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Materials and Structures

*Physical Measurements Program
Pyrolytic Graphite*

SEMIANNUAL TECHNICAL REPORT
(1 January - 30 June 1962)

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MATERIALS AND STRUCTURES

Physical Measurements Program

Pyrolytic Graphite

SEMIANNUAL TECHNICAL REPORT

(1 January - 20 June 1962)

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ABSTRACT

Studies on pyrolytic graphite have been made with respect to its possible use as a re-entry heat shield material. Preliminary work is reported on changes in x-ray parameters and physical dimensions caused by heat treatment above the temperature of deposition. Data are presented which indicate that the pyrolytic structure becomes similar to that of natural graphite after treatment to 3000°C. Initial studies on structural changes as a function of time are reported.

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I. INTRODUCTION

Unique anisotropic thermal properties and high temperature strength make pyrolytic graphite tremendously interesting as a material for re-entry nose caps, leading edges, or rocket nozzle inserts. However, initial tests have revealed several problems associated with its uses such as severe dimensional changes at high temperature, a tendency to delaminate, and poor thermal stress resistance. These properties in question appear to be intimately dependent on microstructure of the as-fabricated material. An understanding and prediction of the behavior of pyrolytic graphite at high temperature can be accomplished only through a basic understanding of the changes in microstructure that occur at high temperature, and the effect of these changes on thermal and mechanical properties.

Studies have been undertaken during this report period aimed at identifying the scope of selected problems associated with the use of pyrolytic graphite as heat shield material. This report summarizes the results to date.

II. DISCUSSION

A. MICROSTRUCTURE STUDIES

Pyrolytic graphite is formed by the pyrolytic decomposition of a hydrocarbon gas in successive batches on a mandrel heated to about 2200°C. Growth proceeds such that the "c" axes of the individual crystals are all essentially normal to the mandrel surface. The resulting material, although polycrystalline, has the characteristic 0001 cleavage and shows the strong anisotropy typical of graphite single crystals. The pyrolytic graphite studied was obtained from High Temperature Material Corporation in the form of a plate 6 in. wide, 12 in. long, and 0.250 in. thick. The density was found to be 2.19 g/cc, or about 97 percent of theoretical. The "c" axes of the crystallites were oriented perpendicular to the major surface of the plate.

Microstructure studies have included optical microscopy, electron microscopy, and x-ray diffraction. Optical microscopy studies indicate the initial crystals nucleate from numerous points on the mandrel and grow radially. This radial growth, limited by the nucleation and growth of neighboring grains, results in a cone-like structure with apexes directed toward the mandrel. The cones are, in turn, made up of small crystallites in which the "c" axes are parallel to the growth radii of the cone as shown in Fig. 1.

The structure resulting from the nucleation and growth process described above has been termed "singular nucleation" (Ref. 1), see Fig. 2. Another type of pyrolytic graphite structure, "continuously nucleated," is characterized macroscopically as having fibrous rather than cone-like appearance. An example of continuously nucleated pyrolytic graphite is shown in Fig. 3. In the material studied, the initial and final depositions yielded singularly nucleated pyrolytic graphite. The two intermediate depositions resulted in a continuously nucleated material. Figure 4 illustrates this sequence. The change in the types of structure could be indicative of temperature difference from deposition to deposition.

Specimens of pyrolytic graphite cut parallel to the "c" axes permit excellent qualitative studies of the cone structure as a result of polarization phenomena but are not amenable to standard grain-counting techniques. Information resulting from specimens cut normal to the "c" axes is limited due to lack of both the polarization phenomena and good etching techniques. To overcome these difficulties, a new sample preparation technique was devised at this laboratory. Specimens have been prepared with polished surfaces oriented at 45 deg to the "c" axes, yielding measurable grain shapes which exhibit polarization phenomena. Figure 5 shows diagrammatically the techniques of sample preparation. Although grain counts could be taken in any random direction, the grain counts in this study were made in the "a" direction. To maintain continuity between specimens, counts were made at the midpoint of the final singularly-nucleated grains. It should be emphasized that the grains to be counted in this study are the cones.

Results of the grain size analysis as a function of temperature are shown in Table 1 with the "as received" value for comparison. Above 2400°C, the grain size measurements were limited by the size of the sample (6 mm). Figure 6 shows the pronounced grain structure of the "as received" material as prepared by the above technique. The larger bounded areas are the grains (cones) with the finer crystallite substructure superimposed. Figure 7 is a photomicrograph of pyrolytic graphite which was heated to 3000°C for 4 hr. The grain size is very large, with only remnants of the crystallite substructure. Upon heating, these changes in structure give strong visual evidence that "a" direction growth proceeds by straightening of the spherical layers resulting from radial growth of the graphite.

The examination of the cone structure of pyrolytic graphite was further extended by examination under the electron microscope. In addition, the areas at the junction of adjacent cones were examined to gain a better understanding of the contraction-expansion processes which result from the heat treatment of pyrolytic graphite.

Negatively shadowed replicas of a polished surface of "as received" pyrolytic graphite cut parallel to the "c" axes have been prepared and have been examined by means of the electron microscope. Figure 8 shows the tip of a cone and the junctions between it and other cones. Long dark areas in the figure correspond to long openings. The junction area structure results from shorter openings. If the openings are interpreted as pullout of crystallites of graphite, the electron photomicrograph substantiates x-ray findings, i. e., the cones are composed of crystallites which are progressively larger from the edge of the cone to the center. The junctions between two grains, although highly populated with small grains, appear to be sharp. Therefore, the presence of any large quantity of amorphous carbon in these boundaries is not probable. As a result, grain growth resulting from assimilation of amorphous carbon from these areas would not be significant.

