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Technical Report No. 32-889

*Analysis of High Temperature Creep
in Pyrolytic Carbon*

W. V. Kotlensky

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ABSTRACT

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Data on short-time high-temperature tensile creep parallel to the substrate for two pyrolytic carbons (pyrolytic graphites) characterized by their microstructures as substrate nucleated (SN) and regeneratively nucleated (RN) have been analyzed by means of the Dorn method. Over the range of approximately 1.5 to 10% creep strain for the SN material and for creep strains above 1.5% for the RN material, the creep data were found to fit the empirical relationship $\epsilon = A + Bt^n$, where ϵ is the creep strain, t is the time, n is a constant that depends on the material, and A and B are parameters that depend on both the material and the test conditions. The SN material was characterized by $n = 0.60$, while the RN material had $n = 0.42$. The same apparent activation energy of about 250 kcal/mole was calculated for both of these carbons. As assumed in the analysis, the structural change that occurs during creep was found to be dependent on the total creep strain, and the same structure was developed at a given load for the same strain, independent of test temperature. These structural changes are discussed briefly with reference to the deformation mechanisms.

Author

I. INTRODUCTION

By carefully varying the processing parameters, it is possible to produce pyrolytic carbons (pyrolytic graphites) varying in structure and properties. The two most distinguishable groups are represented by the regeneratively nucleated (RN) and the substrate nucleated (SN) classifications. These groups are easily identified by their microstructures. Polarized light photomicrographs of the edge of the basal planes show a columnar microstructure with nucleation originating at the apexes of the cones. In the SN classification, the growth cones are nucleated only at, or near, the substrate surface; the RN classification shows continuous cone nucleation across the thickness of the deposit. Differences in thermal expansion

(Ref. 1), strength (Ref. 2), and other properties (Refs. 3 to 5) for these two classifications have been reported.

Previous work at this Laboratory has involved tensile properties (including some preliminary creep studies), structural behavior accompanying deformation, and graphitization of these two structurally different materials (Refs. 6 and 7). As a continuation of this work, an investigation was carried out involving the short-time high-temperature tensile creep behavior parallel to the substrate in an attempt to understand more clearly the creep properties and the relationship between structure and deformation.

II. EXPERIMENTAL MATERIALS AND PROCEDURE

Both of the pyrolytic carbons¹ used in this study were produced at about 2100°C from methane gas and had the following characteristics: a density of 2.20 g/cm³, a unit cell height c_0 of 6.85 Å, and a preferred orientation² parameter $\beta_{1/2}$ of approximately 22 in the as deposited condition. However, the two samples had significantly

different microstructures. Polarized light photomicrographs of the as deposited carbons, parallel and perpendicular to the substrate, are shown in Fig. 1. The difference

²Measured as half-peak width at half-maximum intensity from a tracing of intensity of the (002) X-ray diffraction peak against angle of rotation about an axis parallel to the substrate plane, using small rod-shaped samples.

