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Tensile Properties of Pyrolytic Graphite to 5000° F

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DISCLAIMER

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ABSTRACT

Tensile properties of pyrolytic graphite have been measured parallel to the basal planes from room temperature to 5000°F. The gage section of the test specimen used was 0.06 by 0.10 in. in cross section and ¾ in. long. The specimens were heated in a helium atmosphere by an external graphite heater and were tested at a strain rate of approximately 2 x 10^{-4} in./in./sec. Tensile strengths at room temperature varied from 6,000 to 19,000 psi with elongations of less than 1%. At 3000°F the strength and elongation were approximately the same as at room temperature. At 4000°F there was a very slight increase in the strength and elongation. At 4500°F tensile strengths up to 35,000 psi and elongations up to 3%, and at 5000°F tensile strengths of 64,000 psi and elongations greater than 70% were measured. At test temperatures of 4500°F and above load-deformation curves were recorded. Microstructure and x-ray diffraction patterns showed that marked structural changes accompany deformation at 5000°F. Large changes in room-temperature dimensions, parallel and perpendicular to the basal planes, were also measured after heating, with no load, to temperatures in this same range.

I. INTRODUCTION

The continuing demands for new and more suitable structural materials for use at temperatures above 3000°F have led to the development of several new types of materials. One such type of material, which has undergone extensive work during the past year, is represented by pyrolytic graphite.

Earlier work at this Laboratory (Ref. 1, 2, and 3) dealt with the exploration of the tension and creep behavior of pitch-coke graphites at temperatures up to 5300°F. This has been followed by similar studies of the behavior of pyrolytic graphite.

The results reported are from some of the first high-temperature (above 3000°F) tests conducted on this material; also presented are some of the structural changes which occur when this material is deformed at high temperatures.

II. MATERIAL TESTED

Pyrolytic graphite is a polycrystalline form of carbon having a high degree of orientation. It contains no binder phase, has high purity, and its density may exceed 95% of the theoretical density of carbon.

This material is produced by the deposition of carbon from a dilute hydro-carbon gas onto a substrate which is maintained at a temperature above 3600°F. The as-deposited material has a block-like structure of conical elements called "growth cones." Typical microstructures of pyrolytic graphite and commercial pitch-coke graphite are shown in Fig. 1. The size, shape, number, and origin of these growth cones can be varied greatly by changes in the processing parameters.

Since the material used to determine the properties and behavior herein reported was produced during the early stages of the development of the state of the art, it is not possible to classify it as a specific type of pyrolytic graphite. In fact, it is possible that there may have been block-to-block variations, or even variations of the structure within a given block, which could have affected the results presented.

Nominal characteristics of pyrolytic graphites tested are given in Table 1.

Table 1. Nominal characteristics of pyrolytic graphites tested*

Block No.	Source of carbon	*Deposition* temperature °F	*Thickness of* deposit in.	*Density as* deposited g/cm^{3**}
14601	Natural gas	3990	—	2.20
14801 14802 14803 14804	Natural gas	3810	0.24	2.15–2.16
15601	Natural gas	4080	0.28	2.195–2.203

*Data supplied by General Electric Company Research Laboratory, Schenectady, New York.

**Measured by CCl_4 immersion by authors.

III. TESTING EQUIPMENT AND PROCEDURE

The equipment used for this investigation had been developed and used over a period of several years for the determination of the high-temperature tensile properties of pitch-coke type of graphites. A detailed description of this equipment is given in Ref. 1, 2, and 3.

The important features are that the test specimen was heated by radiation from a separate heating element which had a hot zone at least four times the specimen gage length, and that the temperature of the gage section of the specimen was continually monitored with an optical pyrometer. All heating was done in an atmosphere of tank helium.

Because of the size and shape of the material available for test-specimen blanks, and because of the high values of tensile strength expected, it was necessary to redesign the specimen holders and the specimen for these pyrolytic graphite tests. Figure 2 is a photograph of the complete load train used for this investigation. The specimen had a 0.1-in.-thick × 0.06-in.-wide × 0.75-in.-long gage section. Three-quarter-inch radius fillets at each end of the specimen provide a seating surface against the holders. The specimen holders are made from a high-density, high-strength pitch-coke graphite and have a spherical seat to match the end of the carbon load-transmission rod and to provide alignment of the specimen.

