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

January 1, 1966, to March 31, 1966

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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 January 1, 1966, to March 31, 1966.

The Project is under the general supervision of J. T. Meers. The materials preparation has been carried out by N. F. Graves and E. J. Seldin. The graphite single crystal work has been carried out by D. E. Soule and C. W. Nezbeda. This report was prepared by J. T. Meers.

ABSTRACT

Several compression-annealed pyrolytic graphite disks have been prepared; these await evaluation. Several sets of measured or calculated values of c_{33} and c_{44} are compared with the measured values obtained from this investigation.

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1. INTRODUCTION

The 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 primary objective of this quarter's work has been the production of high quality compression-annealed pyrolytic graphite to be used for irradiation test specimens. Additional work on between-the-planes shear of natural graphite crystals is still in progress. The sonic, ultrasonic, and static measurement program for compression-annealed pyrolytic has been inactive this quarter.

2. SUMMARY

Two furnaces for compression annealing were commissioned this quarter, and three disks have been produced which appear to be of suitable quality for irradiation test specimens. The static tensile test results will establish whether or not the disks are of sufficiently good quality.

The single crystal shear apparatus was modified; the machine compliance and electronic noise were reduced in order to achieve increased sensitivity. Values of c_{33} and c_{44} which were measured and calculated by several different methods are tabulated and compared with each other and with the results of this work. There is reasonable agreement for c_{33} among the several methods of determining elastic constants, but the measured static values of c_{44} are 13 to 35 times smaller than the values calculated from the specific heat.

3. MATERIALS PREPARATION

Two new furnaces for compression annealing were placed in operation, and the initial heats to establish furnace conditions and load train alignment were made with commercial pyrolytic graphite. Because of the large in-plane expansion of pyrolytic graphite during annealing, a two-step sequence was adopted: first, each disk was given a thermal anneal which resulted in approximately a five per cent diametrical expansion, and, second, the disk was stripped to a new surface on each side and reannealed between 2800-2900°C under a pressure of 4,000 to 5,000 lbs/in².

Seven of the ten unannealed disks of pyrolytic graphite which remained from the third furnace load of special methane-based pyrolytic graphite were annealed and examined. These disks, designated the M300 series, were slightly concave in the as-deposited state. This concavity, which persisted through the two-step annealing sequence, was flattened by repressing at 2950° to 3000°C.

A fourth furnace load of special methane-based pyrolytic graphite plates was received during this quarter. This series of plates, designated the M400 series, were unusually bright with relatively narrow and uniform growth cones. A polished edge of as-deposited plate M402 was examined with an optical microscope; a typical section is shown in Figure 1. The cone structure is nearly continuous from substrate to surface and there are no visible soot inclusions or marked renucleation bands. Plates M401, M411, M425, and M421 have been annealed as 3.7-inch diameter plates; plates M401 and M411 were re-annealed after stripping the flat surfaces of each disk. Although side slippage has not been so severe in these anneals as those previously annealed, wrinkles have been observed in the annealed disks which may be due to thermal gradients which cause nonuniform permanent expansion. The temperature uniformity within each disk has been improved by heating more slowly and by increasing the time at maximum temperature.

The surface flatness of several disks were measured by the optical reflectivity method. The values of $\theta_{1/2}$, the half-width taken at half-height of the reflectance curve, are given in Table I. Although the surface orientation of these disks, as measured optically, is not so high as the best previously produced material (M304), samples from some of the disks described in Table I are being prepared for static tensile tests. If the tensile results are satisfactory, radiation test specimens will be prepared from these disks.

TABLE I
Surface Flatness Measured Optically

Samples	$\theta_{1/2}$ (Degrees)	Remarks
M321	0.56	3rd anneal, surface stripped
M321	0.43	3rd anneal, surface stripped, 0.001-inch further
M321	0.28	4th anneal, surface stripped
M325	0.28	3rd anneal, surface stripped
M401	0.28	2nd anneal, surface stripped

FIGURE 1
Growth Cone Structure of Plate M402

N-9610

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

4.1 Apparatus Modification

The characterization of between-the-planes shear of thin natural graphite crystals has necessitated working at the limits of resolution of the apparatus. However, three important improvements have been made, primarily because of the necessary close observation of the apparatus.

First, the diameter of the seven strand stainless steel cable used to transmit the load force to the shear heads has been reduced from 0.015 to 0.0045 inch, permitting greater flexibility and less kinking in the load train; second, the distance of separation of the stainless steel cables at the shear heads was reduced by more than a factor of three, thereby reducing the couple on the sample and the compliance of the system; third, the transducer circuitry and amplifier were rechecked at the factory. Improved impedance matching was attained, and both noise and drift were greatly reduced. These changes have appreciably improved the sensitivity of the system.

The modified system was checked out by measuring the shear modulus of a sample of M311 pyrolytic graphite. This measurement gave the same value as that which had been previously measured on this material.

4.2 Comparison of Moduli Determined in Static, Sonic, and Ultrasonic Tests with Those Calculated from Other Measurements

Prior to the present series of measurements made on graphite, the only reasonably reliable c_{44} values which existed were those which were deduced from cantilever beam, low temperature specific heat, and neutron diffraction measurements. Now that reasonably accurate c_{44} values have been determined for single crystals and compression-annealed pyrolytic graphite, a comparison can be made with values calculated from other types of measurements.

