AD688074

AD

[redacted]

ARMY MATERIALS AND MECHANICS RESEARCH CENTER

D D C
JUN 9 1969
C

Watertown, Massachusetts 02172

19

AMMRC MS 69-01

RECENT DEVELOPMENTS IN PYROLYTIC GRAPHITE

Monograph Series by

R. NATHAN KATZ and CHARLES P. GAZZARA

February 1969

D/A Project 1T062105A330
AMCMS Code 5025.11.296
Ceramic Materials Research for Army Materiel
Subtask 39191

Presented at AMMRC Seminar on

Structural Ceramics and Design With Brittle Materials
IIT Research Institute, Chicago, Illinois
March 1968

CERAMICS RESEARCH LABORATORY
ARMY MATERIALS AND MECHANICS RESEARCH CENTER
WATERTOWN, MASSACHUSETTS 02172

CONTENTS

Page

ABSTRACT

INTRODUCTION 1

MECHANICAL PROPERTIES OF BORONATED PYROLYTIC GRAPHITE 1

THE MICROSTRUCTURE OF BORONATED PYROLYTIC GRAPHITE 3

THE EFFECTS OF A B_4C DISPERSOID 6

THE POST-DEPOSITION HEAT TREATMENT OF PYROLYTIC GRAPHITE 8

SUMMARY 8

LITERATURE CITED 11

ARMY MATERIALS AND MECHANICS RESEARCH CENTER

RECENT DEVELOPMENTS IN PYROLYTIC GRAPHITE

ABSTRACT

A study of the fine microstructure of boronated pyrolytic graphite was made utilizing optical and electron microscopy and X-ray diffraction techniques. The influence of boron content on the laminar structure, the lattice parameter, the lattice strain, the particle size, and the flexural strength of pyrolytic graphite were studied. Significant changes in the behavior of all investigated parameters were observed in the 0.50 to 0.75 percent boron range. A mechanism relating these changes to the appearance of a B_4C deposit is hypothesized.

In addition, the effects of post-deposition thermal treatment on the mechanical properties of unboronated pyrolytic graphite are discussed. Some general remarks concerning similarities in structure of pyrolytic materials are presented.

INTRODUCTION

The structure of graphite, which is formed by the stacking of covalently bonded sheets of carbon in an ABABABA sequence with van der Waals' bonds between layers, results in unusual thermal, electrical, and mechanical properties.[1] The fact that single crystal graphite possesses a thermal conductivity of the same order as a metal in the "a" direction (i.e., graphite = 4, copper = 3.88) but exhibits that of an insulator in the "c" direction,[2] coupled with the fact that its strength increases with increasing temperature,[3] make it highly desirable for use in rocket nozzle liners or heat shields. However, one cannot make a structure from a single crystal of graphite, and artificial graphites, such as polycrystalline bonded graphite, do not possess such a high degree of anisotropy. So the search for an artificial form of graphite which would closely approximate the properties of single crystal graphite led to the use of a material known variously as pyrolytic graphite or pyrolytic carbon. This material is an artificial, polycrystalline, but highly oriented form of graphite made by the high temperature decomposition (usually at 1800 to 2200 C) of a hydrocarbon gas for example CH_4. The structure which results is characterized by growth cones[4] and laminar substructure inside the growth cones;[5] this structure has been described in great detail by many investigators.[6-8] Although pyrolytic graphite had been known as a unique material since its discovery by Edison[9] 85 years ago, it has only been in the past decade that attention has been drawn to its use in bulk form as a structural material.[3-10]

In the past several years attempts have been made to alter the properties of pyrolytic graphite by alloying additions.[7,11-13] An even more recent development, and one which has had only the most preliminary of investigations, is that of altering the mechanical properties of alloyed and unalloyed pyrolytic graphite by post-deposition thermal treatment.[14]

This paper will treat some recent developments in our understanding of the influence of alloying and post-deposition heat treatment on the mechanical properties of pyrolytic graphite.

MECHANICAL PROPERTIES OF BORONATED PYROLYTIC GRAPHITE

The mechanical properties of unalloyed pyrolytic graphite have been thoroughly studied.[3,4,10,15-18] However, there is very little information available in the literature concerning the effects of alloying on the mechanical properties of pyrolytic graphite. What information is accessible is primarily limited to boron additions,[7,11,19] and this is summarized below.

The mechanical properties of pyrolytic graphite are quite strongly influenced by boron. The variation of flexural strength as a function of boron content at room temperature is shown in Figure 1. One observes a decrease in flexural strength with the addition of 0.50 to 0.75 percent boron, while additions of 1.0 percent or more boron significantly increase the strength.