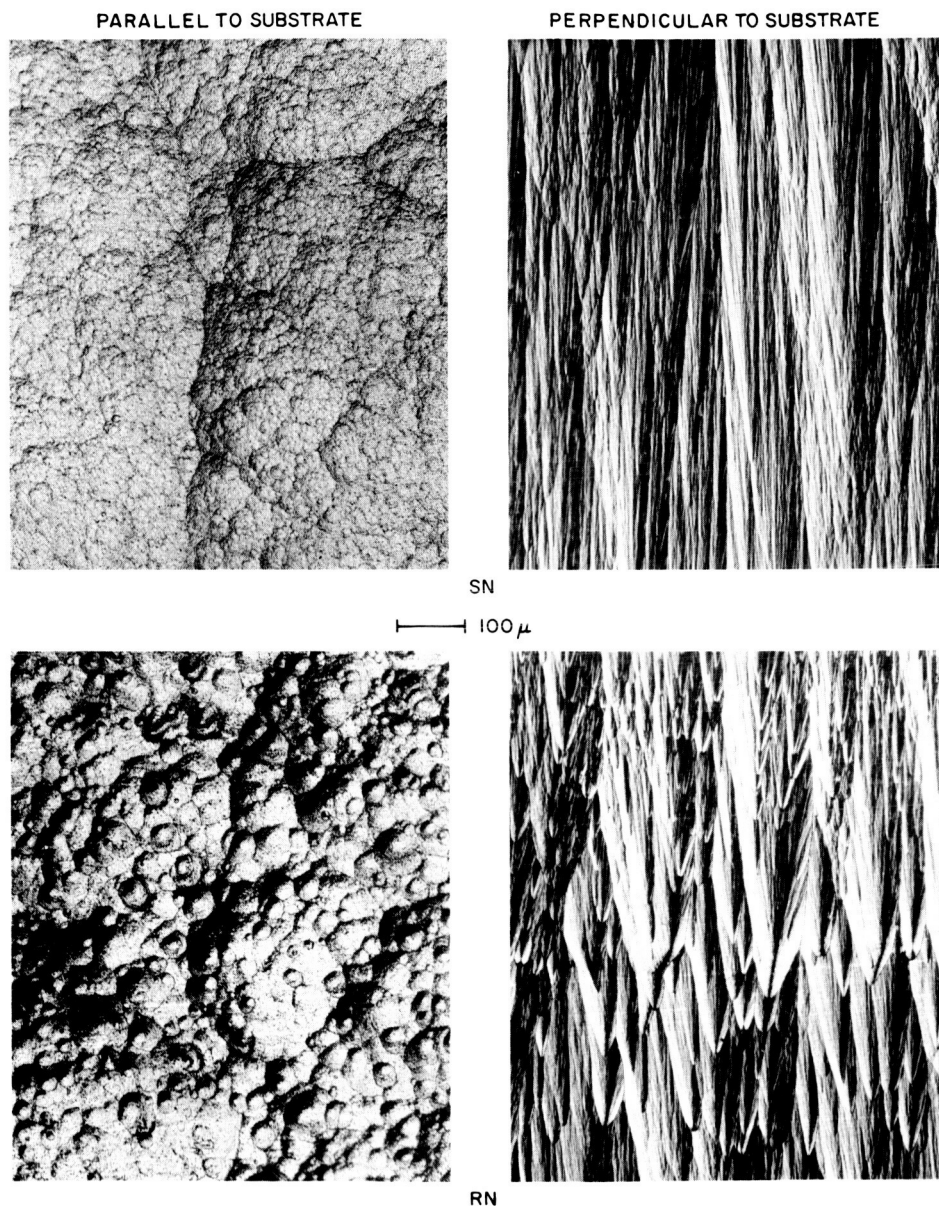


Fig. 1. As deposited microstructures of the substrate nucleated (SN) and regeneratively nucleated (RN) pyrolytic carbons tested

in microstructure is very pronounced with the RN material showing the characteristic continuously nucleated cone structure, a more grainy texture and a larger angle at the apexes of the cones. Although differences in processing conditions undoubtedly account for the microstructural differences, detailed processing data were unavailable from the manufacturers.

Specimens with a $\frac{3}{4}$ -in. gauge length and a 0.10- by 0.06-in. cross section were machined from 3- by 1-in. plates that had been heat treated in He at 2800°C for 30 min. Appreciable structural changes occur when pyrolytic carbons are heat treated at high temperatures. The 2800°C pretreatment was found to be sufficient to normalize the structure prior to testing so that only deformation-induced

structural changes occurred during the tests. After heat treating, the two carbons still had similar X-ray diffraction structures, despite their differences in microstructure. Both materials gave the same c_0 lattice spacing of 6.75 Å and the same $\beta_{1/2}$ of approximately 16.

The uniaxial creep tests were made at an initial stress of 12,000 psi, which was produced by a constant load applied parallel to the substrate; the test equipment used was the same (described in Ref. 8)³ as has been used to study the creep behavior of pitch-coke graphite.

³Described also in a JPL Project Report by H. E. Martens, L. D. Jaffe, and D. D. Button, "High Temperature Short-Term Creep of Graphite," December 1958.

