

# Contrails

## FOREWORD

This work was conducted by National Carbon Company, Division of Union Carbide Corporation, under USAF Contract AF 33(616)-6915. This contract was initiated under Project No. 7350 "Refractory Inorganic Non-metallic Materials," Task No. 735002, "Graphite Materials Development"; Project No. 7381 "Materials Application"; Task No. 738102 "Materials Preproduction Process Development"; and Project No. 7-817 "Process Development for Graphite Materials". The work was administrated under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, with Captain R. H. Wilson, L. J. Conlon and W. P. Conrardy acting as Project Engineers.

Work under this contract has been in progress since May 1, 1960. The work covered in this report was conducted at the Research Laboratory of National Carbon Company, located at Parma 30, Ohio, under the direction of J. C. Bowman, Director of Research, and W. P. Eatherly, Assistant Director of Research. The room temperature breaking strength measurements were made by S. A. Crawford.

This is the sixth of a series of volumes of WADD Technical Report 61-72 prepared to describe various phases of the work. The preceding volumes of this series are:

- Volume I      Observations by Electron Microscopy of Dislocations in Graphite, by Richard Sprague.
- Volume II     Applications of Anisotropic Elastic Continuum Theory to Dislocations in Graphite, by G. B. Spence.
- Volume III    Decoration of Dislocations and Low Angle Grain Boundaries in Graphite Single Crystals, by Roger Bacon and Richard Sprague.
- Volume IV     Adaptation of Radiographic Principles to the Quality Control of Graphite, by R. W. Wallouch.
- Volume V      Analysis of Creep and Recovery Curves for ATJ Graphite, by E. J. Seldin and R. N. Draper.

# *Contrails*

## ABSTRACT

Flexural creep tests have been made on molded carbons and several types of graphites over the temperature range from 2200° to 3000°C. The amount of creep was found to decrease for a carbon as the temperature of graphitization increased and as the holding time at graphitization temperature increased for times up to four hours.

Activation energies were determined for several standard and experimental grades of graphite from the steady state creep rates. The activation energies ranged from 23 to 92 kcal/mole and appeared to be constant for each graphite. The flexure experiments demonstrated a marked dependence of the creep on the grain orientation for the more anisotropic graphites. The grain orientation showing the highest room temperature strength shows the lowest high temperature creep. Some of the factors which influenced the creep behavior are density, crystallite size, and the size, type, and orientation of the particles.

## PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



W. G. RAMKE  
Chief, Ceramics and Graphite Branch  
Metals and Ceramics Laboratory  
Directorate of Materials and Processes

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## 1. INTRODUCTION

Flexural creep tests have been run on several experimental and standard National Carbon grades of molded carbon and graphite. The experiments were mainly exploratory. They indicate that the creep behavior of carbon depends on such fabrication variables as density, binder level, grain size, crystalline orientation and graphitization history. The results offer a comparison between the different grades of carbon and illustrate the great differences in creep behavior that can be found between different grades and types of carbons.

A flexural test was chosen rather than any other kind of test because it appeared to be the simplest test to run experimentally and because of the ease of preparation of test specimens. A standard specimen size was used in all of the experiments so that the results for the different types of carbons could easily be compared. The creep curves obtained in flexure are similar in appearance to those reported in the literature for creep in tension. A typical creep curve shows an almost instantaneous deformation as the load is applied, followed by a slowly decreasing rate of deformation which, after a period of about thirty minutes or longer, tends to become constant. The final "linear" creep rate has been found to be an Arrhenius function of the temperature for almost every type of carbon which has been studied. The activation energies obtained by fitting the linear creep rates to Arrhenius functions have, therefore, been taken as characteristic parameters of the materials.

## 2. EXPERIMENTAL PROCEDURE

The creep tests were performed in a 4-inch diameter horizontal resistance-heated graphite tube furnace in an inert atmosphere. The creep fixture and other parts of the apparatus within the furnace were made of graphite. The standard specimen was a  $3/32 \times 3/8 \times 1-3/4$  inch slab. The specimen was mounted in a vertical position during the test in a graphite fixture with a distance between supports of 1.5 inches. Details of the creep apparatus are shown in Figure 1. During the creep test, the specimen was held in a vertical position within the fixture, and the load was applied against the broad face of the specimen through a single knife edge positioned midway between the supports. The load was transmitted through a series of  $1/2$ -inch diameter spectroscopic carbon rods approximately one foot long which ran through a one-inch inside diameter graphite tube to the outside of the furnace, a distance of about four feet. Running alongside the load transmission rods was a series of  $1/4$ -inch diameter spectroscopic carbon rods also approximately one foot long, the end rod of the series within the furnace making contact with the graphite fixture close to the specimen.

Outside the furnace, a brass water-cooled fixture, on which was mounted a lever, was screwed onto the graphite tube. The lever had a five-to-one mechanical advantage. The short arm of the lever had a one-inch long  $1/2$ -inch diameter

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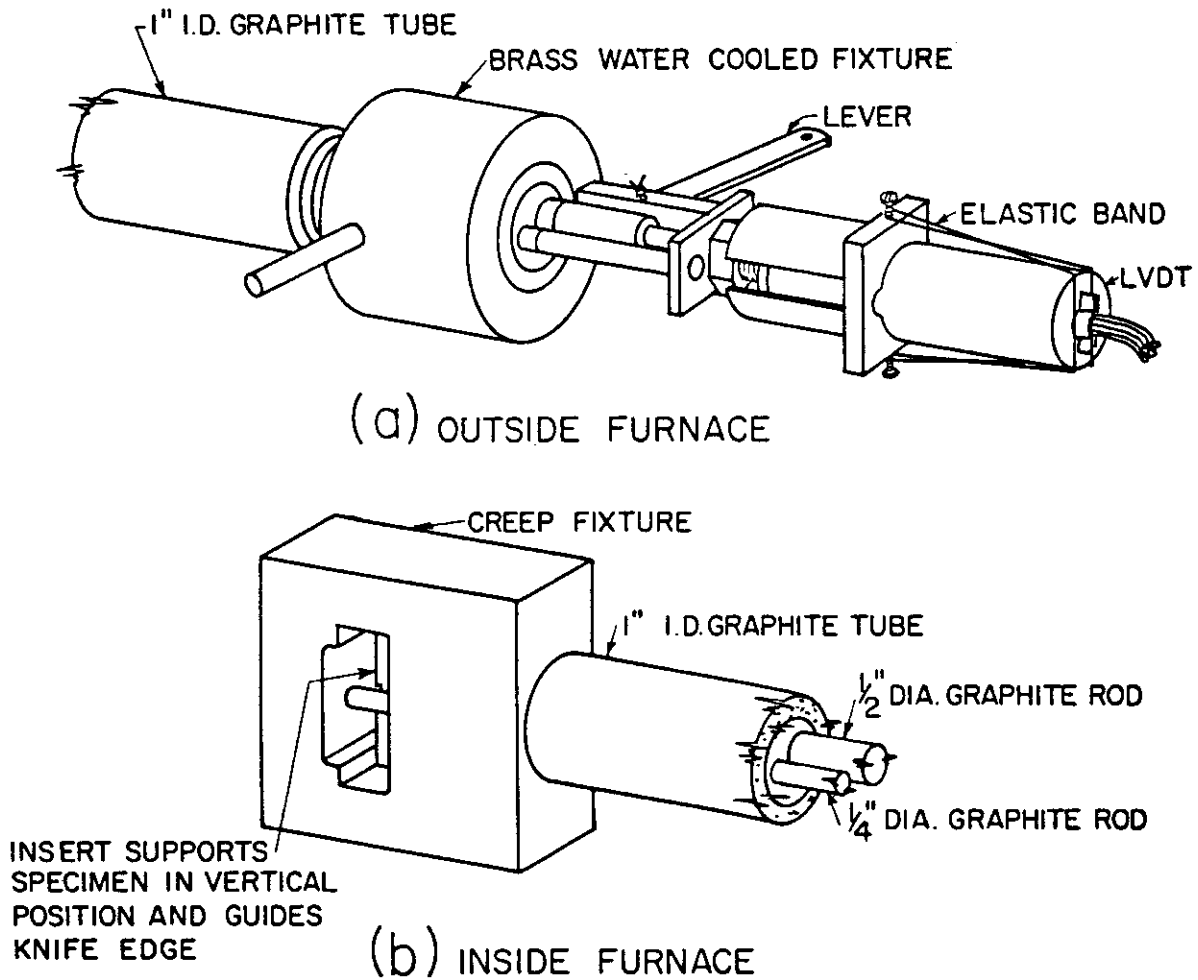


Figure 1. Details of Creep Apparatus

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transite rod which made contact with the load transmission rod, while attached to the end of the long arm of the lever was a string which passed over a pulley. The constant load was attained by hanging a weight on the string. The deformation of the specimen was measured by means of a linear variable differential transformer (LVDT) which was loosely mounted on the brass water-cooled fixture. The body of the LVDT was made to follow the motion of the 1/4-inch diameter spectroscopic rod, and the core of the LVDT followed the motion of the transite rod which was in direct contact with the load transmission rod. The use of two series of graphite rods having the same coefficient of thermal expansion allowed for the automatic compensation of changes in length due to thermal expansion of the load transmission rods, so that the motion of the core of the LVDT was taken to be equal to the motion of the specimen.

In a standard creep test, the apparatus was first set into position, the furnace was raised to temperature, and the load was applied within a few minutes of the time the test temperature was reached. The deformation of the specimen as a function of time was automatically recorded by plotting on a Varian chart recorder the output of the LVDT. The differential transformers which were used were made by Daytronic Corporation of Dayton, Ohio, and had a maximum rated sensitivity of 4.0 mv/0.001-inch and a linear range of approximately 0.08-inch. For most of the tests, the sensitivity had to be decreased by several orders of magnitude in order to get the whole creep curve on the recorder chart. When the magnitude of the deformation exceeded the linear range of the LVDT, the creep curves were recorded in two or three parts by temporarily removing the load and inserting one or two shims of known thickness between the transite rod and the load transmission rod when the end of the linear range of the differential transformer was approached. The differential transformer was calibrated against a micrometer screw at the end of each creep test.

The apparatus occupied half of the tube furnace, so that most often two tests were made at the same time by means of identical sets of apparatus in each half of the furnace. The specimens were positioned about 1-1/2 inches from the center of the furnace, and the temperature at the center of the furnace was read by means of an optical pyrometer. The temperature was regulated by manually controlling the power input to the tube furnace and was usually held to within 25° of the test temperature. The creep tests were run at temperatures ranging from 2200°C to 3000°C. The early creep tests on the effects of time and temperature of graphitization were made on some low density molded stock prepared by the author. These tests were run for 90 minutes with a load of 750g. The later tests on the experimental and standard National Carbon grades of graphite were run for 2 hours with a load of 2500g. In all cases, when the load was removed and the specimens held at temperature, a partial recovery of the deformation was observed. The recovery data are not presented here. They are discussed for the case of ATJ graphite in another report. <sup>(1)</sup>

### 3. RESULTS

The experimental results will be described for each grade of carbon or graphite in turn.

## 3.1 Molded Baked Carbons

This group of carbons was prepared by the author from a mix of 100 parts Continental coke flour and 40 parts of 30-medium pitch by weight. This coke is of dendritic (needle) structure, and the particle size was all less than 0.0164-inch diameter. The mix was molded into cylinders 2-1/2 inches in diameter by approximately 2-3/4 inches in height, which were then baked in protected saggars to 800°C. All of the specimens used in these tests were cut from two cylinders having densities in the baked state of  $1.45 \pm 0.01$  g/cm<sup>3</sup>. The grain orientation was the same in each specimen, the broad face being parallel to the top of the original molded cylinder. This grain orientation will be called grain orientation A.

The creep experiments which were run on this particular set of specimens can be divided into two groups. These experiments demonstrate first the effect of the time of heat treatment on the creep behavior, and secondly, the effect of the heat treatment temperature itself on the total creep, the creep rate, and the activation energy.

