BNWL-1495
UC-25

Battelle

Pacific Northwest Laboratories
Richland, Washington 99352

AEC Research and Development Report

THE EFFECT OF PRESTRESSING ON
THE THERMAL EXPANSION AND
YOUNG'S MODULUS OF GRAPHITE

JUNE 1972

BNWL-1495

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately-owned rights.

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
U.S. ATOMIC ENERGY COMMISSION
Under Contract AT(45-1)-1830

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.95

UNCLASSIFIED

3 3679 00061 7433

BNWL-1495
UC-25
Metals, Ceramics,
and Materials

THE EFFECT OF PRESTRESSING ON THE THERMAL
EXPANSION AND YOUNG'S MODULUS OF GRAPHITE

Patrick E. Hart

Ceramics & Graphite Section
Fuels & Materials Department

June 1972

BATTELLE MEMORIAL INSTITUTE
PACIFIC NORTHWEST LABORATORIES
RICHLAND, WASHINGTON 99352

THE EFFECT OF PRESTRESSING ON THE THERMAL
EXPANSION AND YOUNG'S MODULUS OF GRAPHITE

Patrick E. Hart

ABSTRACT

The effect of preloading on the thermal expansion behavior and elastic modulus of three grades of graphite has been determined. Isostatic, compressive, and tensile preloading loading modes were used. The effect of loading is interpreted in light of the effect of changes in crack size and density.

TABLE OF CONTENTS

LIST OF FIGURES	vii
INTRODUCTION	1
EXPERIMENTAL	3
RESULTS	4
DISCUSSION	21
CONCLUSIONS	23
ACKNOWLEDGEMENTS	24
REFERENCES	25
DISTRIBUTION	27

LIST OF FIGURES

1	Effect of Compressive Preloading on Thermal Expansion of ZTA Graphite	6
2	Effect of Isostatic Preloading on Thermal Expansion of ZTA Graphite	7
3a	Effect of Compressive Preloading at 90% of Ultimate Strength on Thermal Expansion of ATJ Graphite	8
3b	Effect of Compressive Preloading at 60% of Ultimate Strength of Thermal Expansion of ATJ Graphite	9
3c	Effect of Compressive Preloading at 30% of Ultimate Strength on Thermal Expansion of ATJ Graphite	10
4	Effect of Isostatic Preloading on Thermal Expansion of ATJ Graphite	11
5	Effect of Tensile Preloading on Thermal Expansion of ZTA Graphite	12
6	Effect of Tensile Preloading on Thermal Expansion of ATJ Graphite	13
7a	Effect of Isostatic Preloading at 30,000 psi on Thermal Expansion of POCO Graphite	14
7b	Effect of Isostatic Preloading at 15,000 psi on Thermal Expansion of POCO Graphite	15
8	Effect of Annealing on the Room Temperature Length of ATJ Graphite Stressed to 90% of Compressive Strength	19
9	Effect of Annealing on Room Temperature Modulus of ATJ Graphite Stressed to 90% of Compressive Strength	20

THE EFFECT OF PRESTRESSING ON THE THERMAL
EXPANSION AND YOUNG'S MODULUS OF GRAPHITE

Patrick E. Hart

INTRODUCTION

The thermal expansion behavior of polycrystalline anisotropic materials exhibits two interrelated phenomena:

- Expansion accomodation and
- A hysteresis in length change.

Both effects are due to cracks formed during cooling from elevated temperatures. Crack formation* in anisotropic materials results on cooling from graphitization temperature from stress buildup between crystallites of different orientation. Cracking commonly occurs in crystallite directions having high thermal expansion. The resultant removal of these crystallites from the crystallite average yields a decrease in the average thermal expansion coefficient.⁽¹⁾ The difference between the measured thermal expansion and that predicted from an average overall crystallite expansion is termed accommodation.

The modified constant-strain model discussed by Slagle,⁽¹⁾ which predicts thermal expansion behavior in

* *Hysteresis in length change on thermal cycling is attributed to the opening and closing of these cracks.*

agreement with measured expansion, indicates that elastic anisotropy as well as these cracks contributes to accommodation.

Based on experimental observations, Sutton and Howard⁽²⁾ attributed accommodation in polycrystalline graphite to cracks⁽³⁾ formed during cool-down from graphitization temperatures. Open pores do not appear to contribute to accommodation. Prices, Bokros, and Koyama⁽⁴⁾ also attributed accommodation in pyrolytic graphite to microporosity.