Boron content exerts an even more marked effect on the Young's modulus of pyrolytic graphite, as shown in Table I. Since the value of E is higher in tension than in compression for the undoped material (which is generally the case in undoped pyrolytic graphite[15,16]), adding boron causes a reversal of this behavior, that is, boronated pyrolytic graphite is stiffer in compression. Also, there is a maximum in modulus at 0.50 percent boron - just where the flexural strength exhibits a minimum. The modulus of pyrolytic graphite with

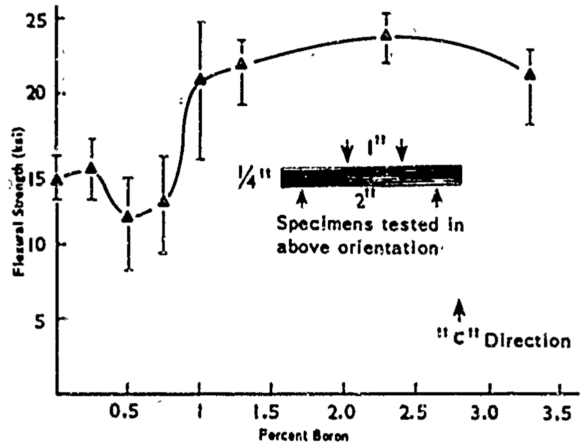


Figure 1. FLEXURAL STRENGTH OF BORONATED PYROLYTIC GRAPHITE VERSUS BORON CONTENT IN WEIGHT PERCENT (After Katz and Gazzara, Ref. 7)
19-066-442/AMC-68

Table I. ROOM TEMPERATURE MODULUS OF BORONATED PYROLYTIC GRAPHITE

	Modulus (psi)	
Boron (%)	Tension	Compression
0	5.55×10^6	5.37×10^6
0.25	--	--
0.50	8.04	8.11
0.75	--	--
1.00	4.00	4.51
1.30	4.45	5.03
2.3	4.52	4.86
3.3	4.57	4.75

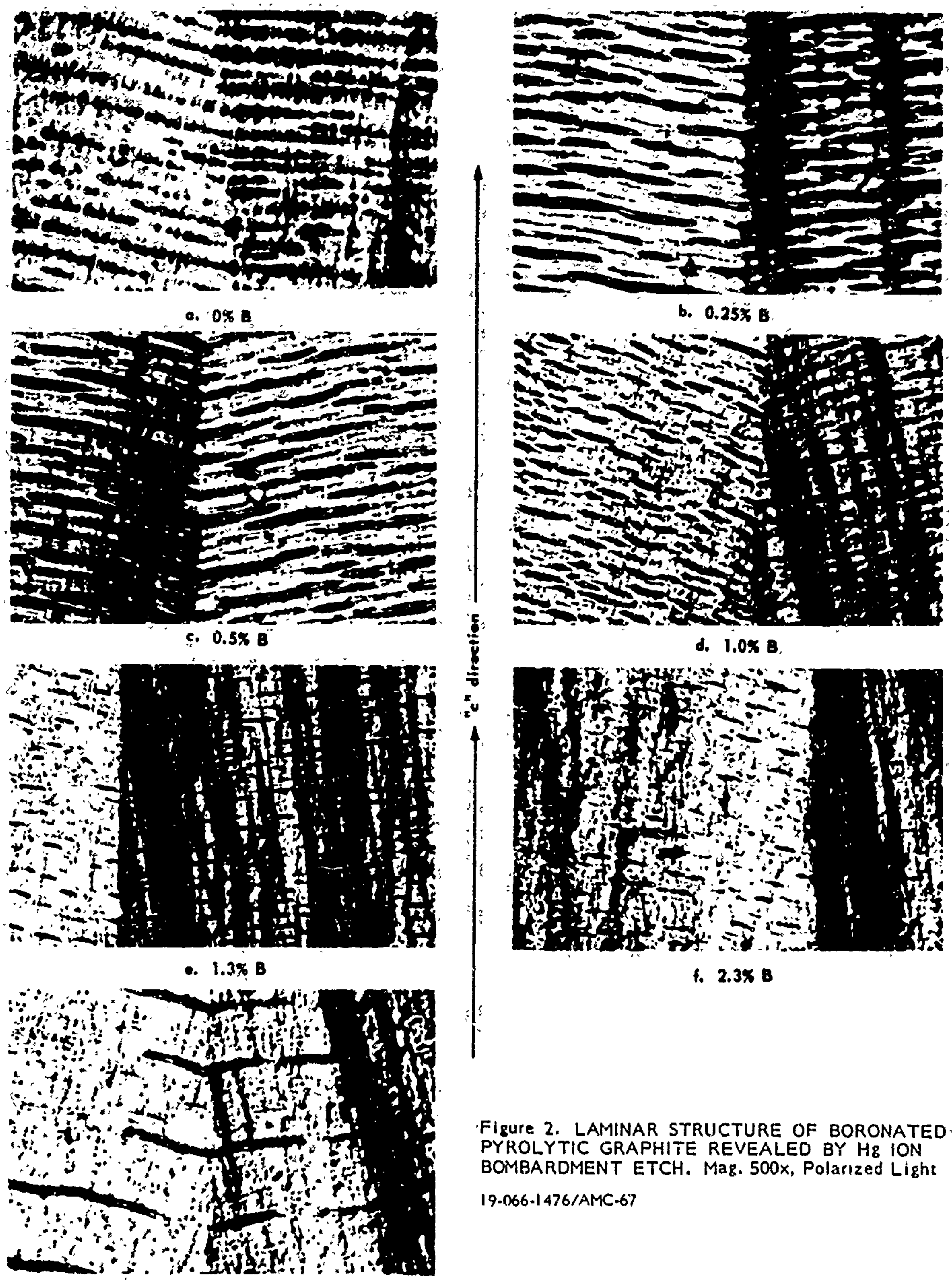
more than 0.5 percent boron is less than the modulus of unalloyed material. This finding is in partial agreement with that of other investigators who also observed a maximum in modulus at 0.5 percent boron but did not find that the modulus fell below the unalloyed value.[20] This may be due to the difference in deposition temperature, the material in Table I having been deposited at 1850 C and the other material having been deposited at 2000 C.