Replicas also were prepared of pyrolytic graphite which had been heated at 3100°C for 15 min. Figure 9 is a photomicrograph of this material showing less curvature and more continuity of the crystallites than the untreated material. This behavior lends support to the observation that layer straightening upon heating is the major mechanism of the permanent expansion in the "a" direction.

The pyrolytic graphite "as received" has a turbostratic structure, i. e., it has completely random stacking of the basal planes. This random stacking results in C_0 spacings which are significantly larger than that of natural graphite. Bacon's (Ref. 2) correlation of percentage turbostratic structure with C_0 spacing indicates the "as received" material with a C_0 spacing of 6.96 \AA has about 93 percent turbostratic character.

The results of x-ray diffraction studies of C_0 contraction, and hence degree of ordering, as a function of heat treatments are shown in Fig. 10. These permanent contractions increase rapidly between 2400°C and 2600°C, and assume a constant value, $C_0 = 6.74 \text{ \AA}$ at about 2800°C. Within the error of the measurement, these results are in agreement with Bragg and Packer (Ref. 1)

at temperatures above 2800°C. The results of Kotlensky and Martens (Ref. 3) are shown for comparison. Additional x-ray diffraction analysis indicates that the turbostratic structure gradually gives way to a more ordered graphite with heating to successively higher temperatures above 2200°C. Strong (100) and (101) reflections replace the (10) two-dimensional reflection above 3000°C. The percentage of turbostratic structure is 36 percent for samples heated above 2800°C.

B. DIMENSIONAL STABILITY

A series of samples in the form of 0.25-in. cubes were heated for 4 hr at temperatures ranging from 2200°C to 3000°C. Room temperature dimensional measurements indicated contraction in the direction parallel to the "c" axes and expansion in the direction parallel to the "a" axes, as predicted by the microstructure investigation. This is shown in Fig. 11. The net reduction in volume agrees well with the change in graphite unit cell volume up to 2800°C (see Table 2). This would indicate that up to 2800°C the reduction in volume is largely due to a unit cell contraction associated with ordering of the graphite lattice. Above 2800°C other mechanisms, such as pore removal, increase in importance.

The thermal expansion of pyrolytic graphite in both the "a" and "c" directions was measured up to 3000°C. An average heating rate of 10°C/min. was maintained during the heating cycle. Results are shown in Figs. 12 and 13. Upon heating, the "a" axes first underwent a negative expansion with a minimum at about 400°C. Above 400°C, the expansion was positive and again reached zero at about 800°C. Above 2500°C, the rate of expansion in the "a" direction increased rapidly. At the upper limit of the test (2900°C) the expansion was 2.5 percent. Upon cooling, the expansion followed along a curve parallel to the initial expansion but displaced by about 2 percent, which represented the permanent expansion. The "c" axes expansion was as expected, up to about 2700°C. At this temperature the cumulative expansion was 7.4 percent. Above 2700°C contraction began, and the percent expansion decreased rapidly to about

minus 2 percent at 3000°C. Upon cooling the net contraction was about 9.1 percent.

Because of the short times involved in ballistic re-entry, knowledge of the time-dependence of structural changes in pyrolytic graphite is necessary. A first experiment indicated that the net expansion and contraction in the "a" and "c" directions, respectively, were considerably less with the rapid heating rates than in the four hour heat treatments described above. The data shown in Fig. 14 indicate that the rate of expansion is almost linear with time, with an observed rate change of 0.01 %/min. This preliminary data indicate a fairly strong time-dependence of structural change. Further experimentation in this area, particularly at higher temperatures, is needed.

III. TECHNICAL RESUME AND CONCLUSIONS

The preliminary work outlined above can be summarized as follows:

- a) As measured at room temperature, there is a dimensional expansion in the direction parallel to the "a" axes and a dimensional contraction in the direction parallel to the "c" axes, caused by heating pyrolytic graphite above its deposition temperature. The expansion in the dimension parallel to the "a" axes is due to the straightening of the spherical surface resulting from the radial growth of the cone structure. The contraction in the dimension parallel to the "c" axes is due to ordering in the individual graphite crystallites, in addition to the straightening process. The ordering also causes a reduction of the C_o spacing.
- b) A net volume reduction occurs as a result of heat treatment and is largely the result of the ordering phenomena.
- c) The net expansion in the direction parallel to the "a" axes is approximately linear with time at a temperature of 2800°C , and at times ranging up to 3 hr. This is significant since it implies that severe dimensional changes may not occur during the short times at high temperatures involved in re-entry. Additional experimental work in this area is urgently needed.
- d) In the direction parallel to the "a" axes, it appears that the structural changes do not change thermal expansion.
- e) The changes in x-ray properties, crystallite size, and density indicate that the structure becomes similar to that of natural graphite after heat treatment to 3000°C . On this basis, at temperatures above 3000°C , some deterioration of mechanical properties and tendencies to laminate would be predicted.

Table 1. Grain Size of Pyrolytic Graphite With Heat Treatment

Temperature, °C	Grain Size
"As Received"	90 μ
2400	200 μ
2600	≥ 6 m. m.
2800	≥ 6 m. m.
3000	≥ 6 m. m.