The purpose of this study was to determine the effect of prestressing on thermal expansion accommodation of polycrystalline graphite. The effect of tensile, compressive, and isostatic prestressing on the thermal expansion behavior and Young's modulus of graphite was determined. Results will be discussed in light of the effect of induced cracking on proposed accommodation mechanisms.

Graphite was selected as the test material because of its extreme anisotropy, i.e., at 25°C the thermal expansion coefficient in the c-axis is about 26 times that in the a-axis direction. Polycrystalline graphites typically exhibit a high degree of thermal expansion accommodation. Measured thermal expansion coefficients of randomly oriented graphites are typically 50 to 75% below the values calculated from preferred orientation parameters and single crystal expansion coefficients.

EXPERIMENTAL

Three grades of graphite with a range of micro-structures and varying degrees of preferred orientation were selected for testing:

- POCO AXF, a fine-grained, high-density, randomly oriented graphite;
- ZTA, a highly oriented, hot-pressed, high-density graphite;
- ATJ, a lower density and more randomly oriented base stock of ZTA grade graphite.

All samples were 0.5 in. diameter. Samples for thermal expansion experiments were 3 in. long, while those for Young's modulus determinations were 5 in. long. ZTA specimens were cut both parallel and transverse to the molding axis. Samples were annealed at 2500°C in helium for one hour to relieve machining stresses.

Uniaxial prestressing was performed at 30, 60, and 90% of measured tensile compressive strengths in an Instron test frame.* Samples loaded in tension were glued to steel grips with epoxy resin which was removed after loading by dissolving with an epoxy solvent. Unstressed specimens were given the same gluing treatment prior to thermal expansion measurements in order to compensate for the

*Cross head speed in tension = 0.005 in./min.; in compression = 0.01 in./min.

effect of gluing on the stressed samples. Specimens cut from the mid-section of the stressed specimens exhibited non-reproducible behavior above 1200°C. Other specimens were isostatically loaded at either 15,000 or 30,000 psi in double-wrapped polyethylene bags. Specimen dimensional changes resulting from tensile, compression, and isostatic loading modes were measured.

Thermal expansion measurements, before and after prestressing, were performed in a Brinkmann Dilatometer, Model 3000, fitted with an alumina sample holder. Measurements were made up to 1300°C in a dry helium atmosphere flowing at 0.3 cu. ft/hr.

In addition to expansion measurements, the effect of prestressing on the room temperature Young's moduli was determined. Moduli were calculated from resonance frequencies measured at room temperatures using the method of Spinner and Teft.⁽⁵⁾ Calculations took into account density changes resulting from preloading.

Degree of preferred orientation in the three grades of graphite was determined using the Bacon⁽⁶⁾ x-ray technique.

RESULTS

The effect of tensile, compressive, and isostatic compression of preloading on fractional expansion of the

three graphites is shown in Figures 1-7.* Compressive and isostatic preloading caused a permanent increase in expansion of ZTA (Figures 1 and 2) and ATJ (Figures 3a - c and 4) graphite. Tensile loading (Figures 5 and 6) caused an opposite effect. However, POCO graphite exhibited no permanent effect after either isostatic or compressive preloading (Figures 7a - b). ZTA and ATJ samples loaded in compression showed an annealing effect during only the first heating cycle after loading. No annealing effect was observed for samples loaded in tension.

**POCO samples were preloaded only in compression. Preloading to stresses less than 80% of reported tensile strength resulted in epoxy failure.*

No other applicable means of preloading was found.

Compressive preloading resulted in no permanent effect and is, therefore, not shown.

FIGURE 1. Effect of Compressive Preloading on Thermal Expansion of ZTA Graphite.

FIGURE 2. Effect of Isostatic Preloading on Thermal Expansion of ZTA Graphite.

FIGURE 3a. Effect of Compressive Preloading at 90% of Ultimate Strength on Thermal Expansion of ATJ Graphite.

FIGURE 3b. Effect of Compressive Preloading at 60% of Ultimate Strength of Thermal Expansion of ATJ Graphite.

FIGURE 3c. Effect of Compressive Preloading at 30% of Ultimate Strength on Thermal Expansion of ATJ Graphite.

FIGURE 4. Effect of Isostatic Preloading on Thermal Expansion of ATJ Graphite.

FIGURE 5. Effect of Tensile Preloading on Thermal Expansion of ZTA Graphite.

FIGURE 6. Effect of Tensile Preloading on Thermal Expansion of ATJ Graphite.

FIGURE 7a. Effect of Isostatic Preloading at 30,000 psi on Thermal Expansion of POCO Graphite.

FIGURE 7b. Effect of Isostatic Preloading at 15,000 psi on Thermal Expansion of POCO Graphite.