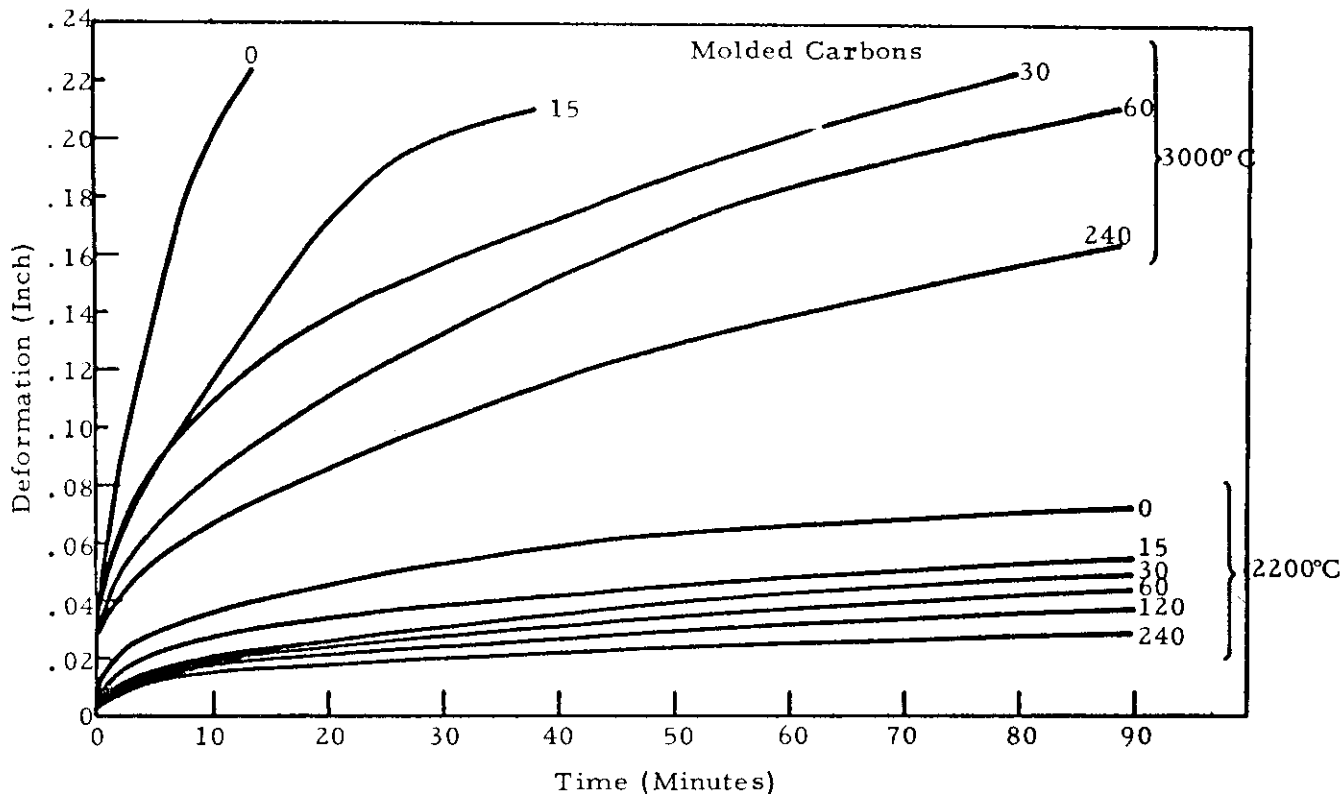
In the first group of experiments, the experimental procedure which was followed was to raise a baked carbon specimen to the test temperature in the furnace as rapidly as possible, usually in an hour or slightly longer, and hold it for a specified length of time at the test temperature before applying the load. The holding time at test temperature was varied from zero to four hours. The test temperatures which were chosen were 2200°C, 2600°C, and 3000°C, and a force of 750 g was used. These creep tests were run for a maximum of 90 minutes.

It is convenient to relate the actual applied load to the maximum fiber stress in the specimen, which is the maximum stress in a small region on the outer face of the specimen directly opposite the knife edge. The equation for the maximum fiber stress,  $S$ , is

$$S = \frac{3PL}{2bd^2} \quad (1)$$

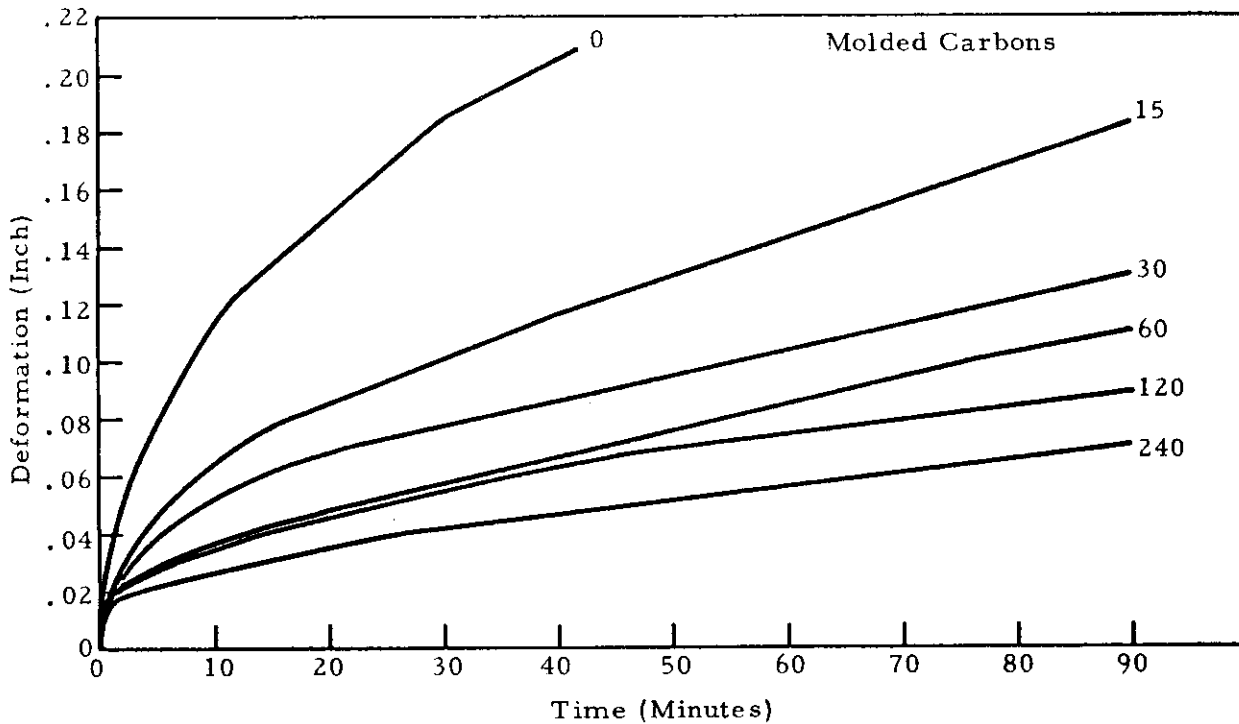
where  $P$  is the force,  $L$  is the distance between supports,  $b$  is the width of the specimen, and  $d$  is the thickness of the specimen. A force of 750 g corresponds to a maximum fiber stress of 1400 lb/in<sup>2</sup>.

The creep curves which were obtained are shown in Figures 2 and 3. It can be seen that at each of the three temperatures, the amount of initial elastic deformation is independent of the holding time, and the magnitude of the creep and creep rate decrease as the holding time is increased. The curves indicate that the changes taking place within the material which influence the creep are taking place most rapidly in the initial few minutes in which the material is at high temperature, but that changes continue to take place for several hours. The creep test, therefore, provides an interesting means of following the kinetics of graphitization. It is interesting to compare these results with data reported by Bowman<sup>(2)</sup> on the half-widths of X-ray diffraction lines of gas-baked spectroscopic rods which were treated at temperatures from 2400°C to 2700°C for various periods of time



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Figure 2. Creep curves for carbons previously baked to 800°C tested at 2200°C and 3000°C. Number on curve is time in minutes the specimens were held at test temperature before the force was applied. Force = 750g.



N-277

Figure 3. Creep curves for carbons previously baked to 800°C tested at 2600°C. Number on curve is time in minutes the specimens were held at test temperature before the force was applied. Force = 750g.

up to four hours. The X-ray data show that after about the first 15 minutes at temperature there is little or no change in the 004 line, but the half-widths of the 022 and 201 lines continue to decrease over a period of four hours. The line widths decrease with heating time in a manner similar to that in which the final creep rates change with holding time. The general conclusion that can be drawn from the creep experiments, therefore, is that the magnitude of the creep decreases because the material becomes more highly graphitized.

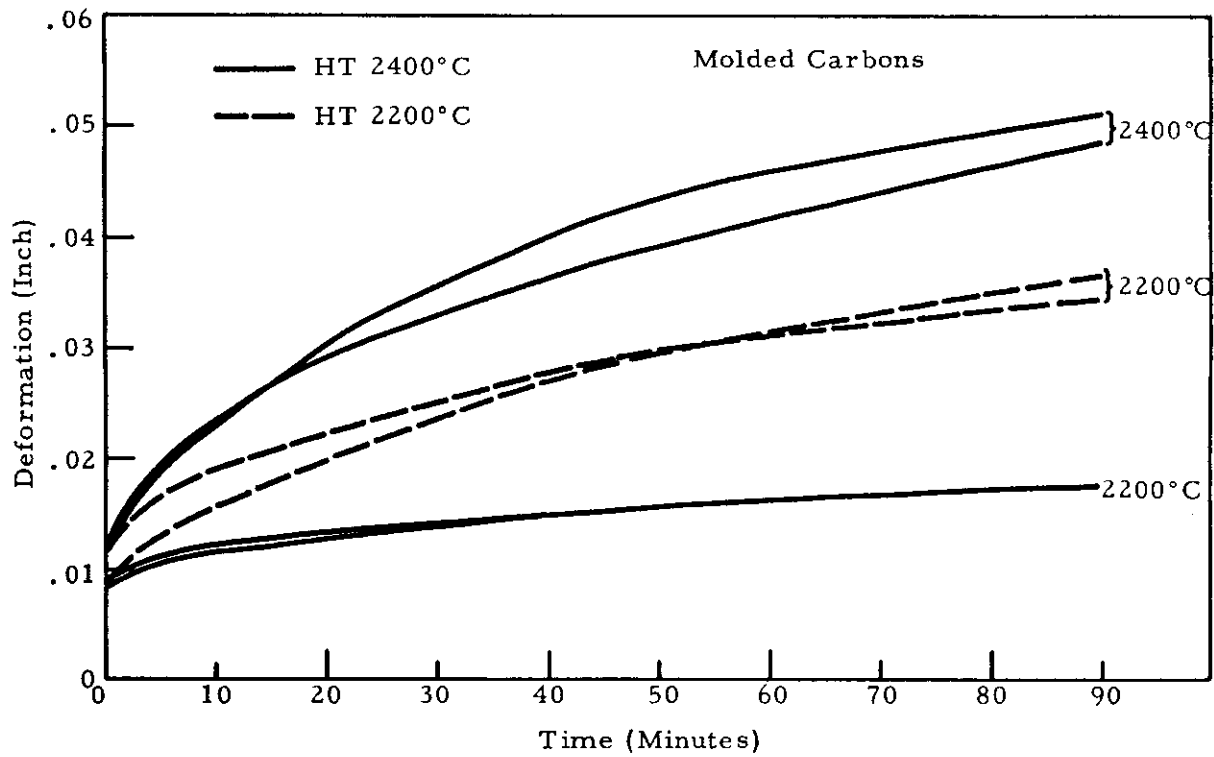
The most common means of increasing the degree of graphitization of a carbon material is to raise the heat treatment temperature. In the second group of experiments, five sets of baked carbon specimens were heated for periods of four hours to temperatures of 2200°C, 2400°C, 2600°C, 2800°C and 3000°C, respectively. Creep tests were then run at temperatures equal to or less than the heat treatment temperature. Again, a force of 750 g was used, corresponding to a maximum fiber stress of 1140 lb/in<sup>2</sup>, and the tests were run for 90 minutes. The creep curves are shown in Figures 4, 5, 6, and 7, where they are grouped according to heat treatment temperature (HT). Two duplicate tests were made in each case, except for the one test at 3000°C. The curves demonstrate the type of deviations in behavior that may be obtained between seemingly identical specimens. They also demonstrate that when the degree of graphitization is increased by raising the heat treatment temperature, the resistance to creep increases.

Figure 8 is a semi-log plot of the steady state creep rate versus 1/T for the curves in the previous four figures. The average creep rate is plotted as well as the spread of the actual values which were obtained. Three parallel lines have been drawn to best fit the sets of points for the three heat treatment temperatures of 2400°C, 2600°C and 2800°C. The activation energy for these three groups of samples, as obtained from the straight lines, is 96 kcal/mole. The line drawn for the samples heat treated to 3000°C gives an activation energy of 60 kcal/mole, and the point at 3000°C falls well above this line. These experiments also demonstrate that the creep rate decreases as the degree of graphitization increases. The change in the activation energy for creep as the heat treatment temperature is increased from 2800°C to 3000°C is interesting to note, though no explanation can be given for it here. Similar observations of the effects on the creep curves of heat treatment temperature and holding time at temperature have been reported by Martens, et al<sup>(3)</sup>.