Table 2. Unit Cell And Macroscopic Volume Contraction As A Function of Temperature (a)

Temperature and Time °C hr		Macroscopic Volume Contraction, %	Unit Cell Contraction, %
2600	4	1.1	1.2
2800	4	1.7	1.8
3000	4	2.7	1.8

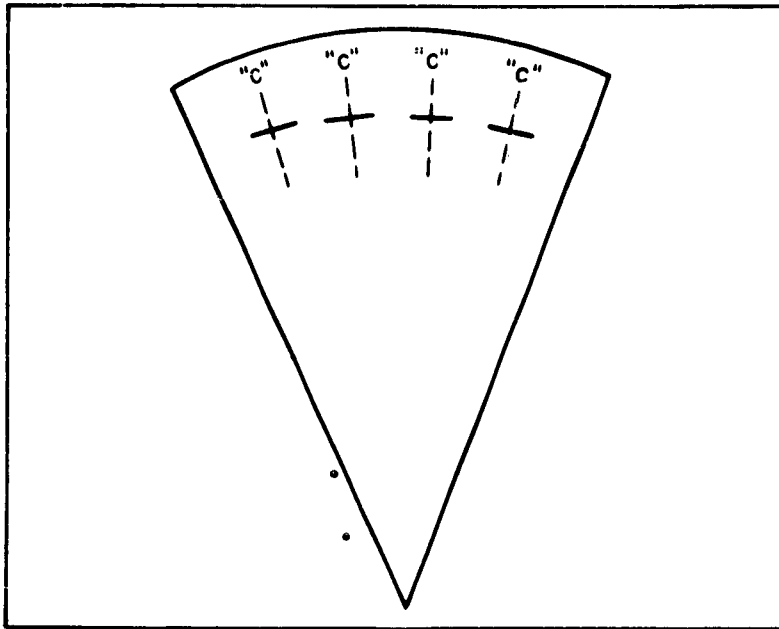


Figure 1. Orientation of Individual Crystallites in Pyrolytic Graphite ("c" Axes Normal to Growth Radii of Cone)



Figure 2. Polished Section of Final Deposition Area in Pyrolytic Graphite Showing Single Nucleation Structure Parallel to "c". (90X, Crossed Polarized Light)

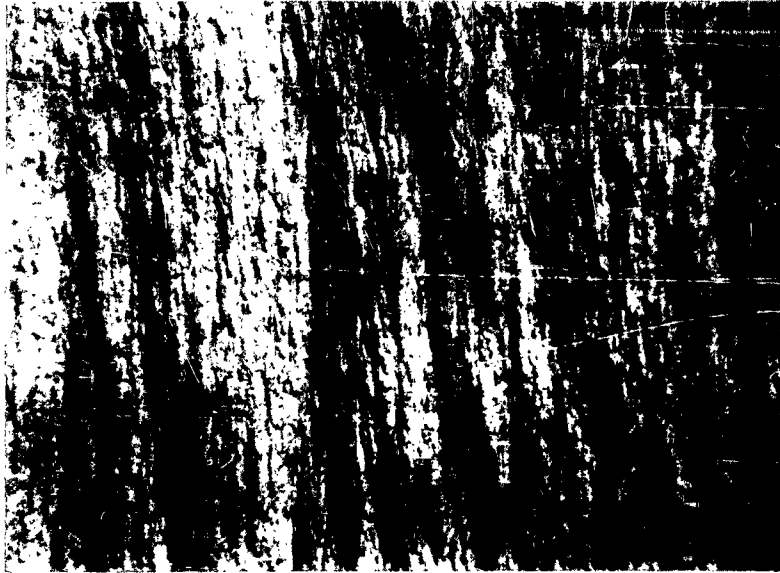


Figure 3. Polished Section of Continuously Nucleated Pyrolytic Graphite Parallel to "c". (90X, Crossed Polarized Light)

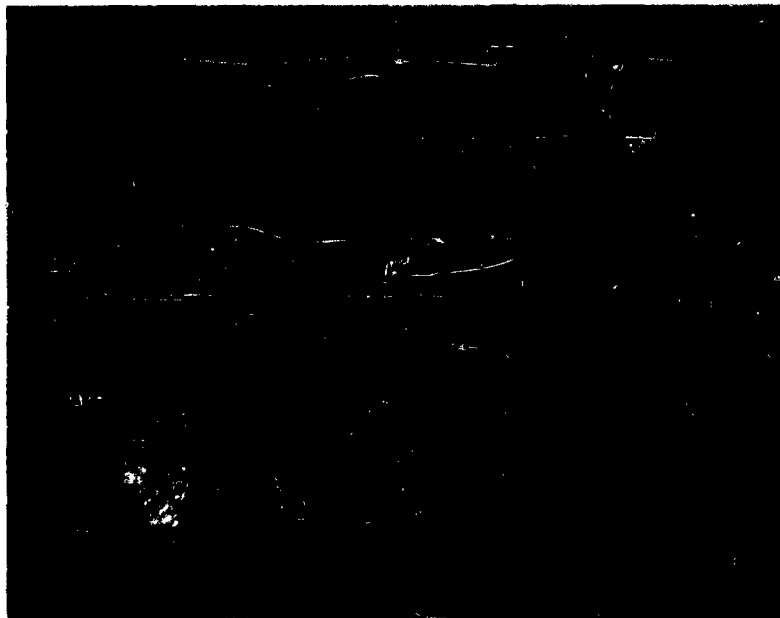


Figure 4. Polished Specimen of Pyrolytic Graphite Parallel to "c" in Cross Section Showing Four Deposition Stages: (1) Initial Singularly Nucleated Area, (2) and (3) Continuously Nucleated Area, and (4) Final Singularly Nucleated Area. (15X, Crossed Polarized Light)