A difference in fracture behavior is also observed. The unboronated material or that with up to 0.5 percent boron content fail in a stepped manner at more or less 45 degrees to the tensile surface, with the steps tending to follow primary growth cone boundaries.[13] The materials with boron contents above 0.5 percent fail in the vicinity of the maximum shear stress by generating a delamination and a large, recoverable elastic displacement, very much like a Volterra edge dislocation.[7] The important point here is that a change in failure mode from cone boundary separation to extensive transboundary shear occurs just beyond 0.5 percent boron.

The mechanical properties of boronated pyrolytic graphite show either a maximum, a minimum, or a change at or near 0.5 percent boron. Perhaps the most singular contribution of metallurgy to science, and the basic unifying factor in the diffuse area known as materials science, is the conception that the properties of materials are determined by their structure. Thus one is led to suspect that "something" is occurring in the microstructure of the boronated pyrolytic graphite which is responsible for the above behavior. The next section of this paper will describe the authors' investigations of the microstructural features of boronated pyrolytic graphite in search of that something.

THE MICROSTRUCTURE OF BORONATED PYROLYTIC GRAPHITE

When attempting to uncover a microstructural rationale for observed property variations, one generally starts with the largest microstructural feature, which in the case of boronated pyrolytic graphite is the growth cone structure described above. Studies of the influence of boron on this level of structure revealed that no identifiable change occurred in boronated pyrolytic graphite with compositions ranging from 0 to 3.3 percent boron. However, upon examination of the next feature encountered as one descends the microstructural scale, namely, the laminar features revealed by mercury-ion bombardment etching, considerable variation was observed. Again two behavioral regimes were encountered. Between 0 and 0.75 percent boron the morphology of the laminar features was essentially constant and could be characterized by very long and thick lamellae exhibiting continuity across the primary growth cone boundaries. By contrast, in going from 0.75 to 3.3 percent boron one observed a continual diminution in the size of these features together with a tendency to become non-continuous across the primary cone boundaries. This is shown in Figure 2. A more complete description of the morphology of these features, including evidence that they are truly microstructural features and not cracks or delaminations, has been previously reported by the authors.[7] Observation of similar laminar features in Ti-doped pyrolytic graphite[13] and in pyrolytic SiC[21] leads



a. 0% B

b. 0.25% B

c. 0.5% B

d. 1.0% B

e. 1.3% B

f. 2.3% B

g. 3.3% B

Figure 2. LAMINAR STRUCTURE OF BORONATED PYROLYTIC GRAPHITE REVEALED BY Hg ION BOMBARDMENT ETCH. Mag. 500x, Polarized Light

19-066-1476/AMC-67

one to speculate that they are a general feature of the pyrolytic deposition process. While these laminar features were interesting, they did not, in themselves, provide an insight into the variation in mechanical properties.

The authors next turned to X-ray diffraction techniques to investigate finer levels of the microstructure. Studies of the X-ray crystallite size, lattice parameter in the "c" direction, and lattice strain were carried out as a function of boron content.[7] The results are shown in Figures 3 through 5. Again, as in the case of the mechanical properties and optically observed microstructure, one notes a distinct transition in behavior in the vicinity of 0.5 percent boron.

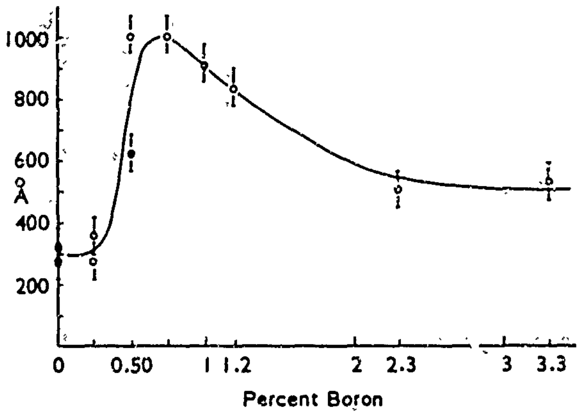


Figure 3. X-RAY CRYSTALLITE SIZE IN "c" DIRECTION VERSUS WEIGHT PERCENT BORON (After Katz and Gazzara, Ref. 7)