III. EXPERIMENTAL RESULTS AND ANALYSIS

Creep curves for the SN and RN materials are shown in Fig. 2; each of the curves has been corrected for A , the instantaneous strain (elastic strain, immediate plastic strain, etc.) associated with the experimental arrangement, but neither set has been corrected for strain associated with deformation in the fillets. This latter correction was not measured during this creep study; however, it was found in previous tensile studies that the deformation in the fillets is a constant factor and, therefore, does not seriously affect the analysis of the creep data. Beyond the first few minutes for the tests at 2500°C and above, the SN material shows a greater time-dependent strain⁴ ($\epsilon - A$) than does the RN material. This characteristic of greater plasticity under similar conditions, which has also been observed in tensile tests (Ref. 6), results from greater strain hardening tendency in the RN material—evidently, caused by the more numerous and severe imperfections and distortions in the RN structure. As do curves from pitch-coke graphite (Ref. 8), these curves show a continuously decreasing creep rate with increasing time; there is no steady-state creep rate nor evidence of a third-stage creep region.

An attempt was made to fit the creep curves to the empirical equation

$$\epsilon = A + Bt^n \quad (1)$$

⁴Hereafter, unless otherwise noted, the term *strain* will refer to ($\epsilon - A$).

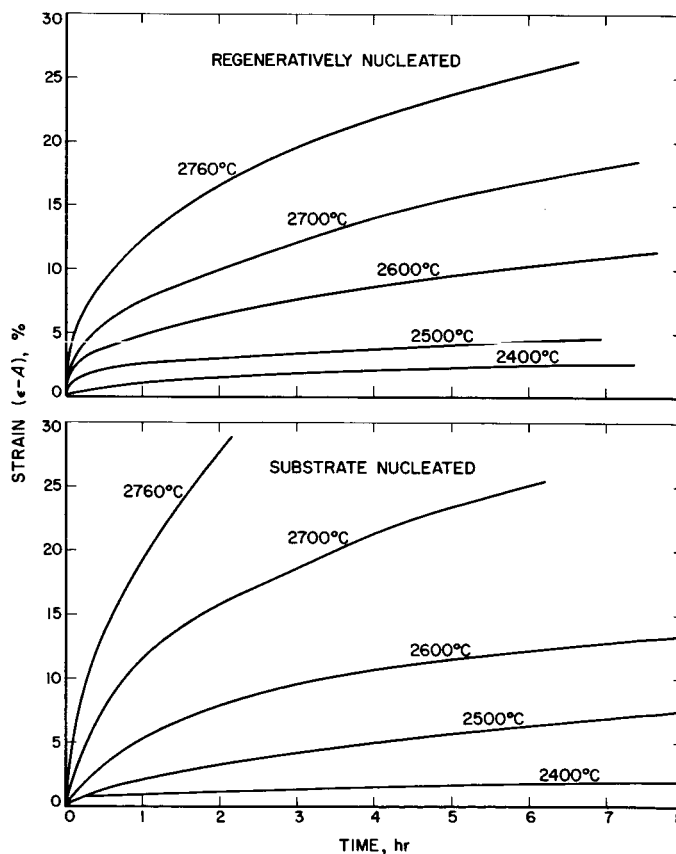


Fig. 2. Creep curves for pyrolytic carbon, initial stress 12,000 psi applied parallel to substrate

where ϵ is the creep strain, t is the time, n is a constant, B is a parameter dependent on stress and temperature, and A is defined as above. Many metals and nonmetals obey Eq. (1) with n values lying between 0.4 and 0.6 (Ref. 9). If the pyrolytic carbon creep data were to fit this equation, then a plot of $(\epsilon - A)$ vs t on a log-log scale should give a straight line. This analysis has been carried out, and the results are given in Fig. 3. The RN data, except for the test at 2500°C in which experimental difficulties were encountered, gave a family of parallel curves above 1.5% strain with an n value of 0.42. The SN data fit Eq. (1) over the range of approximately 1.5 to 10% strain with an n value of 0.60. The scatter in the data at low strains is attributed to lack of sensitivity in measuring small strains and to some uncertainty in estimating the instantaneous strain A . The departure from linearity for the SN data above approximately 10% strain is believed to be associated with the beginning of the second stage of deformation (Refs. 10 and 11) in this material. These deformation stages, which will be considered further in

Section IV, should not be confused with the transient and steady-state stages observed in the creep of metals. Steady-state creep would cause an *upward* curvature on the log-log plot in Fig. 3. The significance of Fig. 3 is that both the RN and SN materials give a family of parallel curves with a reasonable fit to Eq. (1) over the specified range and that n appears to depend upon the structure.