From the preferred orientation parameter, R_x , the measured fractional thermal expansion, $\left(\frac{\Delta L}{L_o}\right)_x$, and x-ray determined a- and c-axes crystallite fractional expansion, $\left(\frac{\Delta L}{L_o}\right)_a$ and $\left(\frac{\Delta L}{L_o}\right)_c$, the c-axis accommodation coefficients, γ_c ,* were calculated at 860°C** using:

$$\left(\frac{\Delta L}{L_o}\right)_x = (1-R_x) \gamma_c \left(\frac{\Delta L}{L_o}\right)_c + R_x \gamma_a \left(\frac{\Delta L}{L_o}\right)_a$$

Fractional expansion was used to determine γ_c at 860°C rather than using coefficients of thermal expansion at 400°C as is normally done. This method alleviates the need to measure slopes of $\frac{\Delta L}{L_o}$ versus temperature curves. Calculated changes in accommodation coefficients are given in Table I. The effect of preloading on Young's modulus on the three graphite grades is given in Table II.

Figures 8 and 9 show the effect of annealing in 200°C intervals in helium on room temperature length and modulus of ATJ specimens stressed to 90% of compressive strength. Annealing time at each temperature was one-half hour.

* An accommodation coefficient of unity represents no accommodation while zero represents completed accommodation.

** Based on coefficients of thermal expansion of Nelson and Riley,⁽⁷⁾ $\frac{\Delta L}{L_o}$ for c-axis = 23.7×10^{-3} , $\frac{\Delta L}{L_o}$ for a-axis = 0 at 860°C. Therefore, the second term is equal to zero.

TABLE I. Percent Change in γ_c Caused by Prestressing

	R_x	Tension 90%	Compression			Isostatic	
			90%	60%	30%	15,000 psi	30,000 psi
AXF ¹ Cycle #1	0.67		+ 3.0%			+ 1.8%	+ 6.0%
Cycle #2			0			+ 0.8%	+ 2.0%
ZTA ² (Parallel)	0.58						
Cycle #1		- 8.2	+29.3				
Cycle #2		- 7.6	+19.6				
ZTA ³ (Transverse)	0.71						
Cycle #1		-27.8	+47.0			+92.5	+134.5
Cycle #2		-25.7	+23.3			+11.3	+ 14.1
ATJ ⁴ Cycle #1	0.69	-12.0	+89.2	+37.5%	+15.0%	+80.5	+105.2
Cycle #2		- 7.4	+ 8.0	+ 7.4	+12.0	+12.0	+ 14.0

	Compressive Strength, psi	Tensile Strength, psi
¹ AXF	18,900	2,266
² ZTA	15,016	1,388
³ ZTA	9,976	2,000
⁴ ATJ	9,625	2,267

TABLE II. *Change in Young's Modulus Caused by Prestressing*

	Tension	Compression			Isostatic	
	<u>90%</u>	<u>90%</u>	<u>60%</u>	<u>30%</u>	<u>15,000 psi</u>	<u>30,000 psi</u>
AXF	---	- 2.4%	---	---	- 0.6%	- 1.6%
After Annealing	---	0	---	---	0	0
ATJ	-1.70%	-18.9%	-8.8%	-4.7%	-24.0%	-33.1%
After Annealing	-0.7%	- 2.5%	-2.0%	-0.6%	- 8.9%	-19.5%

FIGURE 8. Effect of Annealing on the Room Temperature Length of ATJ Graphite Stressed to 90% of Compressive Strength.

FIGURE 9. Effect of Annealing on Room Temperature Modulus of ATJ Graphite Stressed to 90% of Compressive Strength.

DISCUSSION

The observed effect of compressive and isostatic prestressing on accommodation suggest that the models explaining thermal expansion accommodation and hysteresis of anisotropic materials are correct. If crack closure during heating is the source of accommodation, then crack closure resulting from compressive or isostatic preloading should reduce the degree of accommodation as was observed. On the basis of the crack closure model, tensile preloading should cause an opposite effect by increasing crack width or introducing new cracks, thus increasing accommodation. Isostatic and compressive preloading caused an increase in density suggesting that crack closure **did** occur while tensile loading caused an opposite effect. The observed effect of preloading on accommodation suggests that loading effected crack width and/or crack density.

There appears to be no correlation between either the degree of preferred orientation or initial density and the effect of prestressing on the change in accommodation. The finely-grained POCO graphite exhibited no permanent change in expansion after either compressive or isostatic preloading. This may reflect the high degree of perfection of the graphite particles and inter-particle bonding which would result in high loads being required to cause changes in crack density.