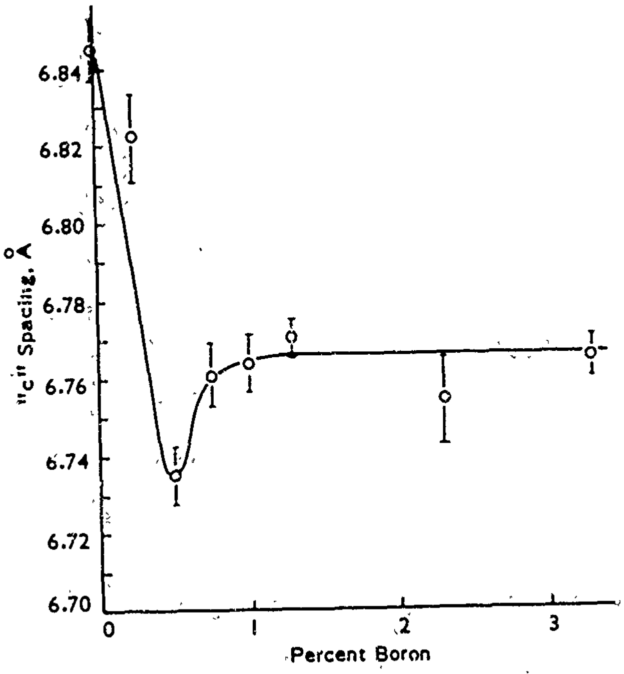


Figure 4. LATTICE PARAMETER IN THE "c" DIRECTION VERSUS WEIGHT PERCENT BORON (After Katz and Gazzara, Ref. 7)

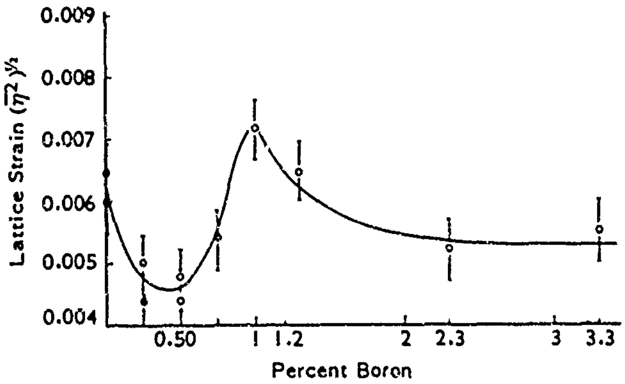


Figure 5. LATTICE STRAIN OBTAINED FROM X-RAY LINE BROADENING VERSUS WEIGHT PERCENT BORON (After Katz and Gazzara, Ref. 7)

While these studies of the microstructure did not themselves directly reveal a structural cause of the observed mechanical properties, they did provide some strong clues for the advancement of a reasonable hypothesis. If one looks at the behavior of the lattice strain beyond 0.5 percent boron in Figure 5 and the behavior of the flexural strength beyond 0.5 percent boron in Figure 1, one is reminded of the precipitation or age hardening behavior often encountered in metallurgical systems. Is it possible that a B_4C dispersoid is present in the material and that this can explain the observed behavior? A review of the available studies of the boron-graphite system[12,22,23] establishes the solubility limit of boron in graphite to be between 0.4 and 1 percent. Lowell[23] found that at the deposition temperature of the material used in this study (1850 C) boron is soluble up 1 percent and that at higher concentration it is present as B_4C. The solubility falls rapidly with temperature so that at about 1600 C it is only about 0.5 percent. In addition, measurements of thermal and electrical properties of boronated pyrolytic graphite carried out by Pappis et al.[11] indicate the presence of B_4C at about 0.75 percent boron. On this basis we can safely assume that B_4C is present, but can it explain the variations in the investigated parameters?

THE EFFECT OF A B_4C DISPERSOID

If one desires to associate the appearance of a B_4C dispersoid with the changes in behavior of the parameters discussed above, one should, at the minimum, be prepared to advance physically reasonable mechanisms to make this association plausible. The authors will now attempt to do this. Consider the variation in lattice parameter with boron content. Boron in solid solution decreases the lattice parameter. However, once B_4C appears* as a second phase or even as a coherent precipitate it is reasonable to assume that the new structural unit can no longer be accommodated in the graphite sheet, and that the new structural unit (i.e., B_4C) acts to separate the layers giving rise to an increase in "c" spacing. The presence of B_4C can also explain the rapid increase and subsequent decrease of microstrains in the lattice beyond 0.5 percent boron. If the B_4C deposits pyrolytically together with the carbon, or if it results from a precipitation reaction, it is probable that for small amounts of B_4C a coherent interface will exist between the carbide and the graphite matrix. Such coherent interfaces produce severe microstrains in the lattice of the matrix.[24] As the boron content increases, it is likely that the size of the B_4C particles will increase. If this were the case, eventually the particles would lose coherency and become a discrete second phase with a noncoherent boundary. The change in the nature of the boundary should relieve the coherency strains and reduce the magnitude of the X-ray strain broadening, which is in fact what one observes.