Tension tests were conducted at room temperature and at various temperatures in the range of 3000 to 5000°F, thus covering the range in which pitch-coke graphites show a peak in the tensile strength vs temperature curve (Ref. 1).

The load was applied parallel to the basal planes. The reported stress was calculated on the initial cross-sectional area of the specimen gage. The cross-head speed of the testing machine was held constant during any given test and was used to calculate the strain rate.

IV. DISCUSSION OF RESULTS

More than fifty tension tests have been run on six lots of pyrolytic graphite from various producers. However, the data herein reported (Table 2) were selected from three lots and are representative of all the data obtained.

Table 2. Tensile properties of pyrolytic graphite

Specimen No.	Test temperature °F	Strain rate × 10^{-5} sec^{-1}	Ultimate tensile strength psi	Recorded elongation in 0.75 in. %
14601 2587	RT	2	8,900	0.2
14601 2592	RT	67	14,700	1.9
15601 2925	RT	4.4	6,200	3.8
14601 2591	4000	21	24,400	6.1
15601 2924	4000	21	24,600	6.9
14601 2589	4500	21	30,600	8.2
15601 2922	4500	21	26,600	5.2
14804 2937	4500	21	32,700	12.2
14601 2588	4750	21	51,900	20.4
14801 2936	4750	21	52,600	27.0
14601 2590	5000	21*	65,800	58.4
14601 2593	5000	21*	>60,800	>49.0
15601 2926	5000	21	46,200	43.9
14802 2601	5000	21*	46,000	78

*Strain rate increased to 42 x 10^{-5} sec^{-1} for last 10 min of test.

Typical engineering stress–strain curves obtained during this study are shown in Fig. 3. At 4500°F and below the shape of these curves is not markedly different from that obtained for pitch-coke graphites (Ref. 1) except that the ultimate strength values are appreciably higher for pyrolytic graphite. The curve at 5000°F is different from that obtained for pitch-coke graphite in that the engineering stress of pyrolytic graphite increased continually with strain, and fracture occurred at a strength level which was markedly above the 4500°F fracture strength. The shape of this 5000°F curve is typical of all those obtained, and its unusual features are not understood.

The differences in the temperature–strength relation for pyrolytic graphite as compared to pitch-coke graphite is more clearly seen in Fig. 4. This shows the tensile strength–temperature relation for a large number of commercial pitch-coke graphites as reported in Ref. 1. Tensile–strength values for all pyrolytic graphite specimens tested to date are shown in the same Figure. At all temperatures studied, the tensile strength of the pyrolytic graphite is approximately ten times higher than the tensile strength of pitch-coke graphites. While the scatter in the pyrolytic-graphite values appears to be quite large, two things should be kept in mind: first, that the results of all lots tested have been included, and therefore the lot-to-lot scatter, which is always large in the early stages of development, will show up; second, and more important, that nearly all of the low-strength values reported were measured for specimens which, after testing, were found to contain cracks or other structural flaws. Further development of the processing procedure, and more complete inspection of the material prior to testing, will reduce this scatter.

Besides the generally higher strength level of the pyrolytic graphite, another important difference shown in Fig. 4 is the behavior or the ultimate strength above 4500°F. For the pitch-coke graphites the tensile strength at 5000°F was equal to or less than the strength at 4500°F. For the pyrolytic graphite, however, the ultimate tensile strength increased markedly, and at 5000°F was approximately twice the 4500°F value.

The ductility of pyrolytic graphite at temperatures above 4500°F also increased markedly, and at 5000°F elongations of 60% and greater were recorded. These values are greater than those measured for pitch-coke graphites at the same temperatures (Ref. 1, 2, and 3).