### 3.2 ATJ Graphite

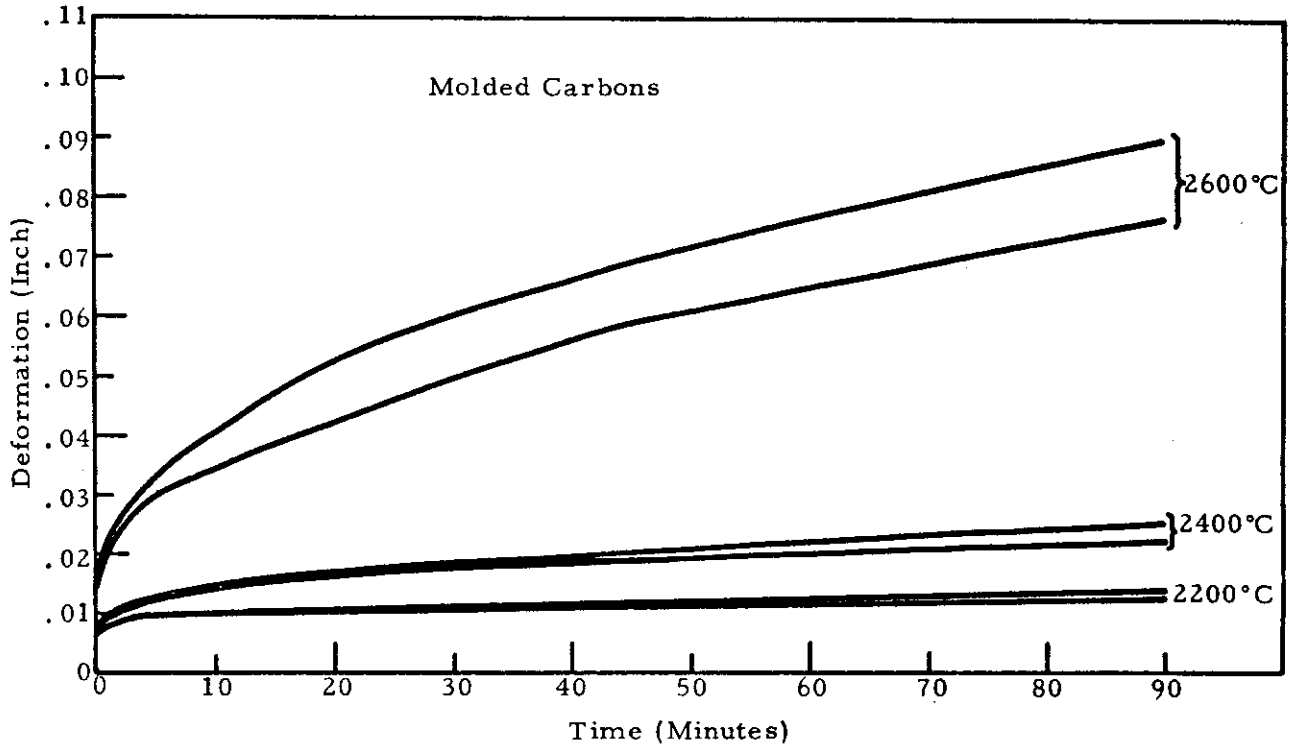
ATJ graphite is one of the standard grades of National Carbon graphite which were tested. This graphite is a fine-grain material which was prepared by molding. It was graphitized at a temperature of approximately 3000°C.

One of the variable factors which was investigated was the effect of the grain orientation in the specimen on the creep. For this purpose, specimens with three different grain orientations were cut from the same large slab of material, as is shown in Figure 9. It is assumed for purposes of illustration, that the grains or crystallites which have a platelet-like structure are oriented during molding so



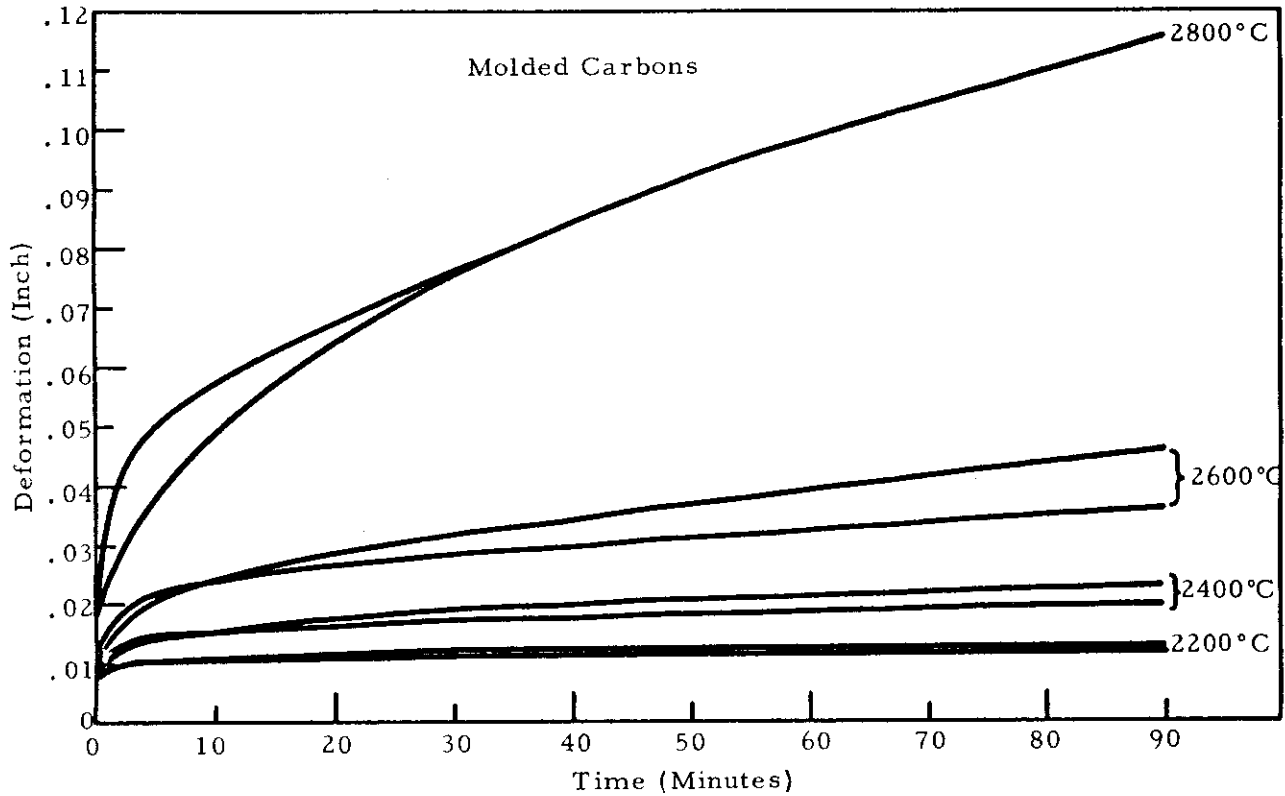
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Figure 4. Creep at various temperatures of molded carbons heat-treated four hours at 2200°C or 2400°C. Force = 750g.



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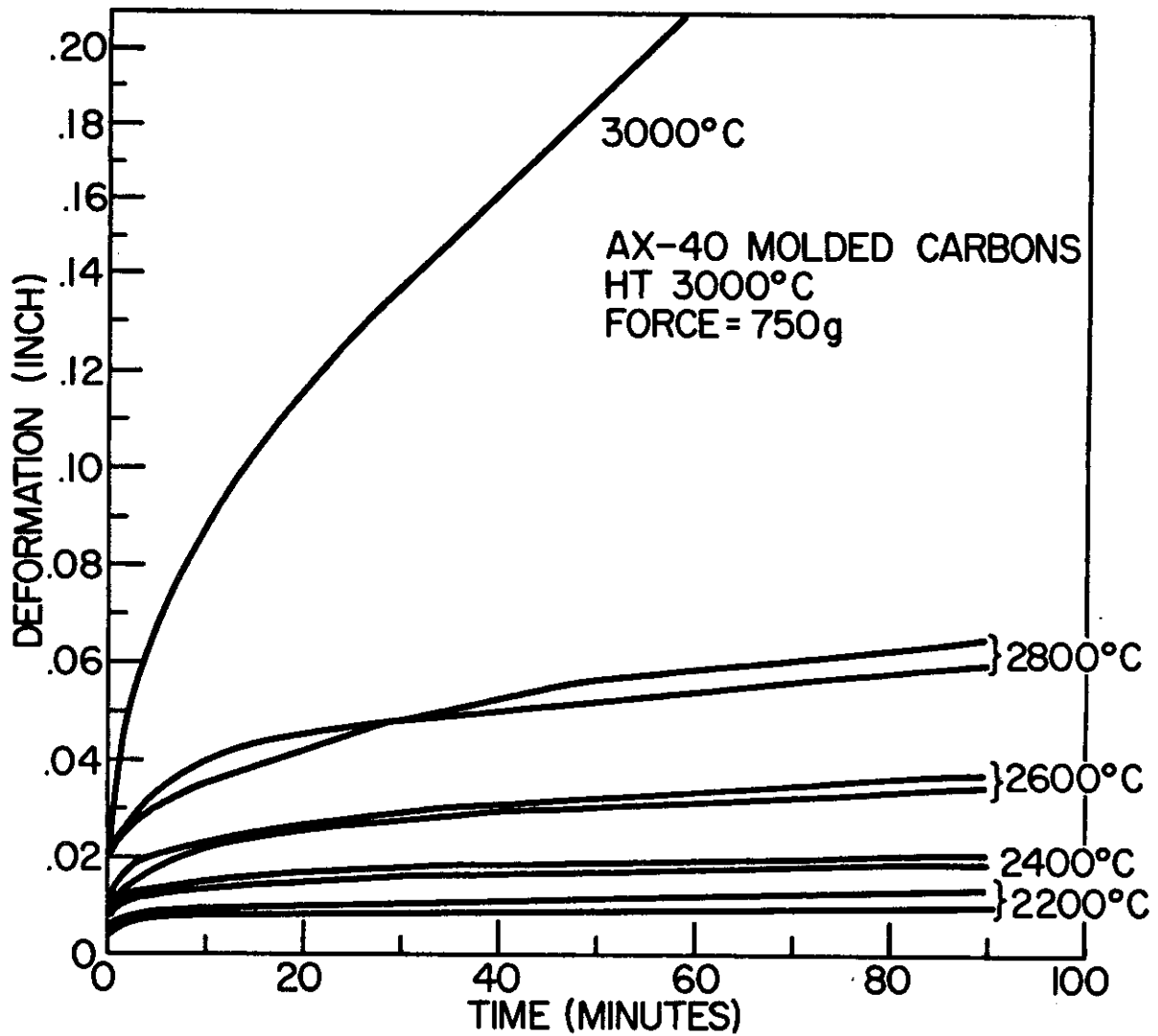
Figure 5. Creep at various temperatures of molded carbons heat treated four hours at 2600°C. Force = 750g.



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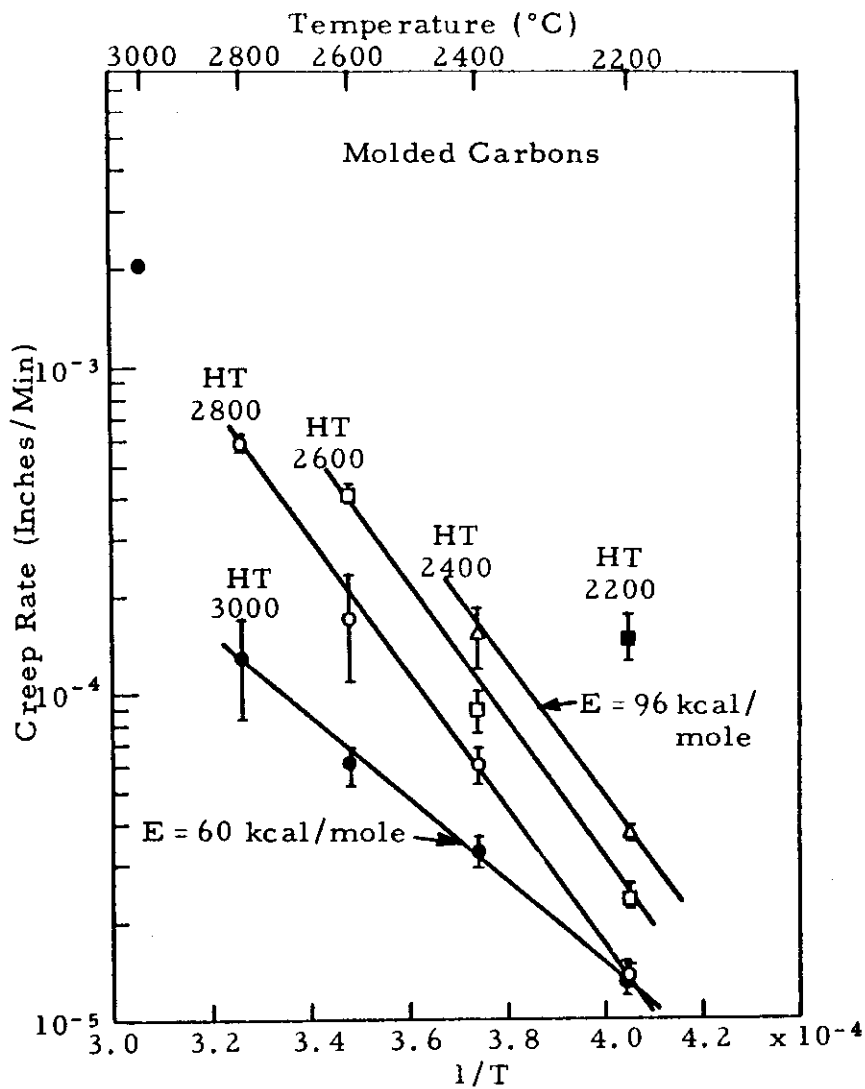
Figure 6. Creep at various temperatures of molded carbons heat treated four hours at 2800°C. Force = 750g.