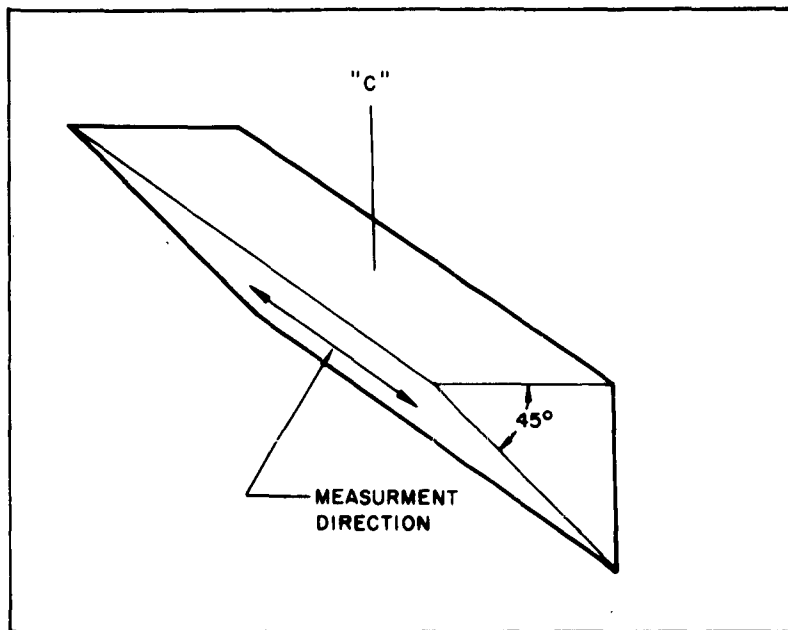


Figure 5. Block Diagram Illustrating the Method of Cutting Pyrolytic Graphite for Grain Size Analysis



Figure 6. Polished Specimen of "As Received" Pyrolytic Graphite Cut 45° to "c" for Grain Size Measurement. (35X, Crossed Polarized Light)

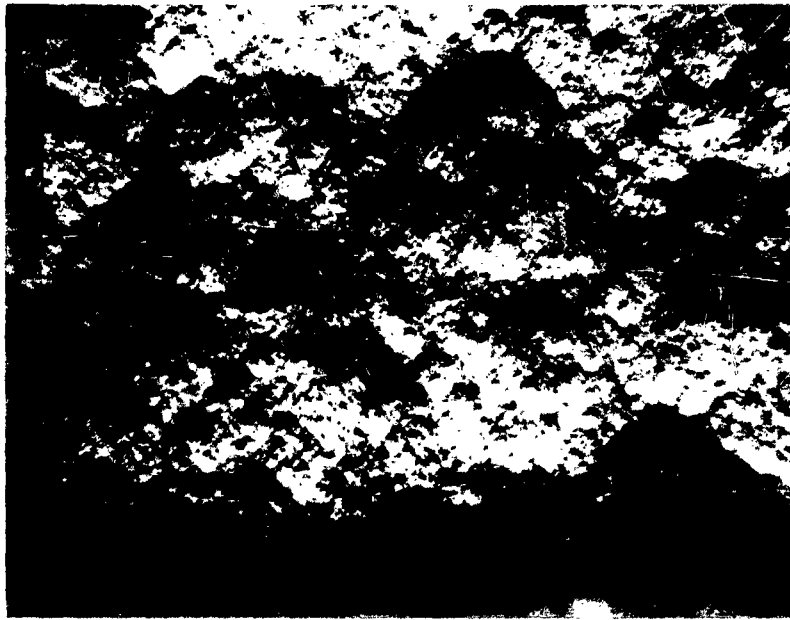


Figure 7. Polished Specimen of Treated Pyrolytic Graphite (3000°C, 4 hr) Cut 45° to "c" for Grain Size Measurement. (35X, Crossed Polarized Light)