**There are two ways in which one could imagine the appearance of B_4C: as a codeposited phase, that is, pyrolytic B_4C and pyrolytic graphite, perhaps with a dissolution into the matrix and a reprecipitation reaction (TiC acts this way[13]); or as a pyrolytically deposited solid solution with a subsequent precipitation reaction.*

One can further imagine that if B_4C is codepositing with the pyrolytic graphite or is precipitating during the deposition, it is possible that the B_4C particles will limit the geometric extent of the laminar features. The greater the amount of B_4C dispersed in the pyrolytic graphite matrix, the greater the restriction on the geometric extent of the laminar features. This behavior is observed in the composition range 0.5 to 3.3 percent boron (if one neglects a banding phenomena in the 3.3 percent boron material, which may be due to favored areas of B_4C deposition).

The increase in strength can also be attributed to the presence of a B_4C dispersoid. However, the coincidence between lattice strains and a coherent/noncoherent precipitate and the increase in strength observed beyond 0.5 percent boron is not presented as evidence that a metallic type of age- or dispersion-hardening mechanism is active. Since plasticity is absent at room temperature in the boronated pyrolytic graphite material, it is difficult to envision a precipitate-dislocation interaction model underlying the observed strength increase. A much less sophisticated type of strengthening mechanism may be at work in this case. It may be, for example, that the presence of B_4C merely increases the interlayer shear resistance. Comparing the flexural strength of a deck of playing cards to a deck of sand paper is a good if somewhat crude model for this type of strengthening.

Thus far our hypothesis rests on inferential evidence provided by metallographic and X-ray studies, and our ability to provide self-consistent mechanisms to rationalize the observed phenomena. It would be much more satisfying to be able to provide direct experimental evidence to substantiate the existence of the B_4C dispersoid. Such direct evidence serendipitously became available in the course of an electron microscope study of boronated pyrolytic graphite utilizing surface replicas of freshly cleaved basal planes. A replica from a 2.3 percent boron sample contained a particulate "pull-out" (Figure 6) which selected area electron diffraction identified as being B_4C. The significance of pulling a particle out of a 2.3 percent boron sample and not a 0.5, 1.0, or 1.3 percent sample is that on the basis of a coherent/noncoherent precipitate or dispersoid model one should not be able to obtain a discrete particle until noncoherency occurs. Referring to the lattice strain data in Figure 5, it is evident that such noncoherency is expected to occur at 2.3 percent boron, the very composition at which the pull-out was encountered.

Figure 6. ELECTRON MICROGRAPH OF 2.3% BORON PYROLYTIC GRAPHITE SAMPLE SHOWING SECOND PHASE B_4C PULL-OUT VERIFIED BY ELECTRON DIFFRACTION. Mag. 21,000X
19-066-1481/AMC-67

Having put the existence of the B_4C particles on firmer ground, one turns to the following question: Since the strengthening of boronated pyrolytic graphite is associated with the presence of a coherent/noncoherent dispersion of B_4C, could one utilize thermal treatments to alter the nature of this dispersion and consequently the strength? In other words, can one apply the traditional metallurgical tools of solutionizing and aging? Some work has been carried out along these lines at AMMRC by Meyer. His findings to date are inconclusive, but encouraging, and will not be discussed here. However, these conceptions in terms of thermal treatment of boronated pyrolytic graphite led to work on the thermal treatment of undoped pyrolytic graphite which is discussed next.

THE POST-DEPOSITION HEAT TREATMENT OF PYROLYTIC GRAPHITE

Post-deposition heat treatments of pyrolytic graphite have been studied previously.[10,25-28] However, the mechanical testing was performed on hot-worked material,[10] rather than material subjected only to a high temperature heat treatment. The only investigations of this nature, to the best of our knowledge, are reported in Reference 14. In that study, unalloyed samples of pyrolytic graphite of a continuously nucleated type, deposited at 2000 C, were heat treated for various times at temperatures between 2500 and 2700 C in an argon atmosphere. The specimens were then quenched in flowing argon and tested in flexure at room temperature. The results of these tests are presented in Figure 7. These curves are based on somewhat limited data since only four tests are represented by each point. Nevertheless, the results are rather dramatic and unanticipated. Since it is well known that the "c" spacing of pyrolytic graphite decreases with exposure to high temperatures and increasing times, one would expect a variation in strength with "c" spacing. This is based on the expectation that the strength of van der Waals' bond between basal planes would be greatly influenced by spacing. The lack of a strength effect would indicate that strength of the growth cone and/or crystallite boundaries determine the strength in this material. This is consistent with metallographic observations of failure along growth cone boundaries in unalloyed pyrolytic graphite.[19] The most interesting finding is that the amount of scatter in the data falls with time at temperature of post-deposition treatment. Decreases in scatter of as much as 91 percent were observed. While no really satisfactory explanation of this observation is available, the implications to the amenability of pyrolytic graphite to rational design processes are obvious.