Rosenfield and Auerbach⁽⁹⁾ have reported the effect of tensile preloading on the thermal expansion of steel while Rosenholtz and Smith⁽¹⁰⁾ have investigated the effect of compressive preloading on the expansion of steel and magnesium. Tensile preloading caused no change in expansion until the elastic limit had been exceeded. After the onset of the plastic flow, expansion increased, passed through a maximum and then decreased. Compressive preloading up to the elastic limit caused a slight increase in modulus. This increase was attributed to plastic deformation in some of the crystallites and resultant stresses in some of the neighboring ones. At the yield point, the observed abrupt drop in expansion was attributed to sudden permanent lattice contractions. At increased loading, expansion increased rapidly to a maximum and then fell. The increase was attributed to induced lattice expansion while the second decrease was due to increased plastic deformation.

The decrease in Young's modulus observed in this work in all loading modes may be a result of: (1) increased crack density, and/or (2) an increase in dislocation density resulting from plastic deformation. Jenkins⁽¹¹⁾ previously concluded that the reduction in the dynamic modulus of graphite observed after prestressing in compression is a result of localized cracking. Mason and Knibbs⁽¹²⁾ have derived an expression inversely relating dislocation

density and modulus. Increased dislocations density accompanying increased plastic deformation could also cause a decrease in modulus. Crack closure has been invoked by Mason and Knibbs to explain the positive temperature dependence of graphites' elastic moduli. Crack closure has been used in the present work to explain the observed effect of compressive loading on thermal expansion accommodations. In the present work, any effect of crack closure on modulus appears to have been overridden by localized cracking and/or an increase in crack density.

Loads of equal magnitude, but opposite sign, caused equal reductions in modulus, even though the measured tensile strength of ATJ graphite is about one-fifth that of the measured uniaxial compressive strength. This effect may reflect like failure modes or equal increased dislocation density in graphite under both tension and compression.

The annealing effects observed in the present work supports Seldin's⁽¹³⁾ observation that structural damage is removed during heat treatment.

CONCLUSIONS

Preloading of graphite in tension reduces graphite thermal expansion c-axis accommodation while compressive and isostatic preloading cause an opposite effect. All loading modes reduce the Young's modulus. The observed effect of

preloading on thermal expansion is attributed to changes in crack size and/or density, while the effect on Young's modulus is due to increased dislocation density and/or cracking. Annealing of induced strains starts to occur at temperatures as low as 200°C.

ACKNOWLEDGEMENTS

Thanks are extended to G. L. Jones for performing experimental work and to Drs. O. D. Slagle and W. J. Gray for helpful discussions.

REFERENCES

- 1a. O. D. Slagle, "Averaging Techniques in Polycrystalline Graphite," *Carbon* 6 (1) 111-121 (1968).
- 1b. O. D. Slagle, "Thermal Expansion Hysteresis in Polycrystalline Graphites," *Carbon* 7 (3) 337-344 (1969).
2. A. L. Sutton and V. C. Howard, "The Role of Porosity in the Accommodation of Thermal Expansion in Graphite," *J. Nucl. Mater.* 7 (1) 58-71 (1962).
3. S. Mrozowski, "Mechanical Strength, Thermal Expansion, and Structures of Cokes and Carbon," *Proc. 1st, 2nd, Conf.*, pp 31-45, Waverly Press, Waverly, New York (1965).
4. R. J. Prices, J. C. Bokros, and K. Koyama, "Thermal Expansion and Preferred Orientation of Pyrolytic Carbons," *Carbon* 5 (5) 423-430 (1967).
5. S. Spinner and W. E. Teft, "A Method for Determining Mechanical Resonance Frequencies and for Calculating Elastic Moduli from These Frequencies," *Proc ASTM* 61 1221-1238 (1961).
6. G. E. Bacon, "A Method for Determining the Degree of Orientation of Graphite," *J. Appl. Chem.* 6 477-481 (1956).
7. J. B. Nelson and D. P. Riley, "The Thermal Expansion of Graphite from 15°C to 800°C," *Proc. Phys. Soc. (London)* 57 (6) 477-486 (1945).