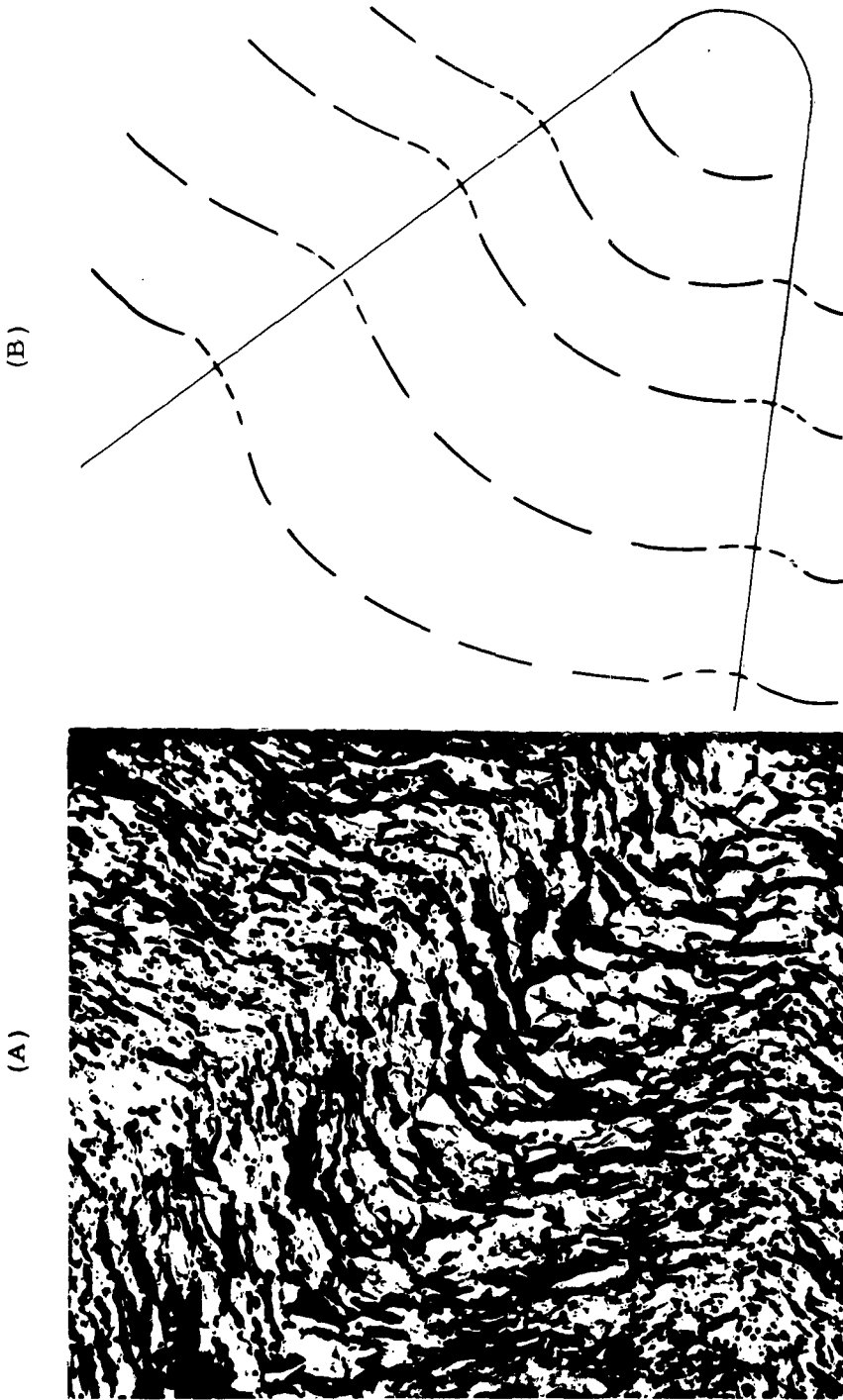


Figure 8. Electron Photomicrograph of "As Received" Pyrolytic Graphite Cut and Polished Parallel to "c". (17, 400X, Negatively Shadowed)



Figure 9. Electron Photomicrograph of Treated Pyrolytic Graphite (3100°C, 15 min.) Cut and Polished Parallel to "c". (13, 200X, Negatively Shadowed)

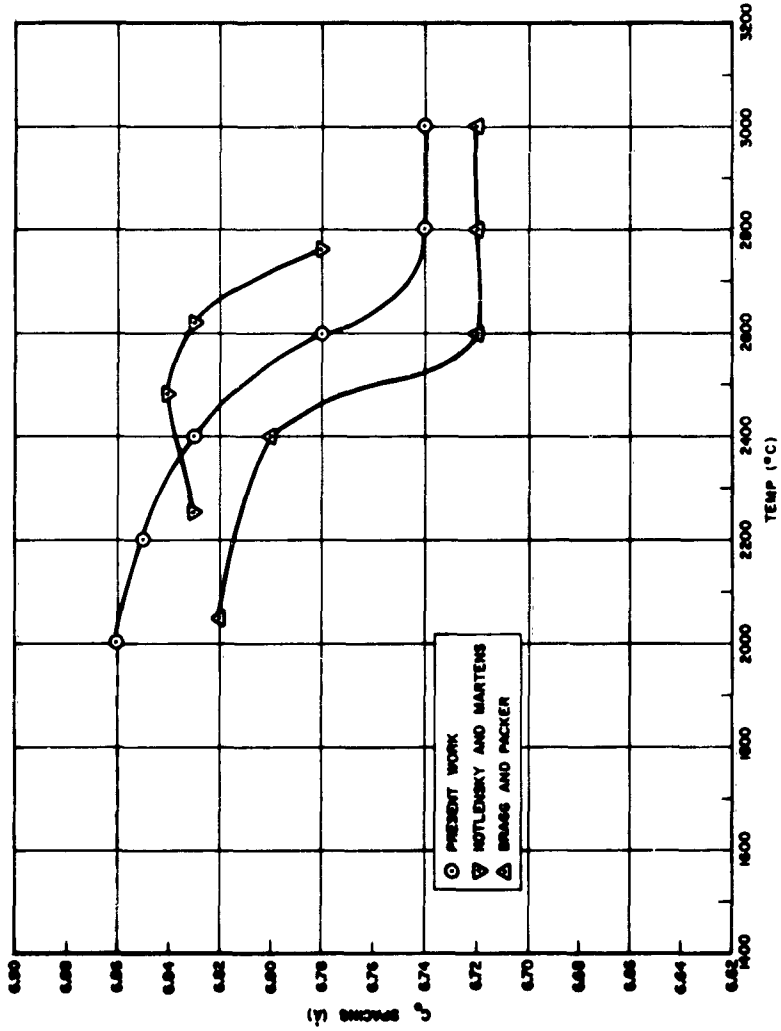


Figure 10. C_o Spacings for Pyrolytic Graphite as a Function of Annealing Temperatures