In considering the phenomenon of high-temperature creep in metals, Dorn (Ref. 12) drew the following conclusions: (1) The observed changes in creep rate with time arise from structural changes that occur during creep; the same structure is developed under a given stress or load for the same strain, independent of test temperature. (2) The creep rate is controlled by some process involving thermal activation. (3) When plotted as a function of log time, creep curves for the same stress or load are identical, except for parallel displacement along the time axis. If the Dorn method of analysis were to be applied satisfactorily to pyrolytic carbon creep, then it must be shown that these three characteristics are observed. For the sake of convenience, the latter two conditions will be considered first, since they are inter-related.

When plotted as shown in Fig. 3, the creep data for pyrolytic carbon give a reasonable set of parallel curves that are identical, except for the displacement along the time axis. Following Dorn, it is assumed that the relationship between these curves is given by

$$\epsilon - A = f \left[t \exp \left(- \frac{\Delta H}{RT} \right) \right] \quad (2)$$

where ΔH is the apparent activation energy, R is the gas constant, T is the absolute temperature, and ϵ , A , and t are defined as in Eq. (1). Then the activation energy can be calculated from the following equation:

$$t_1 \exp \left(- \frac{\Delta H}{RT_1} \right) = t_2 \exp \left(- \frac{\Delta H}{RT_2} \right)$$

where t_1 and t_2 are the times required to reach a given strain at temperatures T_1 and T_2 . This calculation was made for all combinations of t_1 and T_1 at a strain of 2% for the two sets of curves in Fig. 3, and average apparent activation energy values of 240 kcal/mole for the SN and 260 kcal/mole for the RN pyrolytic carbons were obtained.

When ΔH is known, the creep data can be superimposed reasonably well onto a single curve for each material by use of Eq. (2), as shown in Fig. 4. The departure

