximately 3.45×10^{11} dynes/cm². There was no good way to determine a best value of c_{44} , but the ultrasonic data were in good agreement with both the CTO data and the values of $1/s_{44}$ obtained in static torsion tests on the same specimens in the several cases where such comparisons were made.

TABLE 9
RESULTS OF ULTRASONIC AND RESONANT BAR TESTS
(Elastic constants are in units of 10^{11} dynes/cm²)

	As-Deposited Pyrolytic Graphite	Compression-Annealed Pyrolytic Graphite
Resonant Bar Test	$1/S_{11} = 4.3 \pm 1.0$	$1/S_{11} = 69 \pm 30$ $1/S_{44} = .026 \pm .008$
Compound Torsion Oscillator (CTO)		$C_{44} = 1/S_{44} = .0186 \pm .0003$
Compound Longitudinal Oscillator (CLO)		$1/S_{11} = 86$ (one specimen)
Ultrasonic Tests	$C_{33} = 2.45 \pm .50$ $C_{44} = .18 \pm .02$ $C_{11} = 5.2 \pm .8$ $C_{66} = 1.8 \pm .4$ C_{12} (calculated) = $1.6 \pm .1$	$C_{33} = 3.35 \pm .30$ $C_{44} = .028 \pm .008$ $C_{11} = 105.6 \pm 1.6$ $C_{66} = 44 \pm 3$ $C_{12}/C_{11} = .16 \pm .04$

8. ANALYSIS OF RESULTS

G. B. Spence and E. J. Seldin

The elastic constants of compression-annealed pyrolytic graphite have been measured by static, sonic resonance, and ultrasonic time-of-transit tests. Since the material possesses hexagonal symmetry, there are a total of five elastic constants. In terms of the compliances s_{ij} , these are s_{11} , s_{12} , s_{13} , s_{33} and s_{44} , each of which is determined directly in one of the static tests. Alternatively, there are a set of five stiffnesses c_{ij} (c_{11} , c_{12} , c_{13} , c_{33} , c_{44}) which are directly related to the five s_{ij} . The sonic tests yield some of the s_{ij} and the ultrasonic tests yield some of the c_{ij} .

The Young's modulus $1/s_{11}$ is obtained in a static tensile test in which the applied stress is parallel to the a-axis; measurement of the transverse strains along the a-axis and along the c-axis yield s_{12} and s_{13} , respectively. The Young's modulus $1/s_{33}$ is obtained in a static compression test in which the applied stress is along the c-axis; although the transverse strain is

proportional to s_{13} , the Poisson ratio $-s_{13}/s_{33}$ is so low (approximately .01) that s_{13} cannot, in practice, be determined accurately in a compression test. The shear modulus $1/s_{44}$ is obtained in a static torsion test in which the axis of rotation is parallel to the c-axis.

A bar with its long dimension along the a-axis can be made to resonate in either a longitudinal or flexural mode. The longitudinal mode of vibration of this resonant bar yields the elastic constant $1/s_{11}$, whereas the flexural modes of vibration yield, through Timoshenko's equation, $1/s_{11}$ and the shear modulus $1/s_{44}$. A compound torsion oscillator (CTO), consisting of a short cylindrical graphite specimen with its axis parallel to the c-axis and two cylindrical metal end pieces, was used to determine the shear modulus $1/s_{44}$. Unfortunately, this compound oscillator could not be excited in a longitudinal resonance to give the modulus $1/s_{33}$. However, a compound longitudinal oscillator (CLO) was used in which the axis of the graphite specimen was parallel to the a-axis; the longitudinal resonance yielded the modulus $1/s_{11}$, but the values which were obtained were consistently lower than those obtained from the resonant bar and static tests.

Measurements of the transit times of pulses in the ultrasonic frequency range also yielded values for the elastic constants. Depending on whether the wave was longitudinal or transverse, a pulse along the c-axis yielded either c_{33} or $c_{44} = 1/s_{44}$. In a similar manner, a pulse along the a-axis yielded either c_{11} or $c_{66} = (c_{11} - c_{12})/2$.