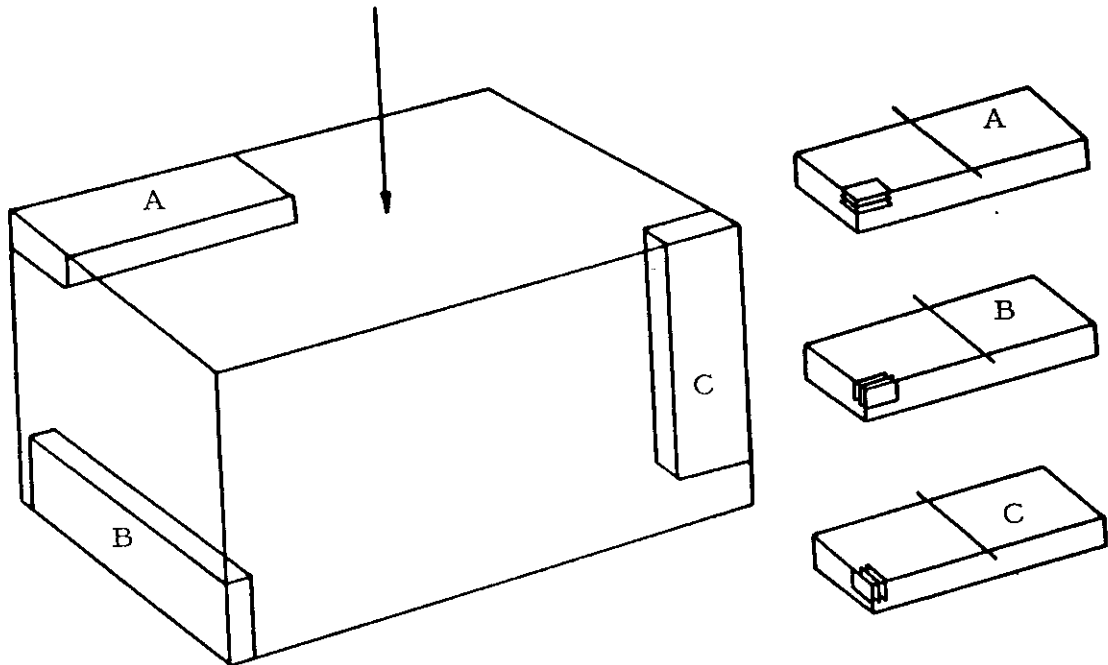
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Figure 7. Creep at various temperatures of molded carbons heat treated four hours at 3000°C.  
Force = 750g.



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Figure 8. Plot of steady state creep rate at various temperatures (T) versus 1/T for molded carbons with different heat treatment temperature (HT). Force = 750g.



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Figure 9. The figure shows three possible grain orientations for flexural specimens taken from an anisotropic material containing layer planes. In the case of a molded graphite, the arrow denotes the direction of the applied force during molding.

that the planes of the crystallites are perpendicular to the direction of the applied molding pressure. The degree to which this is true in an actual graphite determines the anisotropy of the material. The figure shows the three specimen orientations, labelled arbitrarily A, B, and C, the orientation of the specimens relative to the large piece, and the position of the knife edge during flexure.

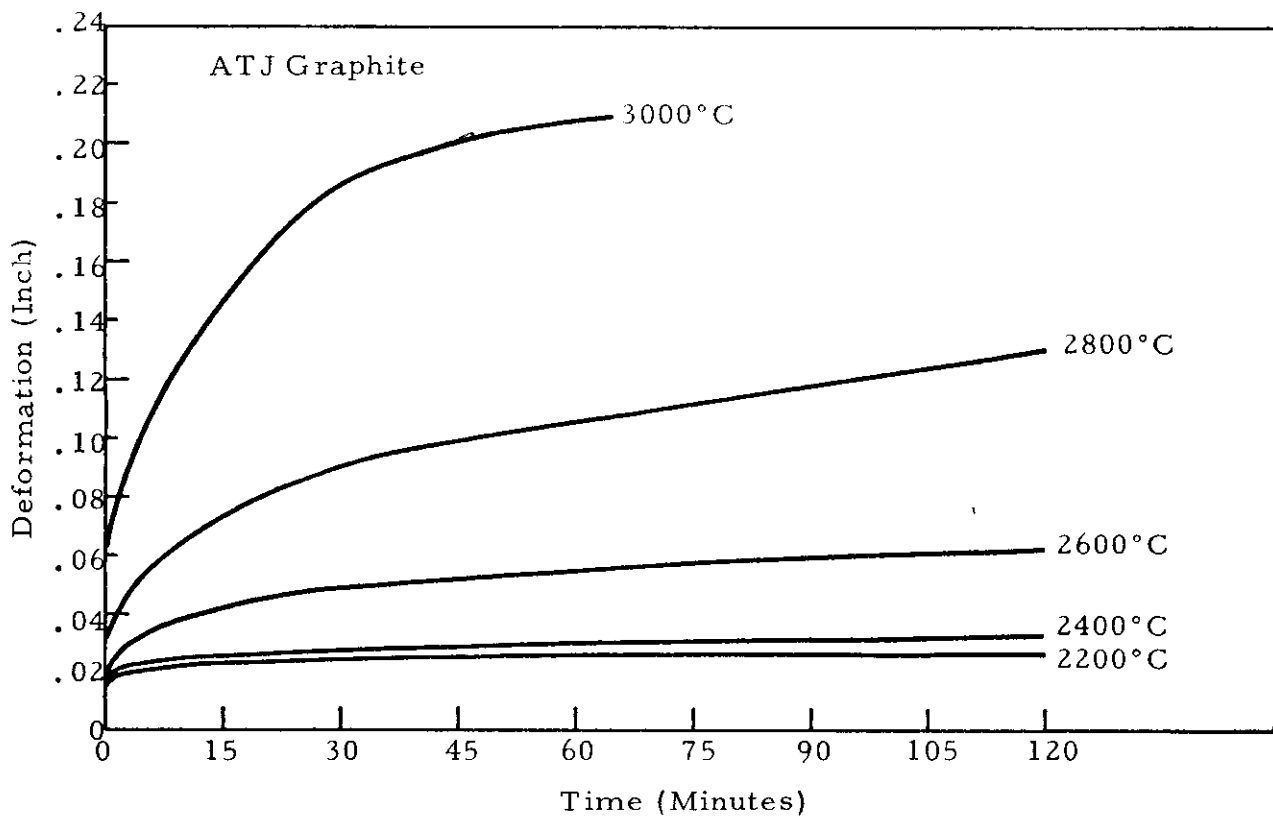
The ATJ specimens had an average density of  $1.755 \text{ g/cm}^3$ . They were tested at temperatures ranging from  $2200^\circ\text{C}$  to  $3000^\circ\text{C}$ , using a load of 2500g, which corresponds to a maximum fiber stress  $S$  of  $3800 \text{ lb/in}^2$ . The creep curves for the three groups of specimens with different grain orientations are shown in Figures 10, 11, and 12. There were no great differences in the creep curves at any temperature due to the grain orientation of the specimens. Specimens with orientation A and B had almost identical creep curves while specimens with grain orientation C showed slightly greater creep at all temperatures. From the linear parts of the creep curves, an activation energy of 76 kcal/mole was determined.

There was a direct correlation between the creep behavior and the room temperature breaking strengths, as the orientations showing the lesser creep showed the greater strengths. The specimens used for breaking strength measurements were  $3/8 \times 3/8 \times 1$ -inch in size. Three point loading was used, the supports and load source being steel cylindrical rolls  $3/8$ -inch in diameter, with a distance between supports of  $5/8$ -inch. The maximum tensile stress in breaking was determined using equation (1). The average breaking strengths for the three orientations were  $5650 \text{ lb/in}^2$  for the A orientation,  $5730 \text{ lb/in}^2$  for the B orientation, and  $4830 \text{ lb/in}^2$  for the C orientation.

### 3.3 ZTB Graphite

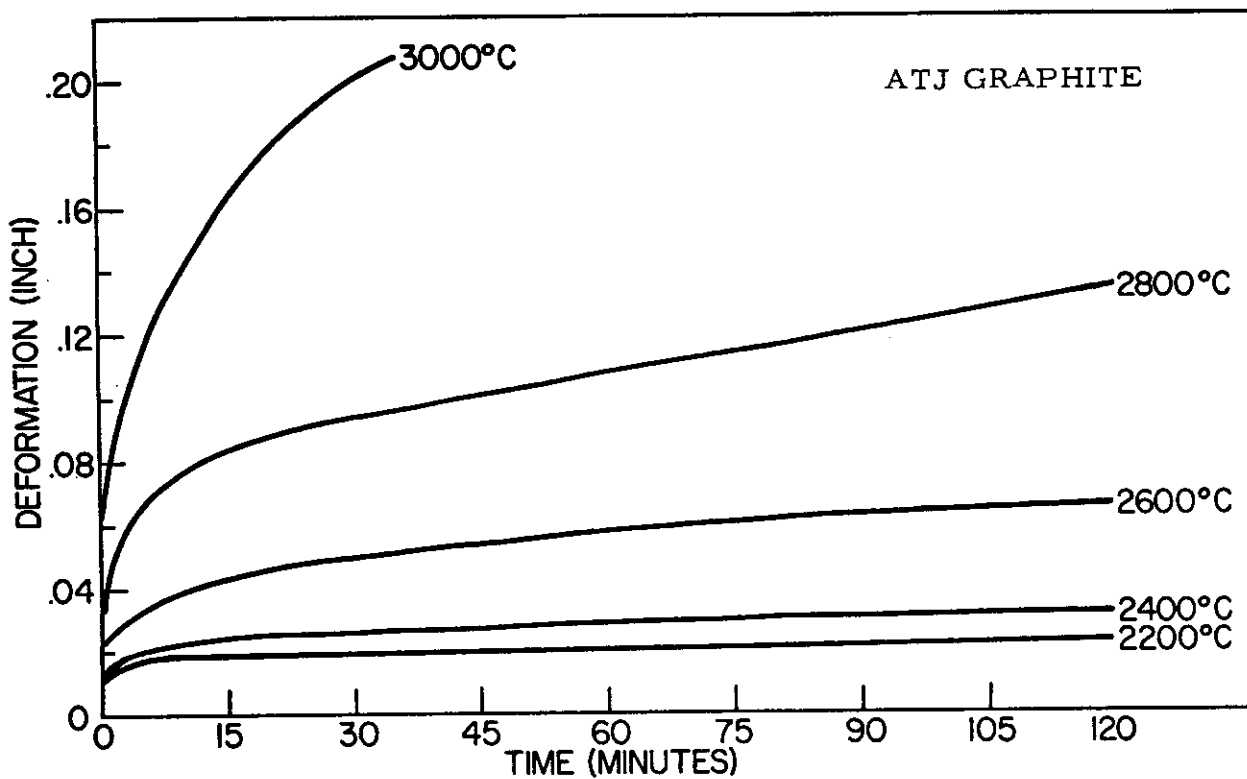
The ZTB graphite was a piece of recrystallized graphite having a density of  $2.008 \text{ g/cm}^3$ . The particle size of this material was comparable to that of ATJ graphite. The original piece from which the specimens were taken was a cylinder  $3\text{-}1/2$  inches in diameter by  $3\text{-}1/4$  inches in length. The material showed a high degree of anisotropy in electrical resistivity and thermal expansion. Specimens were cut having the three orientations shown in Figure 9, and creep tests were run at temperatures ranging from  $2200^\circ\text{C}$  to  $3000^\circ\text{C}$ , using a load of 2500g.

The creep curves for specimens with the three different grain orientations are shown in Figures 13, 14, and 15. For this graphite, there are definite differences in the creep curves at every temperature due to the grain orientation. The specimen with orientation B showed the smallest amount of deformation and the lowest creep rate at any given temperature, and the specimen with orientation C had the largest deformation and the greatest creep rate. The creep curves of the ZTB specimens with orientation C were comparable to those of the ATJ graphite, the magnitude of the deformation and creep rate at any temperature actually being slightly greater for the ZTB specimen than for the ATJ specimen with the same grain orientation. However, the specimens with orientations A and B had considerably smaller creep than any of the ATJ specimens at any given temperature. The creep curve for the ZTB specimen with B orientation at  $3000^\circ\text{C}$  is roughly comparable to that for the ATJ specimen of the same orientation at  $2400^\circ\text{C}$ . From the linear parts of the creep curves, an activation energy of 23 kcal/mole was determined.