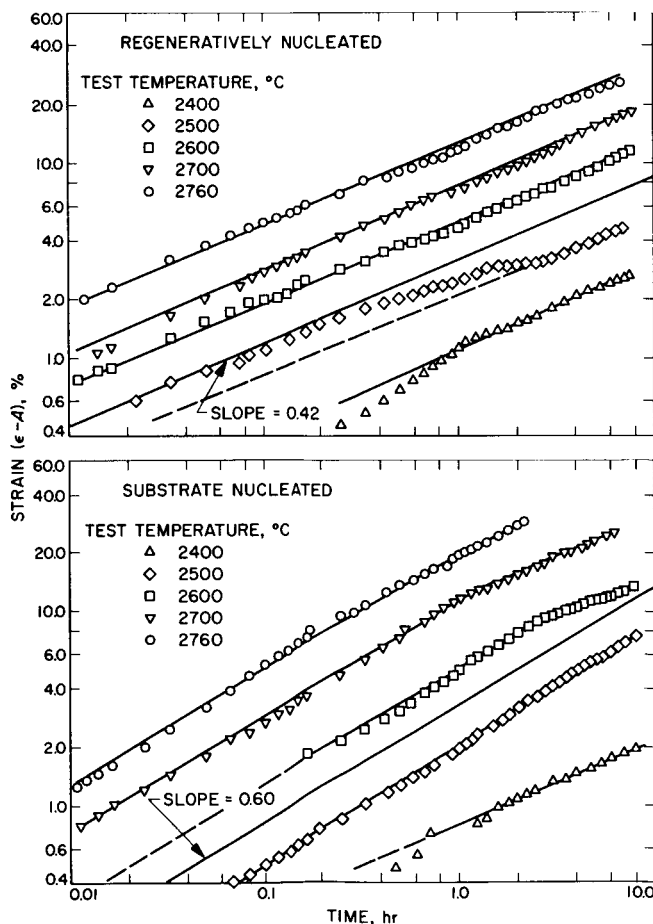


Fig. 3. Log-log strain-time plots for pyrolytic carbon

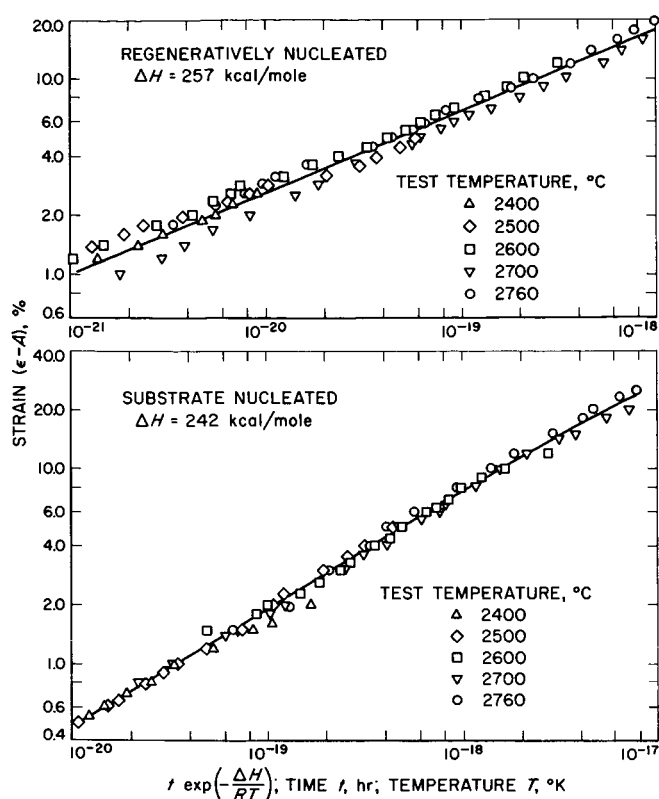


Fig. 4. Creep strain as a function of temperature-compensated time

of the data points from the individual curves in Fig. 4 is not considered to be significant. Errors in temperature measurement, insensitivity of the strain measuring sys-

tem, and errors in estimating the instantaneous strain can account for the scatter. In the RN material, the scatter is approximately $\pm 10\%$ of the measured value; the scatter is somewhat less for the SN material.

Considering now the first condition of Dorn's analysis, it remains to be shown that the same structure is developed for the same strain during the creep deformation of pyrolytic carbon, independent of test temperature. For this part of the study, a detailed structure analysis was carried out only on the SN material. A less rigorous structure analysis on the RN material gave similar, although less pronounced, results.

Figure 5 shows micrographs that were taken from three orthogonal views at the center of the gauge section. These micrographs show the structures developed at three different temperatures for the same nominal 10% strain. Corresponding micrographs of comparable surfaces are indistinguishable. In addition, all three specimens shown in Fig. 5 gave the same unit cell dimensions, $c_0 = 6.73 \text{ \AA}$ and $a_0 = 2.46 \text{ \AA}$, and the same $\beta_{1/2}$ of 6.9 deg and 1.8 deg measured about axes in the substrate plane parallel and perpendicular to the stress. The structure developed by the deformation is a function of the strain. At strain levels between about 5 and 15% the structural changes are strongly anisotropic relative to the stress axis. At higher strains this anisotropy decreases. From the standpoint of the creep analysis, the significance of Fig. 5 and the X-ray data is that the Dorn condition is obeyed, i.e., the same structure is developed at the same strain, independent of test temperature.