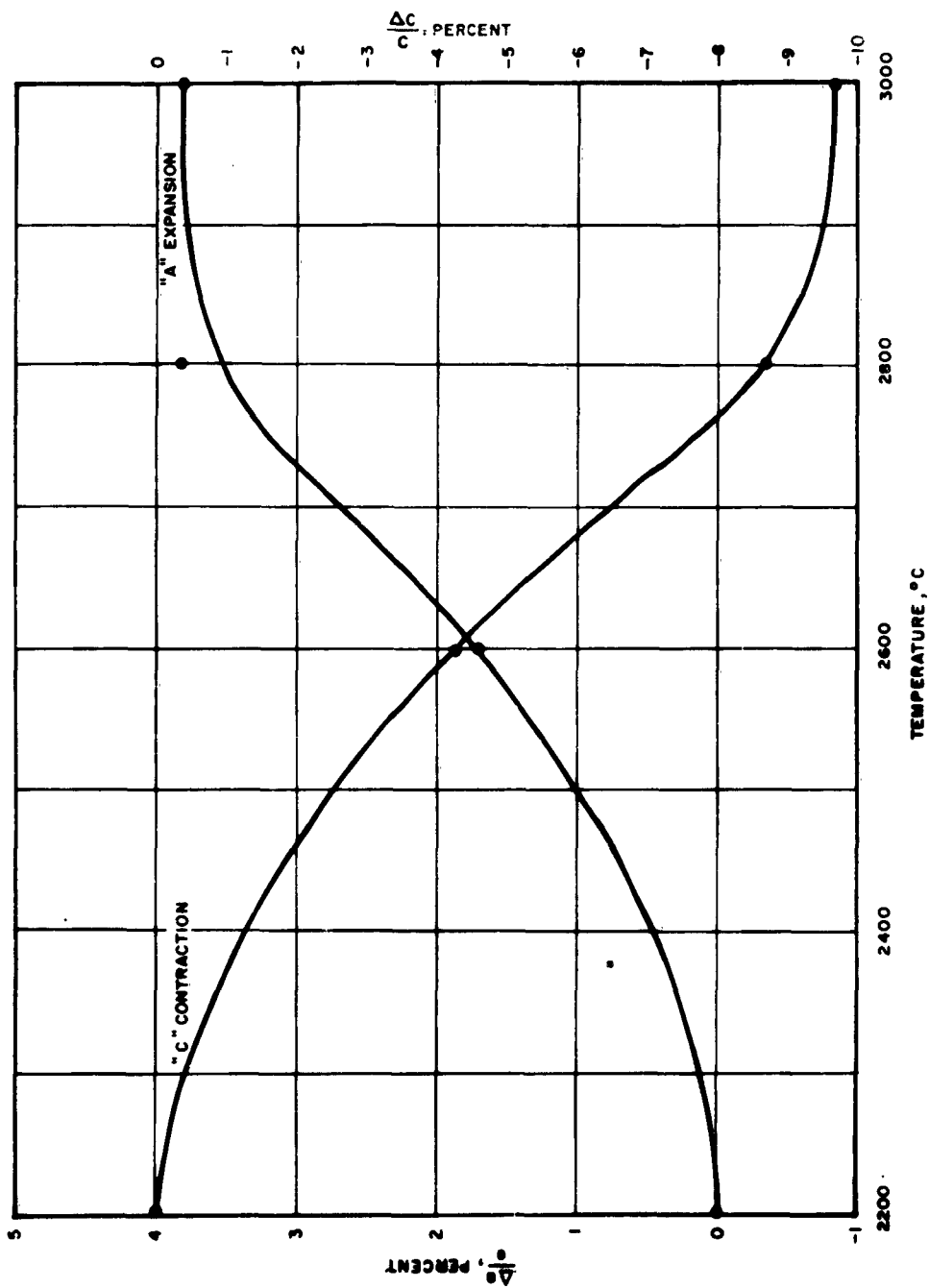


Figure 11. Net Dimensional Changes in Pyrolytic Graphite Due to Annealing for Four-Hour Periods