SUMMARY

In the above we have discussed some recent work contributing to the understanding of microstructure - property relationships in the utilization of pyrolytic graphites. While this was perhaps of interest for its own sake, it also introduced some concepts which may be of broader applicability to the field of pyrolytic materials in general. This is a growing field which now includes such materials as BN, SiC, AlN, Si_3N_4, and PN.[29] Vapor-deposited

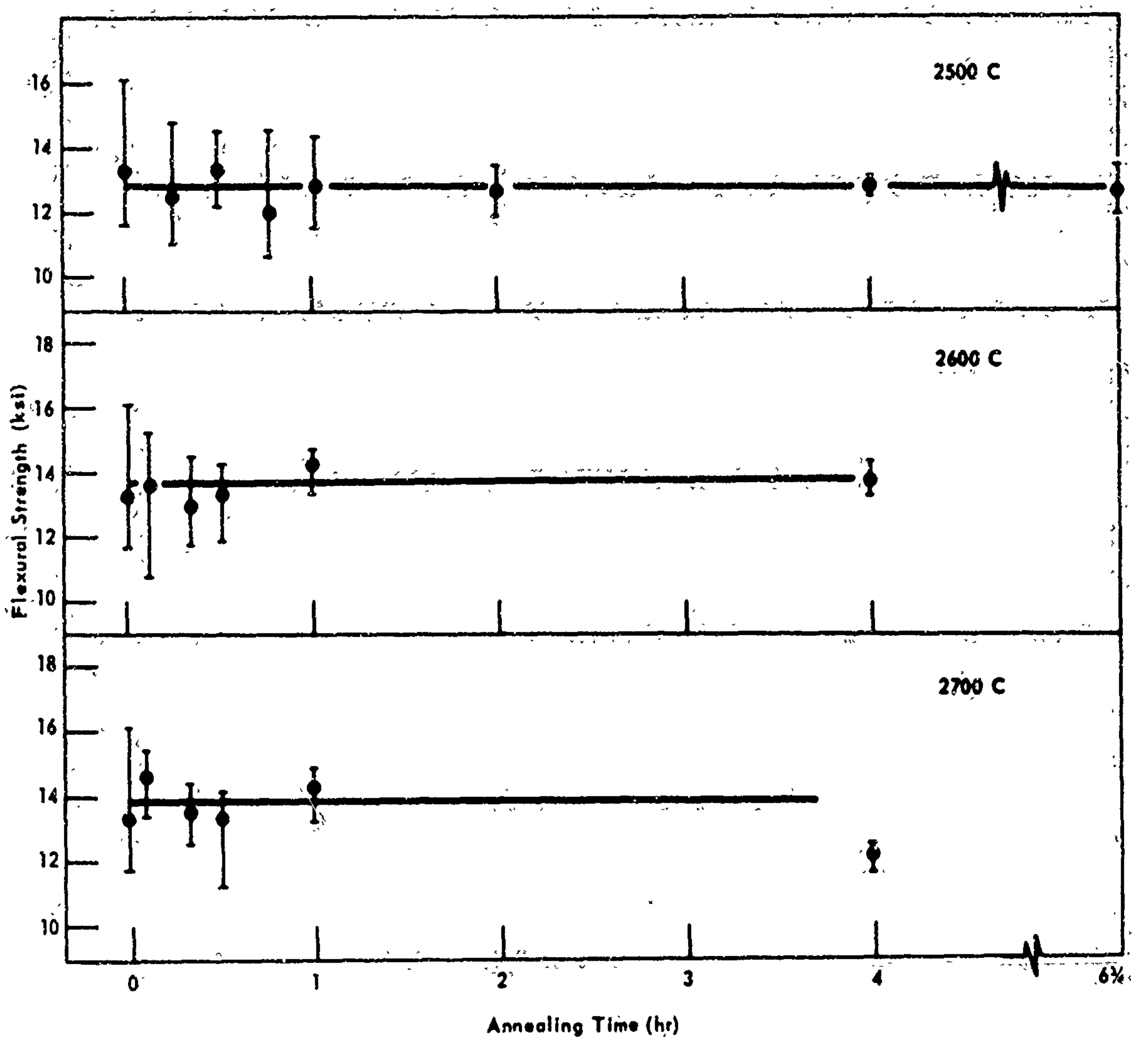


Figure 7. EFFECT OF ANNEALING TIME AND TEMPERATURE ON THE FLEXURAL STRENGTH OF PYROLYTIC GRAPHITE

19-066-526/AMC-68

materials such as Al_2O_3, discussed by Wong and Robinson[30] and Pappis and Ellis,[31] must also be included in this category. While each of these materials possesses its own unique set of characteristics and properties, there are many features which they have in common. These features are a consequence of the method of vapor deposition and are not present in these materials produced by other means. One example of such a common characteristic is the growth cone or columnar feature. The work of Ford et al.[21] shows columnar features in SiC that are of virtually identical morphology to those observed by Wong and Robinson[30] in Al_2O_3. Another example of such similarity can be seen in comparing the laminar features observed in pyrolytic graphite[5] with those observed in SiC.[21] Laminar features have also been observed* in vapor-deposited Al_2O_3 doped with 1 percent Ti (Figure 8, compare with Figure 2), although in this

---

Safran, D. and Robinson, M. Army Materials and Mechanics Research Center, unpublished research.