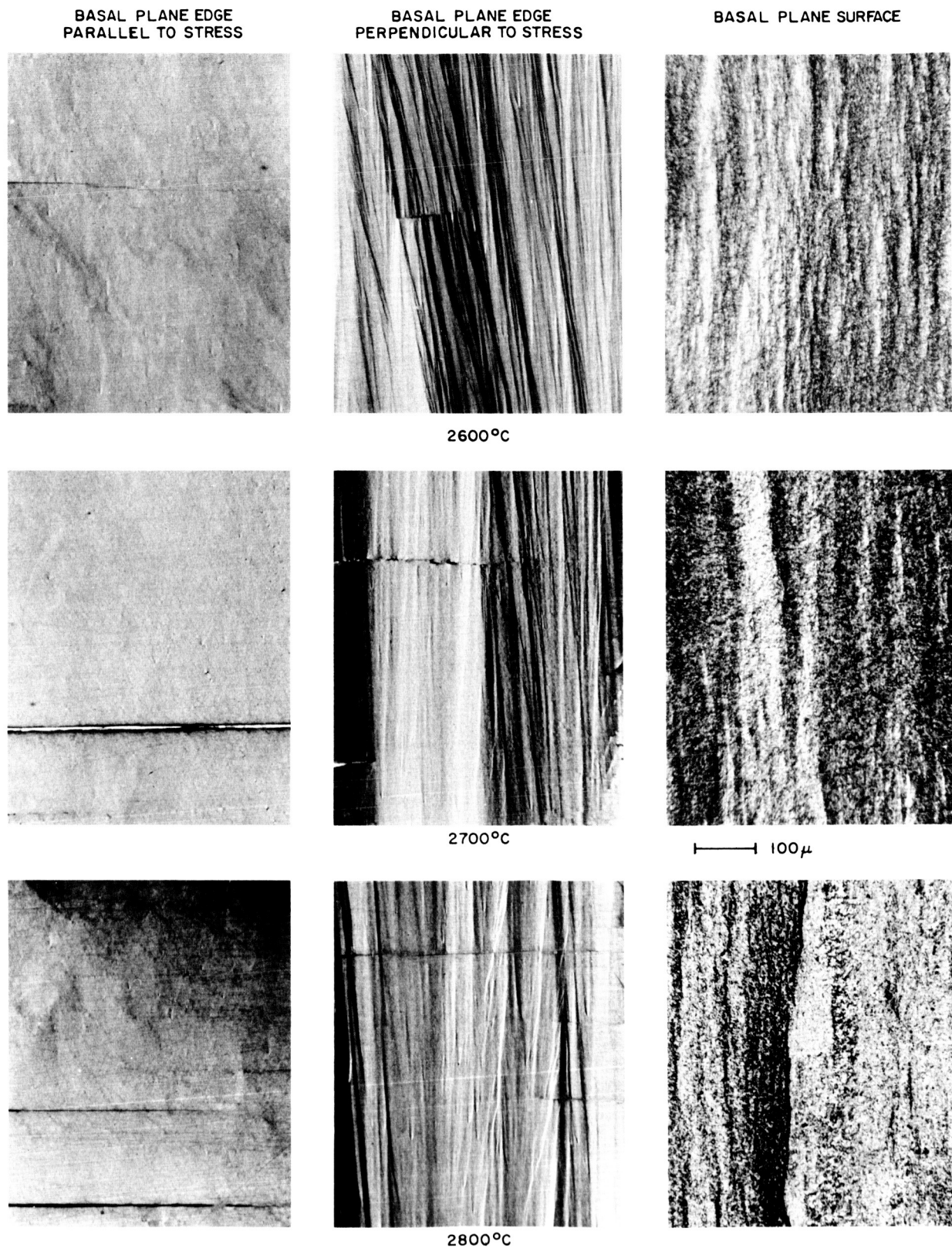


Fig. 5. Microstructures of substrate nucleated (SN) pyrolytic carbon after 10% nominal creep deformation parallel to substrate at three different temperatures