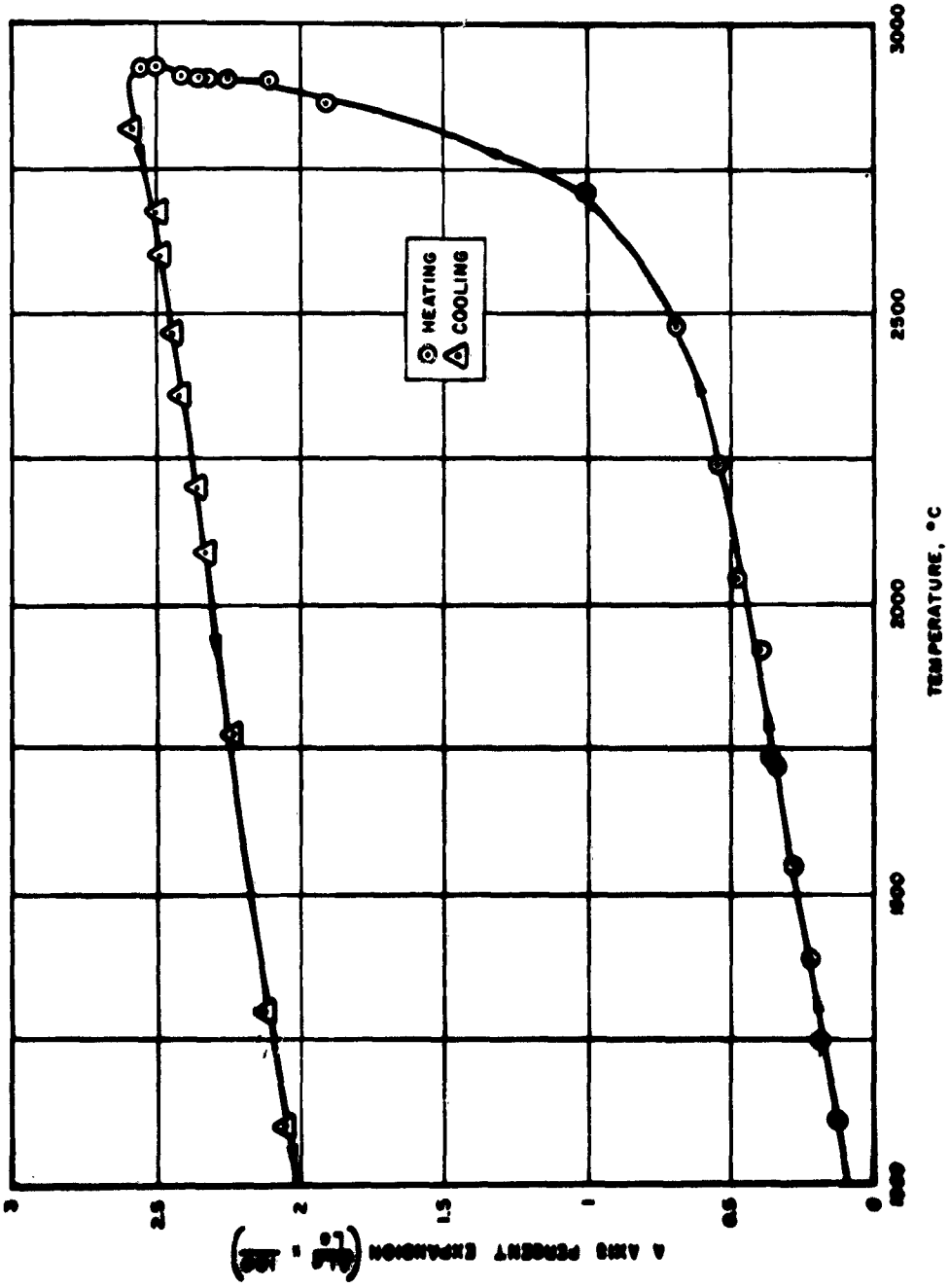


Figure 12. "a" Axis Thermal Expansion

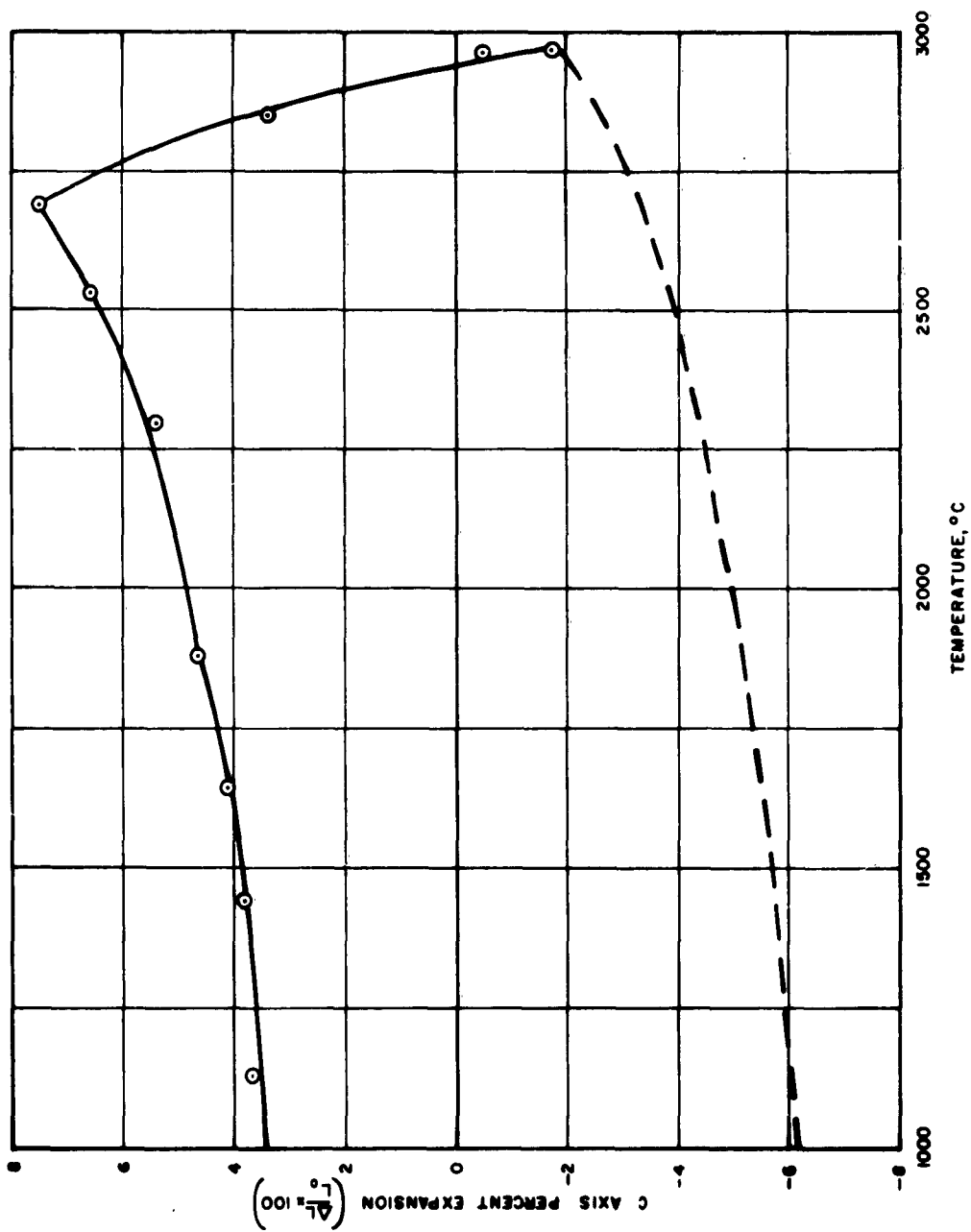


Figure 13. "c" Axis Thermal Expansion