Determination of the properties of pyrolytic graphite after testing at 5000°F is sometimes a difficult procedure because of the fracture behavior of this material. The photographs in Figs. 5 and 6 show a series of pyrolytic graphite specimens after fracture at various test temperatures. Of most interest are the specimens tested at 5000°F which exhibit the kinked regions shown at higher magnification in Fig. 6. It is believed that this kinking occurred after fracture and was caused by the release of elastic energy stored in the load-train assembly.

The angle between the basal planes in the kinked and unkinked regions has been measured and found to be between 29 and 60 deg. There would seem to be no correlation between these "kink angles" and the twinning angle for natural graphite, which is reported to be 20 deg (Ref. 4).

In an attempt to understand and explain the behavior of pyrolytic graphite, it was decided to study the structural changes which occur during heating and straining. Since several of the test temperatures used were above the temperature at which the material was originally deposited, it was possible that just heating to the test temperature could produce changes in the structure which would affect the tensile or fracture behavior.

To study this possibility, the macro-, micro-, and x-ray structures of several lots of pyrolytic graphite were examined before and after heating and straining at temperatures up to 5000°F. The results of these studies are given in Figs. 7-12. The microstructure specimens were mechanically polished using standard metallographic techniques and were photographed unetched using polarized light. Typical photomicrographs taken by looking directly at the top of the basal planes of pyrolytic graphite are shown in Fig. 7. It can be seen that no marked changes occurred upon heating to 5000°F.

Typical microstructures taken by looking at the edges of the basal planes of pyrolytic graphite are shown in Fig. 8. The growth cone structure which is normal for pyrolytic graphite can be seen clearly. The microstructure after heating is not sufficiently different from the as-deposited structure to conclude that a definite change has occurred.

The effects of heating to various temperatures on the three-dimensional ordering in pyrolytic graphite are shown in Fig. 9. These x-ray diffractometer tracings of the two-dimensional (10) reflection, obtained by using CuKα radiation and standard x-ray procedure (Ref. 5), show that heating to temperatures below 5000°F made no measurable change in the ordering of the as-deposited material. Heating to 5000°F resulted in a small degree of three-dimensional ordering.

As part of this study, the effects of tensile deformation on the structure of pyrolytic graphite were also investigated. The changes which occur in the microstructure are shown in Fig. 10. These are views of the top of the basal planes of the material after tensile deformation at room temperature and at 5000°F. If they are compared with Fig. 7, it can be seen that 0.1% deformation at room temperature caused no marked change, but a definite change in the structure occurred after 56% deformation at 5000°F.

Changes also occurred in the microstructure when viewed parallel to the basal planes, as can be seen by comparing the structures after deformation shown in Fig. 11 with the as-deposited structure of Fig. 8. Deformations of 5 to 6% at 4000 and 4500°F seemed to have caused no visible changes. After 20% deformation at 4750°F the growth cone structure has become distorted and less distinct. If 49% deformation is given at 5000°F, the growth cone structure can be completely erased and a "flecking" similar to that reported in Ref. 6 is noted (see Fig. 11).

The x-ray structure shows major changes as a result of deformation at temperatures above 4750°F. This can be seen in the x-ray diffractometer tracings shown in Fig. 12. A marked degree of ordering occurred after 74% deformation at 5000°F, as indicated by the splitting of the two-dimensional (10) reflections into the crystalline (100) and (101) reflections. For some other lots (Ref. 7) this ordering was completed to an even greater degree.

The change in ordering in pyrolytic graphite is accompanied by a change in the height of the unit cell as shown in Fig. 13. These *c* values are averages calculated from the (002), (004), and (006) reflections. The scatter in the data was ±0.02Å. At 4500°F neither heating only, nor heating and straining to a deformation of 8%, produces a decrease in the unit cell height. At 4750°F heating only produces no decrease; however, heating and straining to a deformation of 20% produce a marked decrease in the unit cell height. At 5000°F both heating only and heating and straining to a deformation of 58% produce a marked decrease in the unit cell height; however, these values are still greater than the unit cell height, 6.708Å (Ref .8), for well-crystallized graphite.