IV. DISCUSSION

Apparent activation energy values from 60 to 200 kcal/mole have been reported for pitch-coke graphite creep for temperatures above 2400°C (Refs. 8 and 13 to 15).⁵ Earlier preliminary results on pyrolytic carbon creep gave activation energy values of 100 to 200 kcal/mole (Refs. 6 and 7). This wide variation is dependent on the testing procedure and the method of analysis. The method of analysis used in the current study is believed to be more satisfactory than analyses based on creep rates at constant strain levels, or on steady-state creep rates.⁶ Fischbach (Refs. 16 and 17) has reported a ΔH value of 260 kcal/mole for graphitization of pyrolytic carbons and pitch-coke carbons over the range 2200 to 3000°C in an inert atmosphere. Kanter (Ref. 18) has calculated an activation energy of 263 kcal/mole for diffusion in graphite by a vacancy mechanism, and 113 kcal/mole for diffusion by a direct interchange mechanism, using 170 kcal/mole as the sublimation energy for carbon and the diffusion model proposed by Dienes (Ref. 19). The agreement between the apparent activation energy for pyrolytic carbon creep and the ΔH values reported by Fischbach and calculated by Kanter may be simply fortuitous, or it may indicate the fundamental process that is involved. This process, however, is not well understood, and the creep data are insufficient to definitely establish a rate-determining mechanism. On the other hand, it is significant that creep in pyrolytic carbon can be treated as a thermally activated process and, also, that the apparent activation energy obtained is reasonable. It is also significant that the SN and RN materials, although differing widely in microstructure, give very similar apparent activation energy values.

⁵Also in source cited in footnote 3.

⁶The activation energy may also be determined from B in Eq. (1) if the correct functional form of B is used. By use of Eq. (2), it can be shown that $B = f[\exp(-n \Delta H/RT)]$. In Ref. 9, it was incorrectly assumed that $B = f[\exp(-\Delta H/RT)]$; the ΔH values obtained there from B should be multiplied by 2 ($n \simeq 0.5$) to get the correct value.

Examination of the curves in Fig. 3 reveals that the RN curve is linear over the entire range of reliable data and that the SN curve is not linear beyond approximately 10% strain. As mentioned before, this break in the SN curves has been interpreted as indicating the transition from the first to the second stage of deformation (Refs. 10 and 11). The first stage of deformation in pyrolytic carbons occurs at strains less than 10 to 15%; it involves dewrinkling of the initial wrinkled sheet structure, accompanied by basal plane shear. The second stage occurs at tensile elongations greater than 15% and involves deformation of very well oriented material by mechanisms which are not well understood. The differences in microstructural texture of the basal plane edge surfaces (Fig. 5) and in preferred orientation index, parallel and perpendicular to the stress, resulting from first stage deformation of the SN material are not too surprising and indicate that anisotropic dewrinkling has occurred. This anisotropic dewrinkling phenomenon is consistent with magnetic susceptibility measurements on deformed gauge section samples (Ref. 20) and is what would be expected based upon the reported change in gauge section width and thickness with deformation (Ref. 10). It was first noted (in preferred orientation data) by Stover (Ref. 3) that a tensile stress tends to align the basal planes parallel to the stress axis.

The lack of a similar change in slope in the creep curves for the RN material implies that a single stage is involved in its deformation up to at least 30% elongation. The deformation mechanism in RN carbons has not been investigated in detail, but it is reasonable to assume that the mechanism involved differs from that which occurs in the first stage of SN carbons. The presence of soot particles and other lattice imperfections would be expected to impede or delay complete dewrinkling; this fact was confirmed by micrographic studies on the RN samples.

V. SUMMARY

Differences in the creep behavior have been observed for the structurally different substrate nucleated (SN) and regeneratively nucleated (RN) pyrolytic carbons. When the creep data are plotted as log time-dependent strain vs log time, a family of parallel curves is obtained that obey the empirical equation $\epsilon = A + Bt^n$. The value of n , which appears to depend on the structure, is 0.60 for the SN material and 0.42 for the RN material. The RN data are linear over the entire strain range investigated. The SN data depart from linearity above approximately 10% strain. This characteristic has been interpreted as indicating a single stage in the deformation of the RN material, and a two stage deformation in the SN material consistent with other observa-

tions. The presence of soot particles in the RN material plays an important role in its deformation.

The Dorn method of analysis has been applied satisfactorily. Creep in pyrolytic carbon involves a thermally activated rate process with an apparent activation energy of approximately 250 kcal/mole. The creep curves for each of the two materials, RN and SN, have been superimposed by scaling the time axis.

The same structural features are developed for the same strain, independent of temperature; but different structural features are developed at different strains.

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