Figure 8. LAMINAR FEATURES OBSERVED IN VAPOR DEPOSITED Al_2O_3 DOPED WITH 1 PERCENT Ti. Mag. 250X (Safran and Robinson, Unpublished Research)

case it is not certain whether these are a consequence of the growth process or a result of a preferential precipitation phenomena. As a final example, one can cite similarities in the unusual results obtained from X-ray diffraction data in vapor-deposited tin and pyrolytic graphite.[32] Such similarities among the various vapor-deposited materials indicate that it might be fruitful to consider them as a class for which certain generalized structure-property relationships and property control may be developed.

The primary concept which may have broad applicability with vapor-deposited materials is the utilization of post deposition thermal treatments to alter the structure and thereby modify and control the range of available properties. This concept was utilized to alter the mechanical properties of pyrolytic and boron-doped pyrolytic graphite as discussed above. It would certainly also be of interest in other pyrolytic graphite alloy systems such as Ti, Zr, or Hf doped pyrolytic graphite.

A concept not discussed in this paper is the possibility of grain size control by continuous nucleation during deposition, such as in the production of continuously nucleated pyrolytic graphites. Other avenues to explore may include formation of metastable phases by vapor deposition, or possibly pyrolytic deposition of a solid solution which forms a precipitate upon cooling leading to a one-step precipitation hardening mechanism. It will only be when the full range of materials science has been brought to bear on the post deposition modification of pyrolytic materials, that they will have come of age and be capable of making their full contribution to the world of materials.

LITERATURE CITED

1. UBBELOHDE, A. R., and LEWIS, F. A. *Graphite and Its Crystal Compounds.* Oxford Press, 1960.

2. Ibid., p. 56.

3. PAPPIS, J. *The Mechanical Properties of Pyrographite,* in Mechanical Properties of Engineering Ceramics, Interscience, New York, 1961, p. 429.

4. Raytheon Company, Pyrographite Research and Development. Prime Contract NOrd 17017, Final Report, 1 April 1960 - 1 August 1961.

5. TARPINIAN, A. *Electrochemical and Ion Bombardment Etching of Pyrolytic Graphite.* Journal of American Ceramics Society, v. 47, no. 10, October 1964, p. 532.

6. HARVEY, J., CLARK, D., and EASTABROOK, J. N. *The Structure of Pyrolytic Carbon.* Special Ceramics 1962, Academic Press, London and New York, 1963, p. 181.

7. KATZ, R. N., and GAZZARA, C. P. *The Fine Microstructure of Pyrolytic Graphite as Influenced by Boron.* Army Materials and Mechanics Research Center, AMMRC TR 68-02, 1968; also *The Influence of Boron Content on the Fine Microstructure of Pyrolytic Graphite.* Journal of Materials Science, v. 3, 1968, p. 61.

8. COFFIN, L. F., Jr. *A Note on the Structure-Property Relationships for Pyrolytic Graphite.* General Electric Research Laboratories - Schenectady Report.

9. SKLAREW, S., and ALBOM, M. J. *Pyrolytically Derived Refractory Materials.* Metal Progress, v. 87, no. 2, 1965, p. 102.

10. KOTLENSKY, W. V., and MARTENS, H. E. *Mechanical Properties of Pyrolytic Graphite to 2800 C.* Proceedings of the 5th Conference on Carbon, v. 2, Pergamon Press, p. 625-638.

11. PAPPIS, J., DONADIO, R. N., HAGEN, L. M., and COPRIULO, A. J. *The Properties of Boron Doped Pyrolytic Graphite.* Presented at 2nd ASTM Symposium on Pyrolytic Materials, Palm Springs, California, 10-11 May 1966.

12. KOTLENSKY, W. V. *Effect of Boron Level on Graphitization of Boronated Pyrolytic Graphite.* Carbon v. 5, no. 4, 1967, p. 409.

13. SCHWARTZ, A. S., and BOKROS, J. C. *Catalytic Graphitization of Carbon by Titanium.* Carbon, v. 5, no. 4, 1967, p. 325.

14. KATZ, R. N. *Effect of Post-Deposition Heat Treatment on the Flexural Strength of Pyrolytic Graphite.* Carbon, v. 6, 1968, p. 589-592.

15. DONADIO, R. N., and PAPPIS, J. *The Mechanical Properties of Pyrolytic Graphite.* Raytheon Tech. Memo T-574, 1964.

16. PAPPIS, J., and BLUM, S. L. *Properties of Pyrolytic Graphite.* Journal of American Ceramics Society, v. 414, no. 12, December 1961, p. 592.

17. FISCHBACH, D. B., and KOTLENSKY, W. V. *On the Mechanism of High Temperature Plastic Deformation in Pyrolytic Carbons.* Electro-chemical Technology, v. 5, nos. 5-6, 1967, p. 207.