8. O. D. Slagle, "Deformation Mechanisms in Polycrystalline Graphite," *J. Am. Ceram. Soc.* 50 (10) 495-500 (1967).
9. A. R. Rosenfield and B. L. Auerbach, "Effect of Stress on the Expansion Coefficient," *J. Appl. Phys.* 27 (2) 154-156 (1956).
10. J. L. Rosenholtz and D. T. Smith, "The Effect of Compressive Stresses on the Linear Thermal Expansion of Magnesium and Steel," *J. Appl. Phys.* 21 (5) 396-398 (1950).
11. G. M. Jenkins, "Fracture in Reactor Graphite," *J. Nucl. Mater.* 5 (3) 280-286 (1962).
12. I. B. Mason and R. H. Knibbs, "The Young's Modulus of Carbon," *Carbon* 5 (5) 493-506 (1967).
13. E. J. Seldin, "Stress-Strain Properties of Polycrystalline Graphites in Tension and Compression at Room Temperature," *Carbon* 4 (2) 177-191 (1966).

DISTRIBUTIONNo. of copiesOFFSITE

1	<u>AEC Chicago Patent Group</u> G. H. Lee
4	<u>AEC Division of Reactor Development and Technology</u> J. E. Fox(2) R. E. Pahler J. M. Simmons
1	<u>AEC Division of Research</u> D. K. Stevens
3	<u>AEC, Director, Division of Reactor Licensing</u>
3	<u>AEC, Director, Division of Reactor Standards</u>
192	<u>AEC Technical Information Center</u>
3	<u>Air Force Materials Laboratory</u> G. L. Denman M. L. Minges C. A. Pratt
2	<u>Atomic Energy Establishment - Dragon</u> M. R. Everett L. W. Graham
2	<u>Atomic Energy of Canada, Limited</u> Fuels and Materials Division Fuels Materials Branch Chalk River, Ontario, CANADA J. R. MacEwan J. A. L. Robertson
1	<u>Berkeley Nuclear Lab.</u> Berkeley, Cal., ENGLAND P. P. Jennings
1	<u>Brookhaven National Laboratory</u> D. H. Gurinsky
3	<u>Centre d' Etudes Nucleaires de Saclay</u> Boite Postale No. 2 Gif-sur-Vvette (seine-et-Oise), FRANCE P. Leveque J. Rappeneau (2)

- 3 Culcheth Laboratories
Reactor Materials Laboratory
UKAEA
Wigshaw Lane
Warrington, Lancashire, ENGLAND
B. T. Kelly (2)
P. T. Nettley
- 1 Euratom C.C.R.
Petten, Netherlands
V. Lungagnani
- 1 General Electric Company
Pleasanton, California
G. E. Robinson
- 1 General Electric Company, Ltd.
Hirst Research Centre
Wembley, Middlesex, ENGLAND
Dr. H. H. W. Losty
- 4 Great Lakes Carbon Corporation
Research and Development Department
P. O. Box 637
Niagara Falls, New York
B. L. Bailey
L. H. Juel (3)
- 4 Gulf General Atomic
R. F. Turner
T. R. Moffett
T. Golden
G. B. Engle
- 1 Idaho Nuclear Corporation
E. Fast
- 1 Los Alamos Scientific Laboratory
M. C. Smith
- 3 Oak Ridge National Laboratory
W. P. Eatherly
R. R. Kasten
M. W. Rosenthal
- 1 Pennsylvania State University
P. L. Walker
- 2 POCO Graphite, Inc.
Garland, Texas
R. K. Carlson
- 2 Pure Carbon Company
St. Marys, Pennsylvania
R. R. Paxton

- 1 Reactor Centrum Nederland
 Petten, Netherlands
 R. Blackstone
- 1 Rice University
 Houston, Texas
 J. L. Margrave
- 2 Speer Carbon Products
 Research & Development Laboratories
 Packard Road & 47th Street
 Niagara Falls, New York
 W. E. Parker
- 2 Speer Carbon Products
 Development Department
 St. Marys, Pennsylvania
 W. A. Bauer
 M. B. Redmount
- 1 United Kingdom Atomic Energy Authority
 Atomic Energy Research Establishment - Harwell
 Didcot, Berkshire, ENGLAND
 J. H. W. Simmons
- 1 University of Washington
 D. G. Fischbach

ONSITE-HANFORD

- 1 AEC Chicago Patent Group (Richland)
 R. M. Poteat
- 2 RDT Senior Site Representative
- 1 AEC Richland Operations Office
 W. E. Lotz
- 3 Battelle Memorial Institute
- 3 Douglas United Nuclear, Inc.
 P. C. Carlson
 D. H. Curtiss
 A. Russell
- 15 Battelle-Northwest
 J. M. Batch R. E. Nightingale
 P. L. Farnsworth (2) G. L. Tingey (2)
 J. W. Finnigan Technical Info Files (5)
 W. J. Gray Technical Publications
 W. C. Morgan
 P. E. Hart (8)