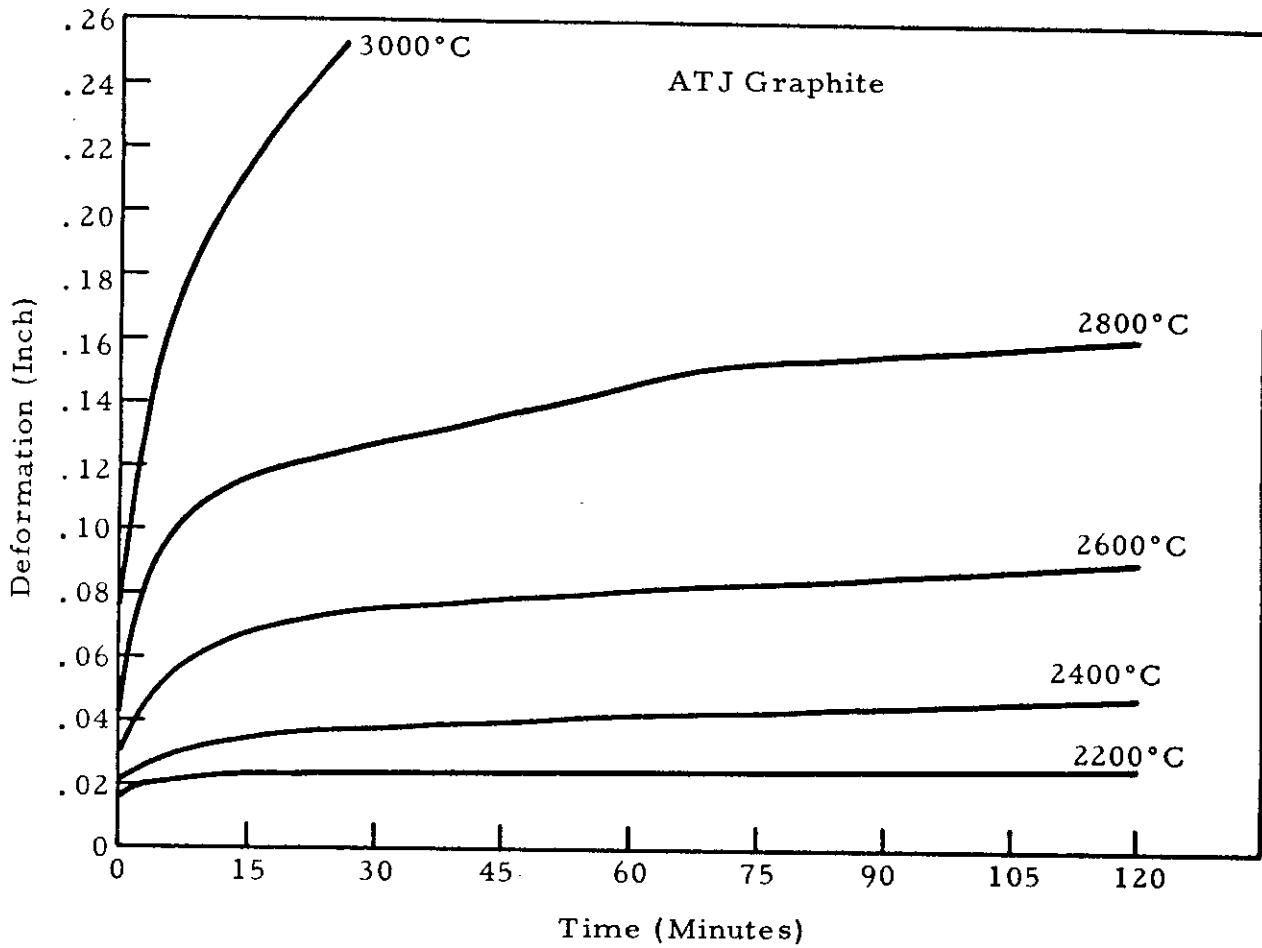
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Figure 10. Creep of ATJ graphite. Grain orientation A.  
Force = 2500g.



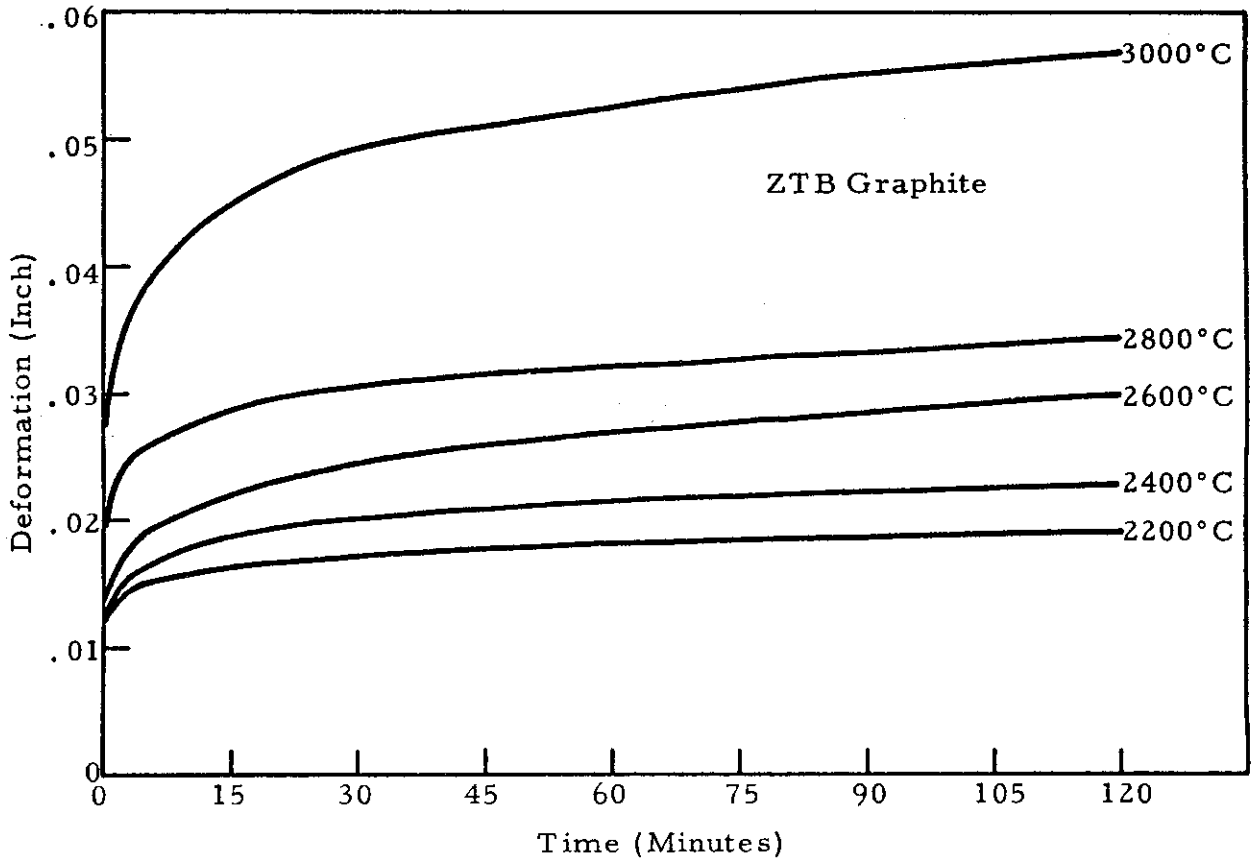
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Figure 11. Creep of ATJ graphite. Grain orientation B.  
Force = 2500g.



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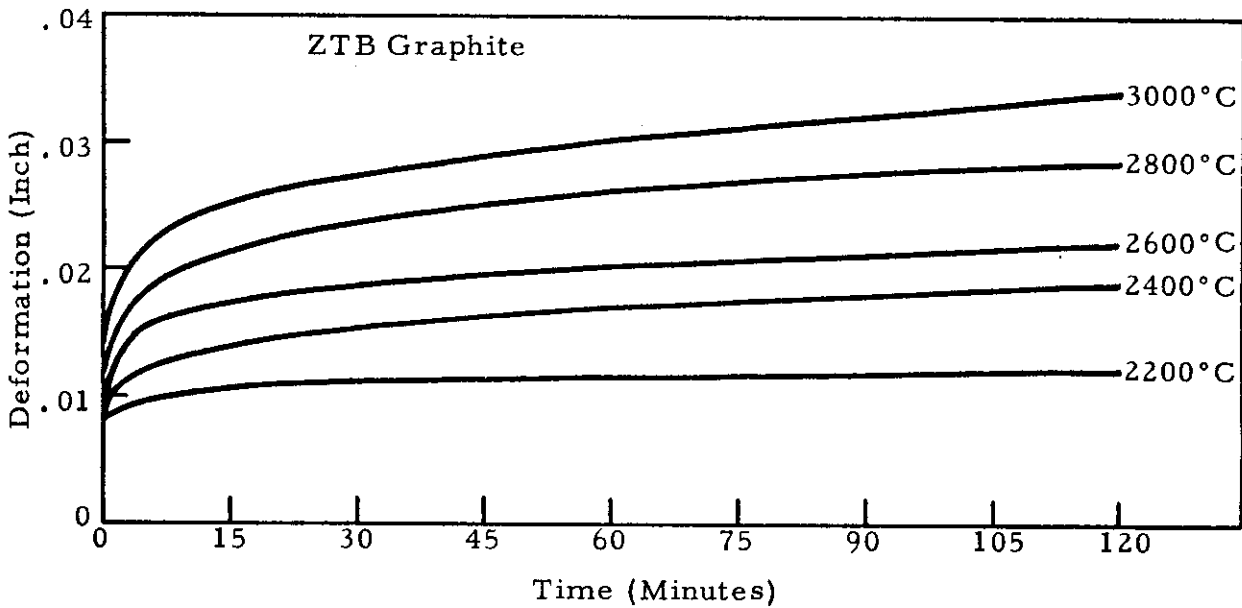
Figure 12. Creep of ATJ graphite. Grain orientation C.  
Force = 2500g.



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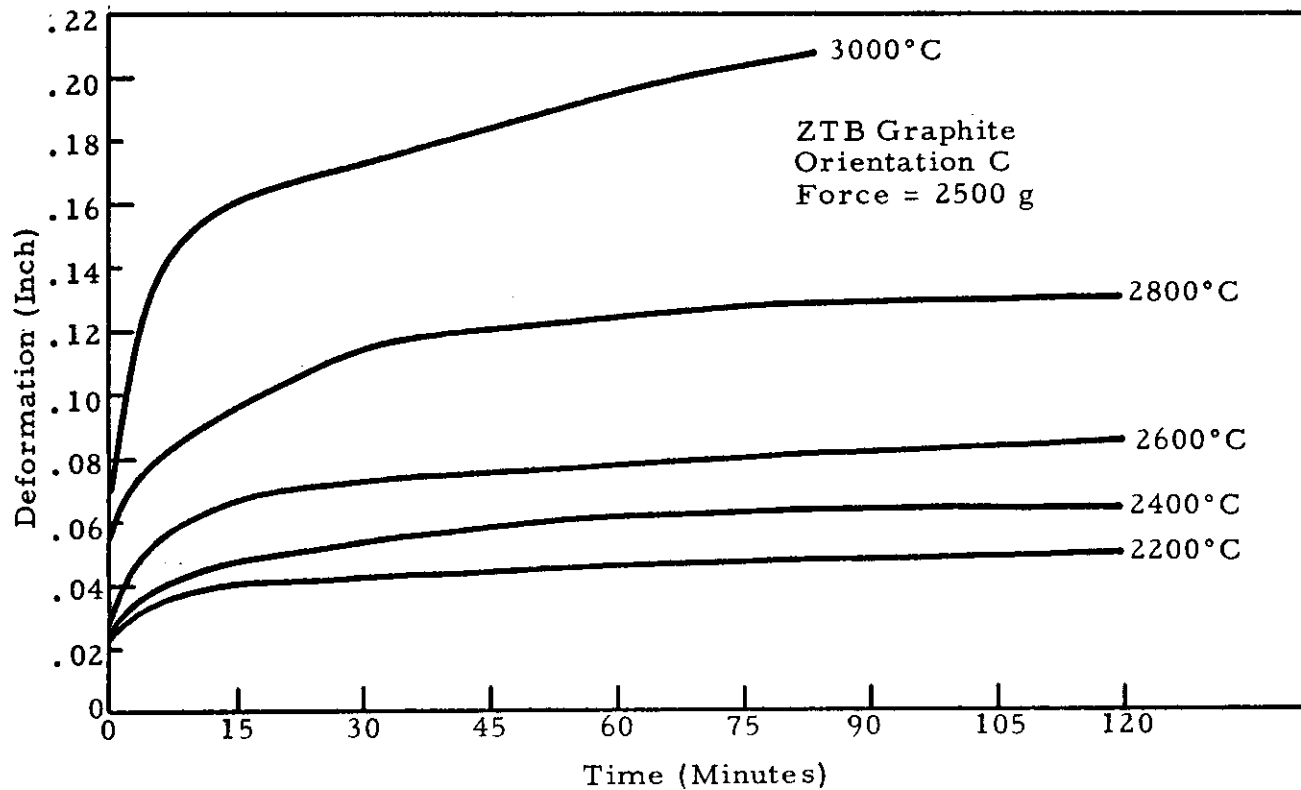
Figure 13. Creep of ZTB graphite. Grain orientation A. Force = 2500g.