18. GEBHART, J. J., and BERRY, J. M. *Mechanical Properties of Pyrolytic Graphite.* American Institute of Aeronautics and Astronautics Journal, v. 3, no. 3, 1965, p. 302-308.

19. ACQUAVIVA, S. J., and KATZ, R. N. *Room Temperature Strength of Pyrolytic Graphite as Affected by Microstructure and Boron Content.* Army Materials and Mechanics Research Center, Watertown, Massachusetts, AMMRC TR 68-04, February 1968.

20. General Electric Company. *Development of Manufacturing Methods for Producing Pyrolytic Graphite in Various Shapes and Structures.* Contract A-T 33-(615) 3136, Proj. NR8-349, Interim Engineering Progress Report, 1 July 1966 - 30 September 1966.

21. FORD, L. H., HIBBERT, N. S., INGLEBY, B. E., and WALKER, D. E. Y. *The Fluidised Bed Coating of Uranium Monocarbide with Silicon Carbide,* to be published in Special Ceramics 1967.

22. ARAI, G. J., and KANTER, M. A. *On the Lattice Parameters of Graphite Containing Boron as an Impurity.* Abstract No. 158, Carbon V., v. 2, 1964.

23. LOWELL, C. E. *Solid Solution of Boron in Graphite.* Journal of American Ceramics Society, v. 50, no. 3, 1967, p. 142.

24. BARRETT, C. S., and MASSALSKI, T. B. *Structure of Metals.* 3rd ed. McGraw-Hill, Book Company, Inc., New York 1966, p. 500.

25. RILEY, W. C. *Graphite,* in Ceramics for Advanced Technologies. John Wiley and Sons, New York, 1965.

26. FISCHBACH, D. B. *Kinetics of Graphitization I.* NAGA JPL Tech Report No. 32-532, February 1966.

27. STOVER, E. R. *Improvement of Pyrolytic Properties by Heat Treating and Hot Working.* General Electric Research Laboratories, Report 62-RL-2991 M, May 1962.

28. MEEIS, J. T. *Some Effects of Annealing Pyrolytic Graphite.* Proceedings of the 5th Conference on Carbon, v. 1, Pergamon Press, p. 461.

29. POPPER, P. *Formation of Non-Oxide Coatings by Pyrolysis*, in Special Ceramics 1962, Academic Press, 1963.

30. WONG, P., and ROBINSON, M. *Chemical Vapor Deposition of Polycrystalline* Al_2O_3. Presented at the Fall Meeting of American Ceramics Society, Basic Science Division, 20 September 1968.

31. ELLIS, R., and PAPPIS, J. *Chemically Vapor-Deposited Alumina*. IIT Research Institute, 12 March 1968.

32. KATZ, R. N., and GAZZARA, C. P., discussion to paper by R. Vook. *X-Ray Studies of Thin Surface Layers*. Proceedings of the 13th Sagamore Conference, Syracuse University Press, 1967.

UNCLASSIFIED
Security Classification

AD 688074

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Army Materials and Mechanics Research Center Watertown, Massachusetts 02172	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE
RECENT DEVELOPMENTS IN PYROLYTIC GRAPHITE

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

5. AUTHOR(S) *(Last name, first name, initial)*
Katz, R. Nathan, and
Gazzara, Charles P.

6. REPORT DATE March 1969	7a. TOTAL NO. OF PAGES 13	7b. NO. OF REFS 32

8a. CONTRACT OR GRANT NO. b. PROJECT NO. D/A 1T062105A330 c. AMCMS Code 5025.11.296 d. Subtask 39191	9a. ORIGINATOR'S REPORT NUMBER(S) AMMRC MS 69-01 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. AVAILABILITY/LIMITATION NOTICES
This document has been approved for public release and sale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY U. S. Army Materiel Command Washington, D. C. 20315

13. ABSTRACT

A study of the fine microstructure of boronated pyrolytic graphite was made utilizing optical and electron microscopy and X-ray diffraction techniques. The influence of boron content on the laminar structure, the lattice parameter, the lattice strain, the particle size, and the flexural strength of pyrolytic graphite were studied. Significant changes in the behavior of all investigated parameters were observed in the 0.50 to 0.75 percent boron range. A mechanism relating these changes to the appearance of a B_4C deposit is hypothesized.

In addition, the effects of post-deposition thermal treatment on the mechanical properties of unboronated pyrolytic graphite are discussed. Some general remarks concerning similarities in structure of pyrolytic materials are presented. (Authors)

DD FORM 1 JAN 64 1473

UNCLASSIFIED
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Pyrolytic graphite Pyrolytic materials Mechanical properties Microstructure Alloys Heat treatment						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization *(corporate author)* issuing the report.

2*a*. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2*b*. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7*a*. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7*b*. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8*a*. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8*b*, 8*c*, & 8*d*. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9*a*. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9*b*. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through
_______________________________."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through
_______________________________."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through
_______________________________."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13. ABSTRACT. Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS)*, *(S)*, *(C)*, or *(U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.