In this section, we summarize the results by giving the average experimental values of all of the elastic constants which were measured and the limits of experimental error. We then invoke the symmetry relationships between the elastic constants in an analysis of the experimental results. The purpose of the analysis is to define the probable limits of accuracy in the data and to deduce a self-consistent set of elastic constants for graphite.

8.1. Between-Plane Shear

The values for the shear modulus $1/s_{44}$ of compression-annealed pyrolytic graphite fell in the range 0.018 to 0.035×10^{11} dynes/cm². Excellent agreement was obtained between the values of $1/s_{44}$ measured in

sonic, ultrasonic, and static tests on the same specimen; this agreement is evidence that the experimental techniques give true and accurate measurements of the shear modulus. However, because of the spread in values from specimen to specimen, the limiting value of $1/s_{44}$ as crystalline perfection is approached is still not known.

8.2. All Other Moduli

The experimental values of the elastic constants are summarized in Table 10, which gives an average value and spread of values for each of the constants which were measured. Characteristically, the sonic and ultrasonic measurements are determined to a higher degree of accuracy than the static measurements. There is also much less variation in the sonic and ultrasonic values of the elastic constants from one material to another. Therefore, the values of c_{11} , c_{12} , and c_{33} in Table 10 impose strong limitations on the values of the compliances which are obtained in the static tests.

TABLE 10

EXPERIMENTAL VALUES OF ELASTIC CONSTANTS
FOR COMPRESSION-ANNEALED PYROLYTIC GRAPHITE
(c_{ij} in 10^{11} dynes/cm², s_{ij} in 10^{-11} cm²/dynes)

c_{11}	=	105.6 ± 1.6	$1/s_{11}$	=	88 ± 11
c_{12}	=	16 ± 5	s_{12}	=	$-.0018 \pm .0006$
c_{13}	=	-----	s_{13}	=	$-.0033 \pm .0008$
c_{33}	=	$3.35 \pm .30$	$1/s_{33}$	=	$3.7 \pm .5$
c_{66}	=	44 ± 3	$s_{13}^2/s_{11}s_{33}$	=	$.0035 \pm .002$
c_{12}/c_{11}	=	$.16 \pm .04$	$c_{44} = 1/s_{44}$	=	$.025 \pm .010$
$K_3 = s_{33} + 2s_{13} = .28 \pm .01$ (Reference 21)					

The hexagonal symmetry of graphite causes the following relationships⁽²⁰⁾ to exist between the compliances s_{ij} and the stiffnesses c_{ij} :

$$c_{11} + c_{12} = s_{33}/X, \quad c_{11} - c_{12} = 1/(s_{11} - s_{12}),$$

$$c_{13} = -s_{13}/X, \quad c_{33} = (s_{11} + s_{12})/X, \quad \text{and} \quad c_{44} = 1/s_{44},$$

$$\text{where } X = s_{33} (s_{11} + s_{12}) - 2s_{13}^2.$$

From these relationships, the following equations have been derived:

$$1/s_{11}c_{11} = (1-p) [1 - (c_{12}/c_{11})^2],$$

$$1/s_{33}c_{33} = (1 - c_{12}/c_{11}) / [(1+p)/(1-p) - c_{12}/c_{11}], \quad \text{and}$$

$$s_{12}/s_{11} = p - (1-p) c_{12}/c_{11},$$

$$\text{where } p = s_{13}^2/s_{11} s_{33}.$$

The equations above are plotted in Figure 41 as three nomograms in which the ordinate is the left side of the equation and the abscissa is c_{12}/c_{11} . The curves in each nomogram correspond to fixed values of the parameter, p , which is a small dimensionless number. Since the value of c_{12}/c_{11} from experiment is $0.16 \pm .04$, the abscissas were made to extend only to 0.2. Although curves are drawn for several values of p , the data indicate that p is approximately 0.0035; thus, practically, it is equal to zero on the nomograms.