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Figure 14. Creep of ZTB graphite. Grain orientation B. Force = 2500g.



N-1171

Figure 15. Creep of ZTB graphite. Grain orientation C. Force = 2500g.

Room temperature breaking strengths were determined for ZTB graphite in the same manner as was done for ATJ graphite. The average breaking strengths for the three orientations of ZTB graphite were 6915 lb/in<sup>2</sup> for the A orientation, 7550 lb/in<sup>2</sup> for the B orientation, and 2652 lb/in<sup>2</sup> for the C orientation. As in the case of ATJ graphite, there was again a definite correlation between breaking strength and creep behavior for the three grain orientations. The ZTB specimens were strongest with B orientation and weakest with C orientation. The ZTB graphite had a higher breaking strength than ATJ graphite in the A and B orientations and a lower breaking strength than ATJ in the C orientation.

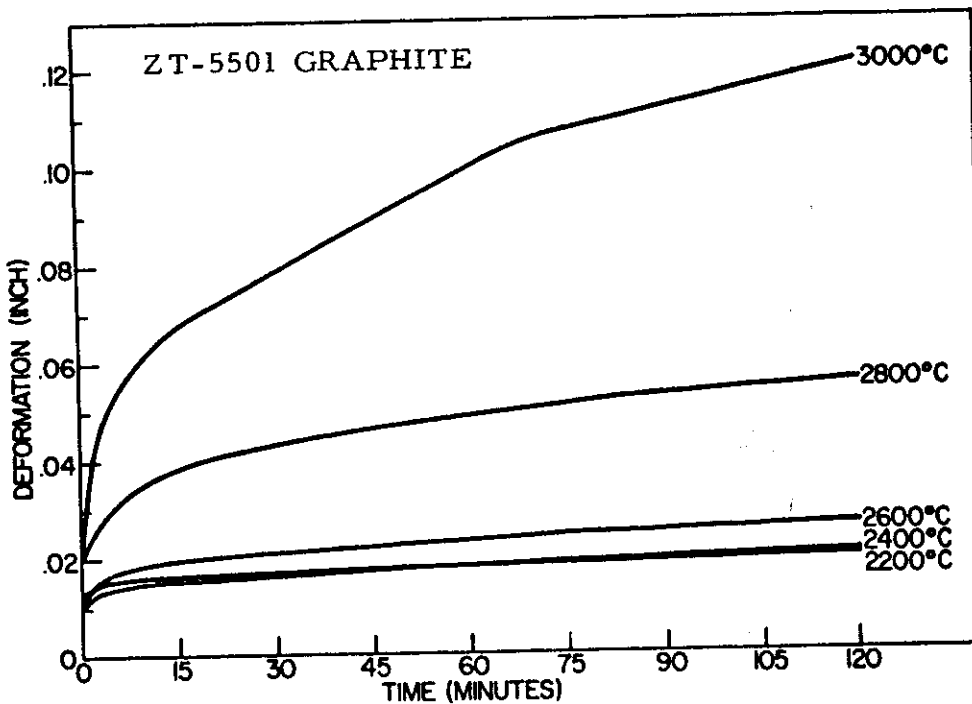
### 3.4 ZT-5501 Graphite

The graphite labelled ZT-5501 was an experimental grade of recrystallized graphite. This material had a density of 2.02 g/cm<sup>3</sup>, and had a little larger particle size than the ZTB graphite. Specimens were cut having the three orientations shown in Figure 9, and creep tests were run at temperatures ranging from 2200°C to 3000°C, using a load of 2500g.

The creep curves for the specimens with the three different grain orientations are shown in Figures 16, 17, and 18. There was not much difference between the behavior of the specimens with A and B orientation. At some temperatures the specimens with A orientation showed greater creep than the specimens with B orientation, and at other temperatures the situation was reversed. The specimens with C orientation showed the greatest amount of deformation and the highest creep rates, much greater than for either the ATJ graphite or the ZTB specimens with C orientation. Only three curves are shown in Figure 18 for the specimens with C orientation because the specimen at 2200°C broke when the load was applied, and the creep curve was so steep at 2800°C that no test was run at 3000°C. No breaking strength measurements were made at room temperature because there was not sufficient material for such tests. The creep of this material was, in general, low as compared to standard grades of graphite. The creep curves for the specimens with A orientation are close to those for the ZTB specimens with A orientation between 2200°C and 2600°C, but the ZT-5501 specimens showed greater creep than the ZTB specimens at 2800°C and 3000°C. The specimens with B orientation all showed greater creep than the corresponding specimens with B orientation of the ZTB graphite. However, for specimens with C orientation, the creep was very great and the specimens appeared to be very weak. From the linear parts of the creep curves for the ZT-5501 specimens with A and B orientations, an activation energy of 33 kcal/mole was determined.

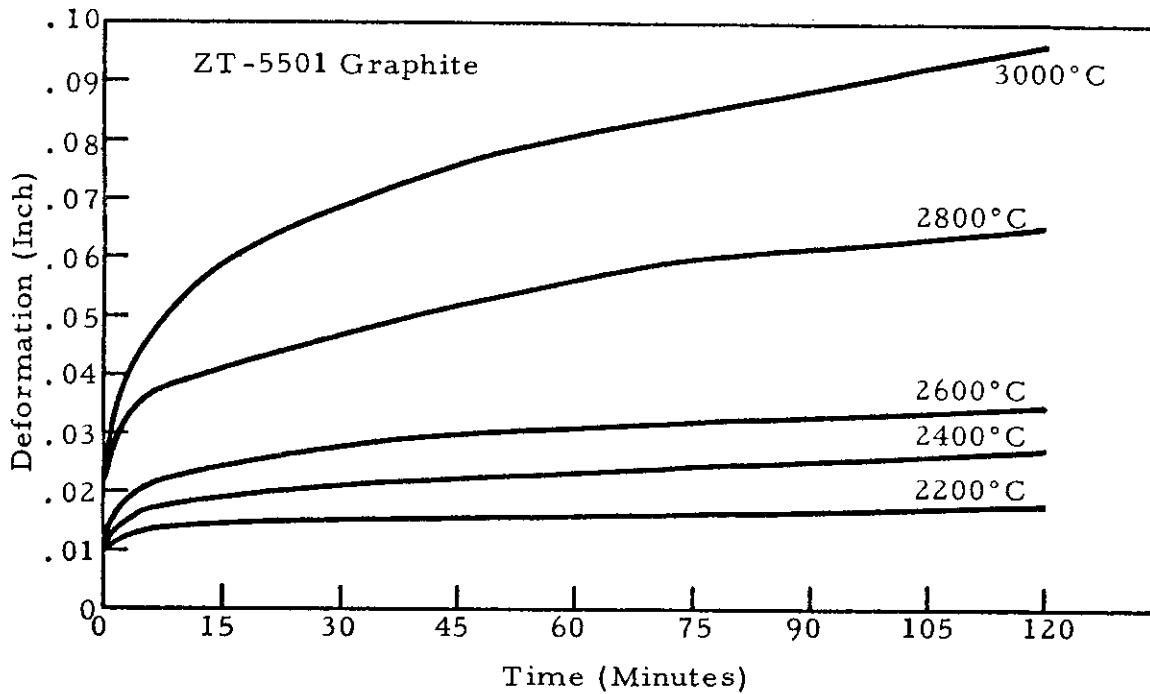
### 3.5 RVA Graphite

Creep tests were run also on specimens of RVA graphite having all three grain orientations shown in Figure 9. This graphite had a density of 1.83 g/cm<sup>3</sup> and had been fully graphitized. Figure 19 shows the creep curves which were obtained for specimens with A orientation at temperatures ranging from 2200°C to 3000°C, using a load of 2500g. The creep curves for the specimens with the other grain orientations are not shown. There was not a great deal of difference between the curves for specimens with A and B orientations, though the A specimens showed slightly greater creep than the B specimens. As in the case of the other graphites, the specimens with C orientation showed the greatest amount of creep.



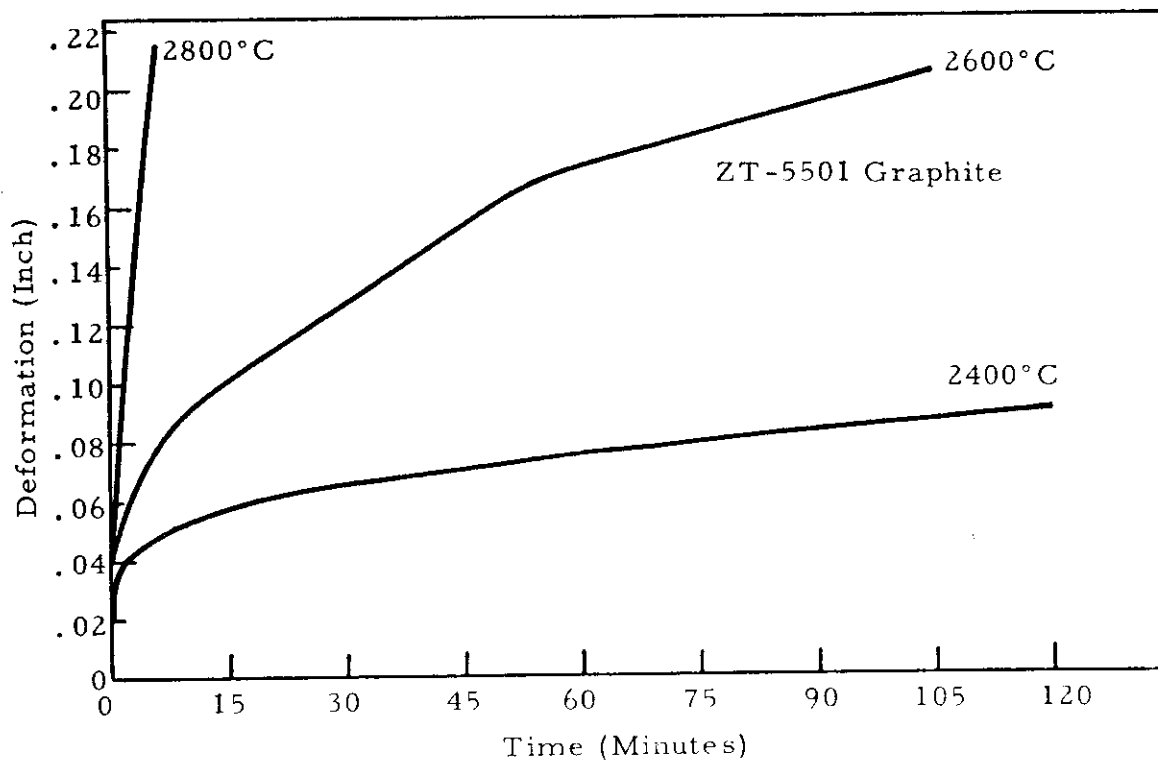
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Figure 16. Creep of ZT-5501 graphite.  
Grain orientation A. Force = 2500g.



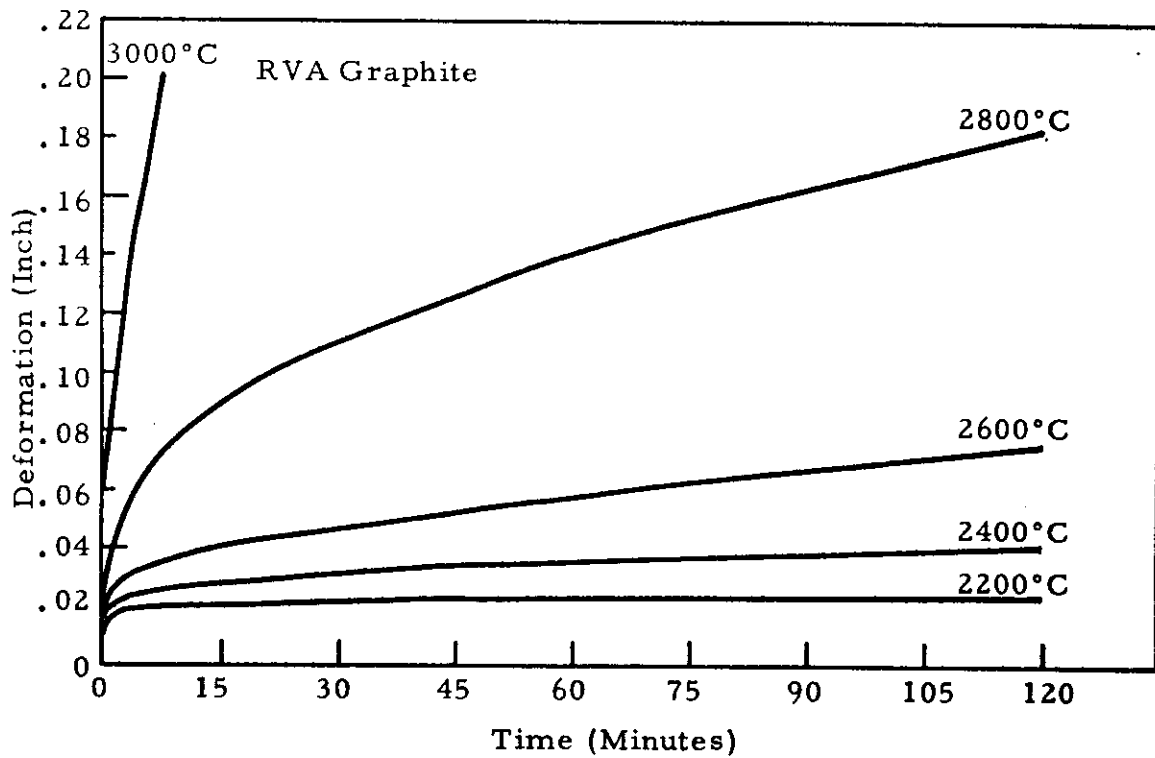
N-1173

Figure 17. Creep of ZT-5501 graphite.  
Grain orientation B. Force =  
2500g.