The data in Table II have been compiled from the literature in order to demonstrate several significant points about both c_{44} and c_{33} as they relate to different measurements made on several types of graphite. Included in Table II are those characteristics of the lattice, plus its imperfections, which may affect these elastic constants. The data cover a range of graphites extending from the

TABLE II

Values of c_{33} and c_{44} as Determined by Different Methods
for Various Graphites

Material	Crystallite Size	Crystallite Tilt	Layer Spacing (Å)	Stacking Fault Degree	c_{33} (10^{11} d/cm ²)	T (°K)	Measurement	c_{44} (10^{11} d/cm ²)	T (°K)	Measurement
Single Crystal Essex County	≥1 mm		3.35	Almost negligible	---	---	---	0.011-0.026	300	Pure shear
Madagascar	>100μ		3.35	Very low	3.56	0.4-2	Spec. heat ^(5,6) (Compressibility)	0.452	0.4-2	Spec. heat ^(5,6)
Canada	~100μ		3.35	Low	3.56 ≥1.8	1.3-4.2 "	Spec. heat ^(2,3) " " (2,4)	0.405 0.23	1.3-4.2 "	Spec. heat ^(2,3) " " (2,4)
Ceylon			3.35	Low	3.50	300	Compressibility ⁽⁷⁾ with X-ray			
Compression- annealed pyrolytic	~30-60μ	<1°	3.35		3.44±0.10 3.65	300 300	Ultrasonic ⁽¹⁾ Static compression ⁽¹⁾	0.018-0.035	300	Pure shear ⁽¹⁾ Diagonal shear ⁽¹⁾ Torsional shear ⁽¹⁾ Sonic resonance ⁽¹⁾ ultrasonic ⁽¹⁾
Thermally- annealed pyrolytic	~100μ	~5°	3.35		3.9±0.4	300	Neutron diffraction ⁽⁸⁾	0.42±0.2	300	Neutron diffraction ⁽⁸⁾
Pile graphite (H-CS-11)	~240Å		3.35	Low	3.56	1.3-4.2 0.4-2	Spec. heat ^(2,3) " " (5,6)	0.292 0.312	1.3-4.2 0.4-2	Spec. heat ^(2,3) " " (5,6)
As-received pyrolytic	~230Å	≤40°	≤3.44	Very high	2.03	0.4-2	Spec. heat ^(5,6)	0.0702	0.4-2	Spec. heat ^(5,6)
Lampblack- based (SA-25)	~100Å	Almost random	3.40	High	2.88	1.3-4.2 0.4-2	Spec. heat ^(2,3) " " (5,6)	0.0702	1.3-4.2 0.4-2	Spec. heat ^(2,3) " " (5,6)

The measurement temperatures and methods are listed after their respective elastic constant values.

most nearly perfect single crystals, Essex County, to the very fine-grain and practically isotropic lampblack-based graphite, CEP. The physical characteristics presented in Table II are:

- 1) crystallite size as determined from the broadening of the (00 l) X-ray lines,
- 2) average crystallite basal plane tilt,
- 3) layer spacing, and
- 4) degree of stacking faults as qualitatively inferred from the resolution of the ($h0l$) lines.

Considering the low temperature specific heat results, the only vibrational modes which may be excited are those with low frequencies ($\sim 10^{11}$ cps), where $\hbar\omega \leq kT$. Because of the weak van der Waals interlayer bonds, the only moduli which must be considered are c_{33} , which is related to the longitudinal vibration of the planes along the c -axis, and c_{44} , which is related to a shearing type transverse vibration of the planes with respect to each other. The values shown in Table II indicate that:

- 1) the c_{44} values determined from the specific heat are much larger than those determined statically by factors of 13 to 35;
- 2) the c_{33} values determined from the specific heat values agree quite well with those determined statically;
- 3) c_{44} is very sensitive to the degree of stacking faults, or degree of turbostraticity, whereas c_{33} is only slightly affected; and
- 4) the crystallite size does not appear to be a major factor by itself.

The room temperature neutron diffraction results of Dolling and Brockhouse⁽⁸⁾ for a good thermally annealed pyrolytic graphite gives $c_{44} = 0.42 \times 10^{11}$ dynes/cm², which agrees very well with the values of 0.452 and 0.405×10^{11} dynes/cm² obtained by Komatsu⁽⁶⁾ from the specific heat of Madagascar and Canadian natural graphites. This agreement is considered to be significant because the neutron diffraction experiment looks directly at the lattice vibrational mode involved.

The values of c_{33} calculated from the specific heat data agree well with those values determined by entirely independent measurements such as neutron diffraction, ultrasonic, sonic resonance, static compression, and compressibility (determined by direct X-ray measurements of the lattice spacing change) tests. The average value of c_{33} obtained for nearly perfect pyrolytic graphite, ⁽⁹⁾ omitting the rough estimate of reference (4) and the values for those graphites with interlayer spacing not equal to 3.35 Å, is $3.61 \pm 0.13 \times 10^{11}$ dynes/cm². This value appears to be valid for both the single crystal and coke-base polycrystalline graphites. On the other hand, a discrepancy exists between the values of c_{44} determined directly by static, sonic, and ultrasonic tests and those values calculated from specific heat and neutron diffraction data. Since the specific heat and neutron diffraction values agree well with each other, this discrepancy suggests that some mechanism or set of mechanisms is operative in the mechanical testing of the graphites which is not active in either the specific heat or neutron diffraction tests. These mechanisms very likely involve dislocations and larger scale structural defects such as twins, kinks, and tilt boundaries. Unfortunately, no good model exists at the present time to explain this discrepancy in the values of c_{44} .

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