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FIGURE 41. Relations Between Elastic Constants for Material with Hexagonal Symmetry

When the above values for c_{12}/c_{11} and p are used, the first plot in Figure 41 indicates that $1/s_{11}$ should be about 3 per cent lower than c_{11} . If we assume that the ultrasonic measurement of c_{11} given in Table 10 is correct, the true value of $1/s_{11}$ is slightly greater than any value we have measured. Apparently, the static measurement is more sensitive to material imperfections than the sonic and ultrasonic measurements; thus, imperfections in the material will substantially lower the effective $1/s_{11}$.

The second plot in Figure 41 indicates that, although $1/s_{33}$ is always equal to or less than c_{33} , the low value of p should cause the two to be almost identical for graphite. If we assume that the value of c_{33} in Table 10 is correct, the average value of $1/s_{33}$ in Table 10 must be slightly high.

The third plot in Figure 41 indicates that the ratio $-s_{12}/s_{11}$ must be equal to or less than c_{12}/c_{11} . The value of s_{12}/s_{11} as determined from the average values of s_{12} and s_{11} in Table 10 is about -0.20, which is outside of the allowable values indicated by Figure 41. We conclude from this reasoning that $1/s_{11}$ must be greater than the average value in Table 10 and/or s_{12} must be numerically smaller than the average value in Table 10. The third nomogram indicates that, for $c_{12}/c_{11} = .17$, the value of $-s_{12}/s_{11}$ should be between .16 and .17, values which fall within the range of those measured.

Unfortunately, no direct measurement could be made of c_{13} , and the equations and nomograms which provide the checks on the other elastic constants are very insensitive to the absolute value of s_{13} . We rely, therefore, entirely on the static tensile test for the measurement of s_{13} . There is one other piece of evidence, however, which may be considered. The c-axis compressibility K_3 , as measured by Kabalkina and Vereshchagin,⁽²¹⁾ on Ceylon graphite and spectroscopically pure polycrystalline graphite, depends on s_{33} and s_{13} and is given in Table 10. The best that can be said about s_{13} from this analysis is that the measured values are reasonable.

In conclusion, the symmetry relationships which must be satisfied by a self-consistent set of elastic constants cause us, through this analysis, to believe that the true elastic constants are, in some cases, different from the

average values which are listed in Table 10. We place greatest faith in the sonic and ultrasonic measurements of c_{11} , c_{12} , and c_{33} , and we use the value of s_{13} from the static tensile test as the only available measurement of this constant. From careful consideration of the data and the quality of the material used in the different tests, we present in Table 11 a self-consistent set of elastic constants, with probable errors, which represents our best estimate of the true elastic constants of compression-annealed graphite. By setting a relatively high value for $1/s_{11}$, we are, in effect, saying that in a static tensile test, one can only approach the true Young's modulus. The value of s_{12} in Table 11 is consistent with experiment, and the values of $1/s_{44}$ represent the observed values for which there is no crosscheck with other elastic constants. The greatest uncertainty is in the value of c_{13} .

TABLE 11

ESTIMATE OF ELASTIC CONSTANTS FOR GRAPHITE
 $(c_{ij}$ in 10^{11} dynes/cm², s_{ij} in 10^{-11} cm²/dynes)

c_{11} =	106 ± 2	$1/s_{11}$ =	101.5 ± 3
c_{12} =	18 ± 2	s_{12} =	$-.0015 \pm .0004$
c_{13} =	$2.72 (x 2^{\pm 1})$	s_{13} =	$-.0063 (x 2^{\pm 1})$
c_{33} =	$3.6 \pm .1$	$1/s_{33}$ =	$3.48 \pm .2$
c_{12}/c_{11} =	$.17 \pm .01$	$c_{44} = 1/s_{44} = .018 \text{ to } .035$	

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