N-1174

Figure 18. Creep of ZT-5501 graphite.  
Grain orientation C. Force = 2500g.



N-1175

Figure 19. Creep of RVA graphite.  
Grain orientation A.  
Force = 2500g.

The specimen with C orientation also broke at 2200°C when the load was applied. From the linear parts of the creep curves, an activation energy of 92 kcal/mole was determined.

### 3.6 CEP Graphite

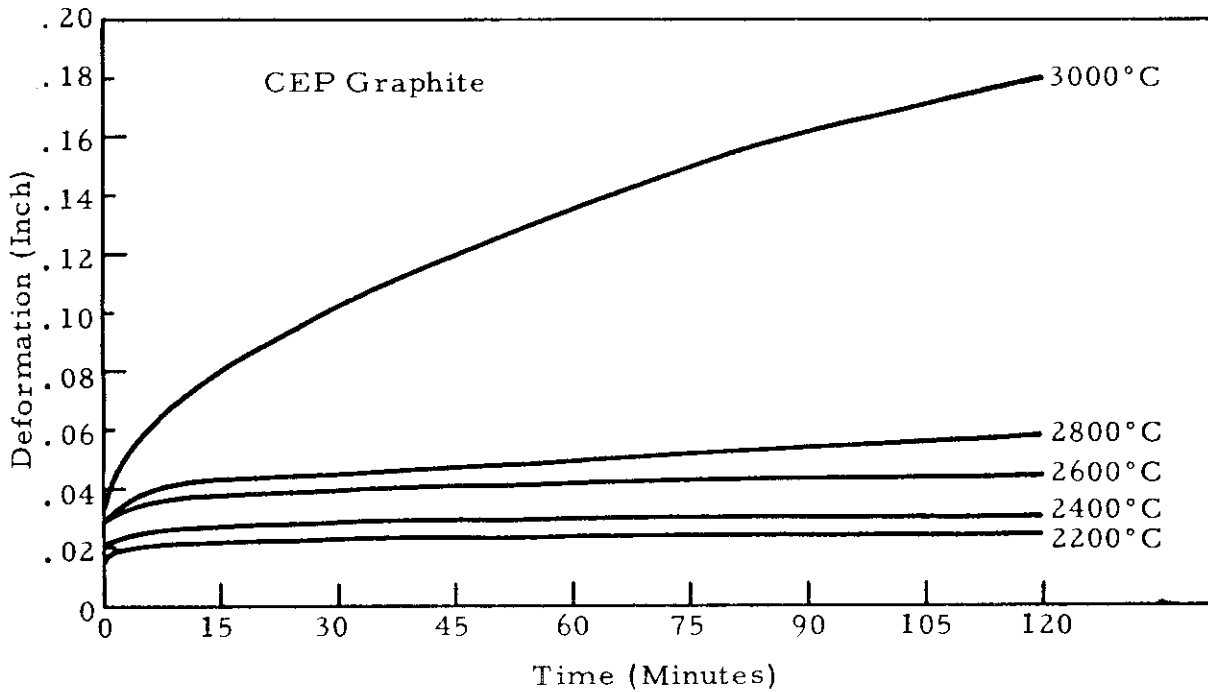
CEP is a lampblack-base graphite which is graphitized at approximately 3000°C. The CEP graphite which was tested had a density of 1.61 g/cm<sup>3</sup>, and creep tests were run on specimens with the three grain orientations shown in Figure 9. The temperature range which was covered was again 2200°C to 3000°C, and a load of 2500g was used. The creep curves for the specimens with A orientation are shown in Figure 20. The curves for specimens with the other grain orientations are not shown, but it was found that the curves for specimens with B orientation were very close to those for the specimens with A orientation, and the curves for specimens with C orientation showed only slightly greater creep at all temperatures than the specimens with the other orientations. The CEP graphite showed much less creep than the other standard grades of graphite at the higher temperatures. The only specimens which showed less creep than the CEP specimens were the ZT specimens which had either A or B orientation. The CEP specimens with C orientation showed much less creep than the corresponding ZT specimens with C orientation. It was not possible to determine an activation energy from the creep rates, as the creep rates could not be fitted to an Arrhenius function.

### 3.7 ZTD Graphite

The ZTD graphite was a piece of recrystallized graphite, which had a much larger grain size than either of the previous ZT graphites. The particle size of this material was comparable to that of large graphite electrodes. This graphite had a density of 2.05 g/cm<sup>3</sup> and had an anisotropy similar to that of a molded graphite. Specimens were cut having the three orientations shown in Figure 9. Creep tests were run at temperatures ranging from 2200°C to 3000°C, using a load of 2500g, for specimens with A and B orientation. These creep curves are shown in Figures 21 and 22. Specimens with C orientation broke under this load. When compared under a lower load, specimens with C orientation showed much greater creep than specimens with either A or B orientation.

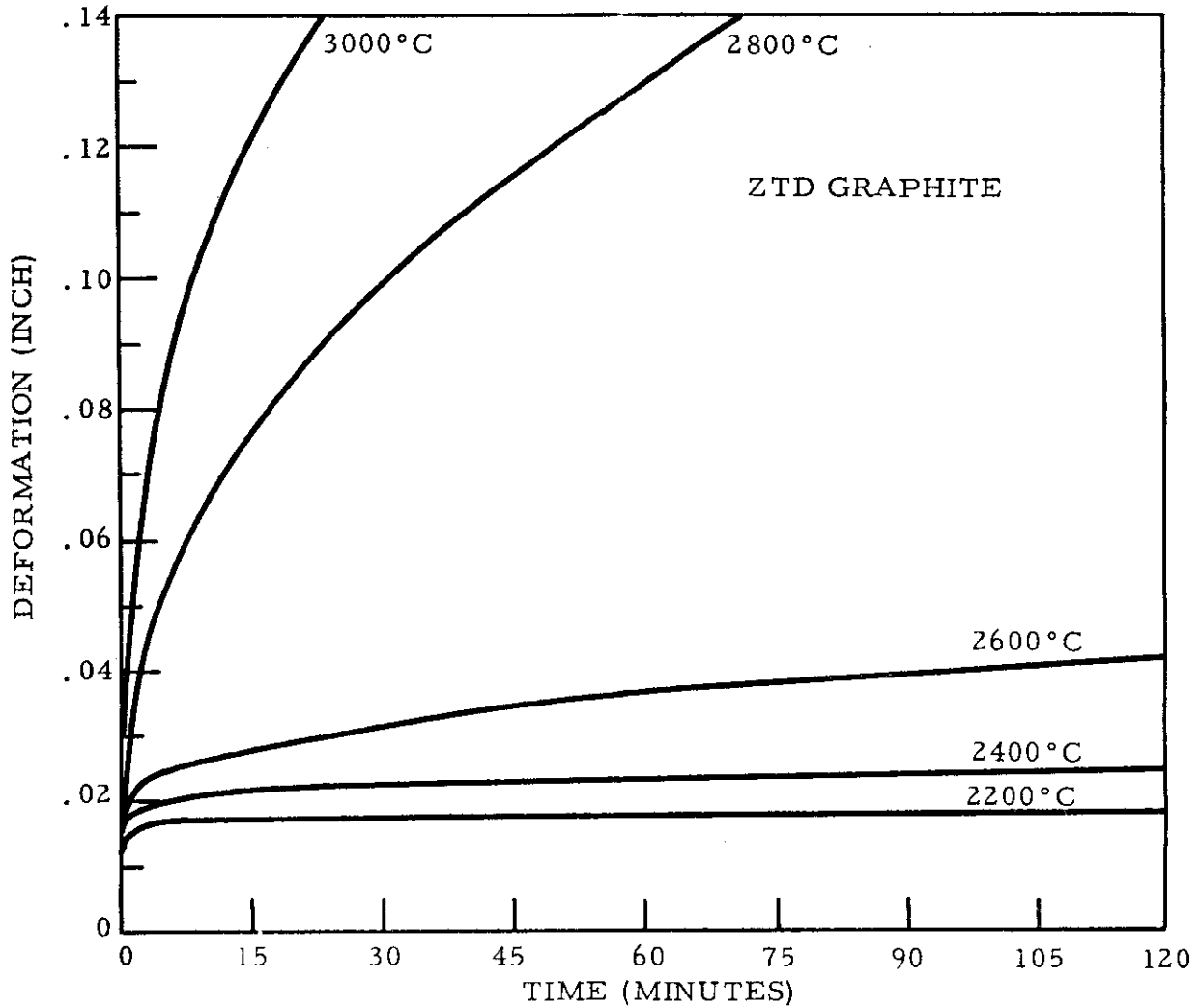
Unlike the other ZT graphites, there was no great difference between the creep specimens with A and B orientation. In comparing the creep curves for ZTD graphite with those of the other graphites, it can be seen that the creep of this graphite is much greater than that of the other ZT graphites with smaller grain size. The creep curves are much more like those for ATJ graphite. The surfaces of the ZTD specimens had a mottled appearance, which is typical of a coarse-grain material. Some surface cracks on the outer surfaces of the bent specimens in the region of maximum fiber stress could be seen with the unaided eye after testing at 2800°C and 3000°C, and these cracks may have been breaks along particle boundaries. No activation energy for creep could be determined from the slopes of the creep curves.





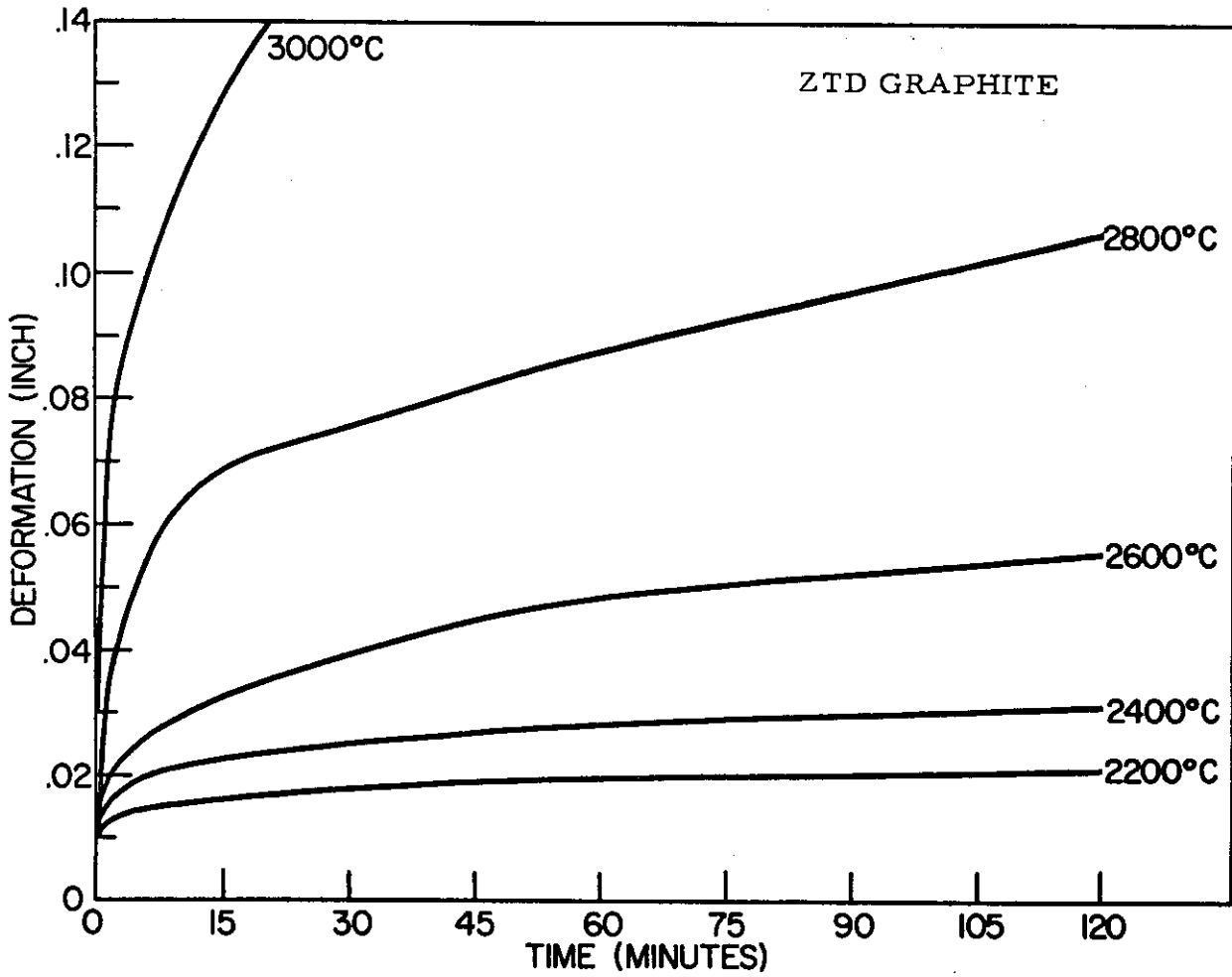
N-665

Figure 20. Creep of CEP graphite.  
Grain orientation A.  
Force = 2500g.