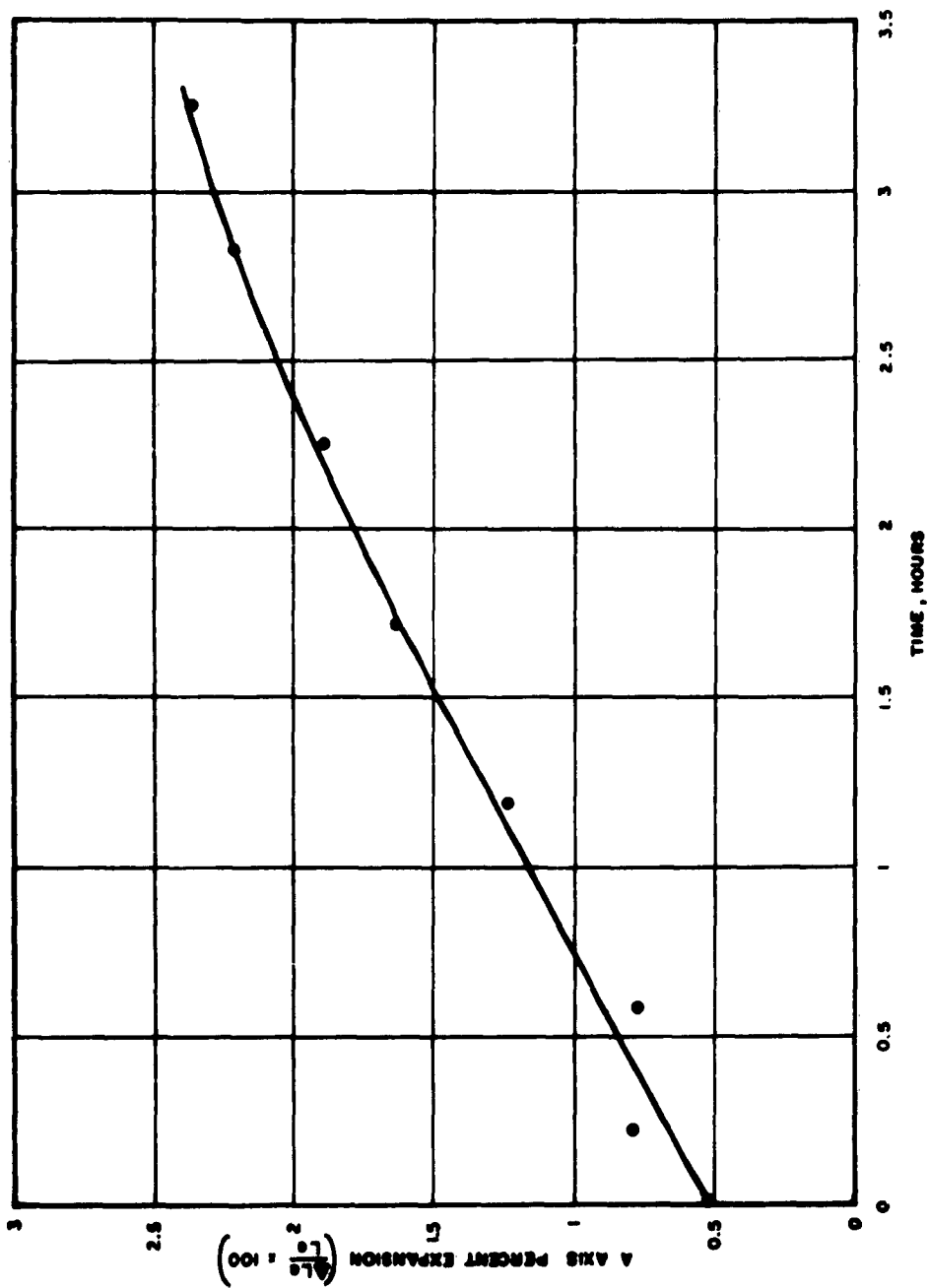


Figure 14. Time-Dependence of "a" Axis Expansion at 2800°C

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