N-1385

Figure 21. Creep of ZTD graphite.  
Grain orientation A.  
Force = 2500g.



N-1386

Figure 22. Creep of ZTD graphite.  
Grain orientation B.  
Force = 2500g.

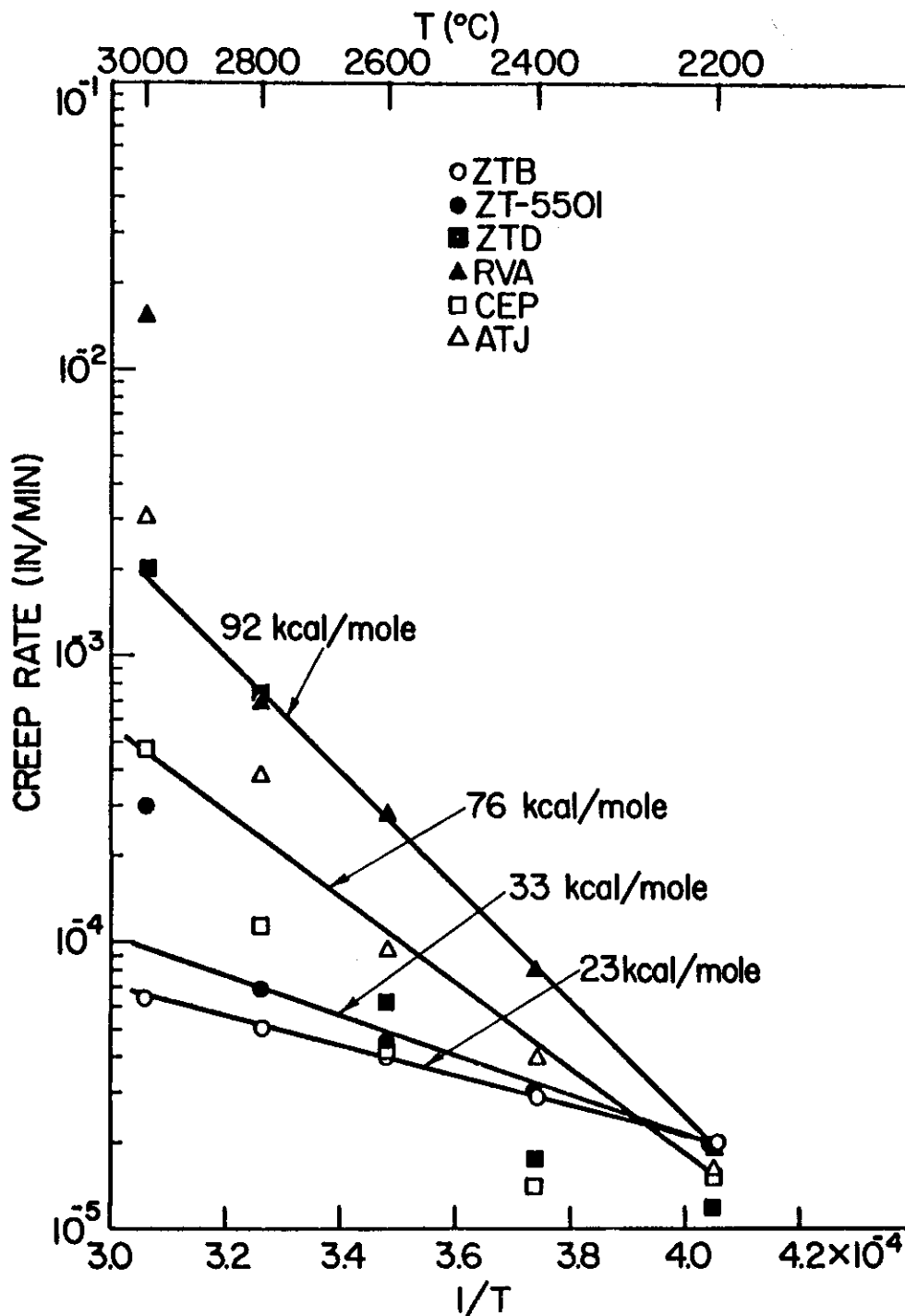
## 4. DISCUSSION

The different grades and types of carbons which have been tested showed remarkable differences in creep behavior. Since the materials themselves differed considerably in such factors as density, grain size, crystallinity, and anisotropy, there are some indications from the data as to how some of these variable factors in polycrystalline carbons and graphites influence the creep behavior. Except for the activation energy, which appears to be a number characteristic of a given graphite, the conclusions which can be drawn from a comparison of the data for the different graphites are largely qualitative.

The activation energies which were quoted for the different graphites were obtained from semi-log plots of the steady-state creep rate versus  $1/T$ . Figure 23 shows such a plot for specimens with grain orientation A for the six graphites which were tested, where the applied load was 2500g. Several features of the figure are of interest. The most striking feature which was noted was that the creep rates for all of the graphites were approximately equal at 2200°C. There is, in fact, little difference between the creep curves themselves for all of the graphites at that temperature. The differences between the creep rates become more noticeable as the temperature is raised above 2200°C.

The activation energy for any graphite, which is obtained from the slope of the straight line on the semi-log plot, is in effect a measure of the rate at which the creep rate for that graphite increases as the temperature is raised. It would be expected that the lines in Figure 23 cannot be extrapolated toward lower temperature, because it would then present the anomaly that the graphite which shows the lesser amount of creep at temperatures above 2200°C would show the greater amount of creep below 2200°C. The temperature of 2200°C is close to the lowest temperature at which a non-zero steady-state creep rate can be observed, and the rates which are plotted for that temperature are, in fact, close to the lower limit of creep rate that can be measured with any degree of accuracy with the apparatus.

From observation of the high end of the temperature range in Figure 23, it can be noticed that the point for the creep rate at 3000°C for any particular graphite usually falls above the straight line which best fits the other points for that graphite. The one exception to this is the ZTB graphite, where the point at 3000°C fell directly on the line. The usual relatively high creep rate at 3000°C is probably due to the fact that the deformation was usually so great at 3000°C with the applied load which was used, that a steady-state creep rate was actually not attained by the end of the creep test. The points at 3000°C in most cases represent the final creep rate which was attained by the time the specimen had been deformed about 0.22-inch, which was close to the limit to which the specimen could be deformed with the apparatus. It has been observed elsewhere, in the case of ATJ graphite, that the points for the creep rates at 3000°C do fall on the straight lines along with the points at lower temperatures when smaller loads are used.<sup>(1)</sup> From plots similar to Figure 23 which were made for the creep rates for specimens of the same graphites with grain orientations B and C, it appears that the activation energy may be independent of the grain orientation. Other evidence indicates that the activation energy may be independent of the density of the graphite for any given graphite.<sup>(4)</sup>



N-1629

Figure 23. Plot of steady state creep rates at temperatures (T) versus 1/T for six graphites.

The apparent density alone gives no indication of the creep behavior to be expected from a piece of graphite. For example, the first two ZT graphites which were tested had very high densities and they had the lowest creep rates and the lowest activation energies, but ZTB graphite, which had a lower density than the ZT-5501 graphite, had a lower activation energy and showed less creep at every temperature than the ZT-5501 graphite. On the other hand, the coarse grain ZTD graphite had the highest density of all, and it showed comparatively large creep when compared to the other graphites. Of the three standard grades of graphite (ATJ, RVA, CEP) which were tested, the RVA had the highest density and the highest creep rate at any particular temperature and the CEP had the lowest density and the lowest creep rate. For any particular type of graphite, however, the creep rate will decrease as the density increases.<sup>(4)</sup> These experiments offer dramatic evidence that differences in grain and crystallite size and type can have greater influence on the creep behavior than density variations.

The experiments demonstrate that creep in a graphite will be smaller as the degree of graphitization increases and as the crystallites grow in size. On the other hand, the creep is smaller as the grain size within the material is smaller, as can be seen from a comparison of the creep curves for the different ZT-type graphites. In postulating possible mechanisms for creep, it is assumed that creep takes place with the greatest ease through "nongraphitic carbon" by the motion of individual atoms and vacancies, since all of the evidence points to the fact that as the material becomes more graphitic, the creep decreases. The term "nongraphitic carbon" is used here to describe in a very general manner those regions where the carbon atoms are not in the perfect graphitic structure, as for example, between crystallites within grains or in the relatively disordered regions which result from the binder phase of the green carbon. With considerably less ease, creep might also take place within or between crystallites by means of the motion along basal planes of either vacancies or dislocations. The differences between the creep of specimens with different grain orientations indicate that creep occurs more easily when the deformation can take place by some type of gliding along crystal planes, as in the A and C orientations. Where such type of motion is less possible, as in the B orientation, the material is more resistant to creep.

In highly anisotropic specimens with C orientation, the maximum fiber stress is perpendicular to the basal planes and acting against the weakest forces within the crystallites. In some of the highly deformed specimens with C orientation, cracks were observed in the region of maximum fiber stress which indicated that some rupture between grains or crystallites along the basal planes was taking place. In the vast majority of cases, no cracking could be observed within the specimen by optical methods. The experiments presented here are not sufficient to resolve the many factors which influence the creep or to delineate the mechanisms which are involved. They demonstrate that creep in carbons and graphites is a fairly complicated process, and they indicate some of the factors which contribute to complicate the process.

## 5. REFERENCES

1. E. J. Seldin and R. N. Draper, WADD Technical Report 61-72, Volume V, 1961, Analysis of Creep and Recovery Curves for ATJ Graphite.
2. J. C. Bowman, Unpublished Data, National Carbon Company, Research Laboratories, NCRL-19, 1952.
3. H. E. Martens, D. D. Button, D. B. Fischbach and L. D. Jaffe, Proc. of the Fourth Conference on Carbon, 1959, p 511, Pergamon Press, Inc.
4. E. J. Seldin, Unpublished Data, National Carbon Company, Research Laboratory, NCRL-20, 1961.

APPENDIX I

6. APPROXIMATE PHYSICAL CHARACTERISTICS FOR  
MATERIALS USED IN CREEP TESTS

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Table 1 gives approximate room temperature physical characteristics for the materials used in the creep tests in Section 3. The bulk densities reported are those appropriate to the particular specimens used in the creep tests and, whenever available, the physical properties pertain to samples with these densities rather than average density for the grade. The values of flexural strength for Grades ATJ and ZTB quoted in Sections 3.2. and 3.3. were obtained with three-point loading which is known to give higher values of strength than four-point loading (the so-called "third-point" loading method\*) used in Table 1.

TABLE 1  
APPROXIMATE PHYSICAL CHARACTERISTICS FOR  
MATERIALS USED IN CREEP TESTS

		ATJ	ZTB	ZT-5501	RVA	CEP	ZTD
Bulk Density, g/cc		1.755	2.01	2.02	1.83	1.61	2.05
Resistivity $\mu$ ohm-cm	w.g.	1100	700	450	1200	4800	540
	a.g.	1450	2000	1700	1500	*	780
Flexural Strength**, psi	w.g.	4000	7000	3200	3700	4200	2650
	a.g.	3580	2200	1700	2900	*	1310
Young's Modulus, $10^6$ psi	w.g.	1.45	3.0	1.80	1.7	1.25	1.76
	a.g.	1.15	0.7	0.65	1.3	*	0.80
Coeff. Thermal Expansion, $10^{-6} \text{ } ^\circ\text{C}^{-1}$ (Mean RT to $100^\circ\text{C}$ )	w.g.	2.2	0.5	0.60	1.8	3.9	1.0
	a.g.	3.4	10.0	9.0	2.7	*	9.0

All properties measured at or near room temperature; w.g. - with grain,  
a.g. - across grain.

\* Across grain values not measured but would be close to with grain values.

\*\* Measured with four-point loading.

\* American Society for Testing Materials, Book of Standards, Test C-78-49,  
3, 1323-1325 (1955).