A plot of the $(00l)$ peak widths against temperature for the heated only and the heated and strained portions of tensile specimens (Fig. 14) shows more clearly the effects of heating and deformation on ordering. From the data for 5000°F it is seen that the magnitude of the (002), (004), and (006) peak widths and the difference between the (002) and (006) peak widths for the portion that was heated only is considerably less than the magnitude and difference for the portion that was heated and strained. The lower $(00l)$ peak-width data for the portion that was heated and strained is thought to be due to an increase in crystallite height and a decrease in distortion broadening.

Other changes which occur when pyrolytic graphite is heated are shown in Fig. 15. This Figure shows changes in the room-temperature dimensions after specimens of pyrolytic graphite have been heated to various temperatures. For one block (14601) the changes were large (5 to 10%) but were not measurable until temperatures of 4750°F and above had been reached. For another block (14803) the changes were small (2 to 4%) but were measurable for temperatures as low as 4300°F. According to Ref. 9, these room-temperature dimensional changes with heat treatment suggest a mechanism of mechanical straightening of tilt boundaries between crystallites. It is also suggested that the magnitude and temperature range of these dimensional changes would be markedly affected by units in the structure which inhibit the straightening of neighboring crystallites.

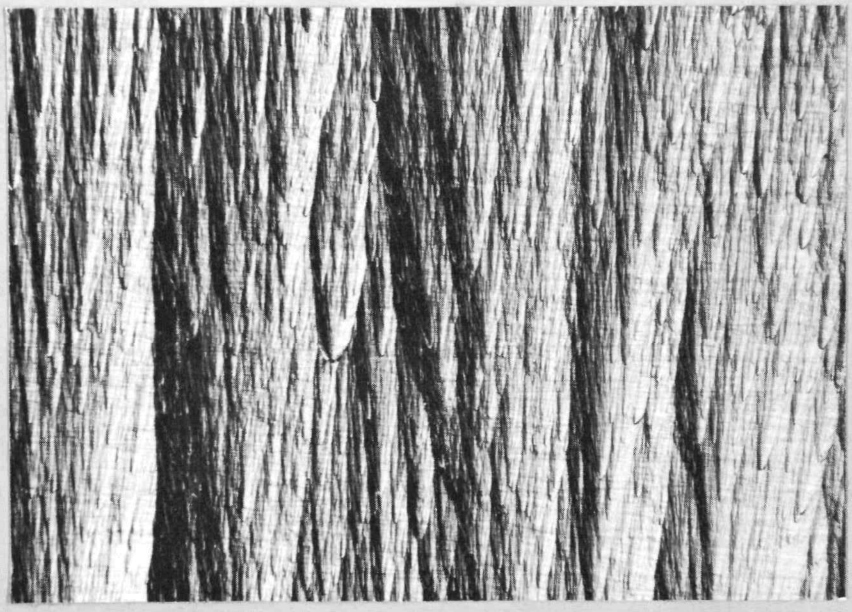
V. CONCLUSIONS

This preliminary study of the tensile properties and behavior of pyrolytic graphite at temperatures up to 5000°F indicates the following:

1. The ultimate tensile strength of pyrolytic graphite at any given temperature in the range studied is approximately ten times as great as that of commerical pitch-coke graphites.
2. Above 4500°F the ultimate tensile strength of pyrolytic graphite continues to increase with temperature rather than decrease or remain constant as is the case with pitch-coke graphites.
3. Heating pyrolytic graphite to temperatures in the range of 4000 to 5000°F produces a measurable change in the room-temperature dimensions, a small degree of three-dimensional ordering, but no visible change in the microstructure.
4. Graphitization is enhanced by heating pyrolytic graphite to temperatures of 4750°F and above, as indicated by a decrease in unit cell height and an increase in three-dimensional ordering of the x-ray structure.
5. If the heating of pyrolytic graphite to temperatures above 4500°F is accompanied by tensile deformation, the x-ray and microstructural changes occur at a lower temperature, or to a greater degree at any of the temperatures investigated.

REFERENCES

1. Martens, H. E., Jaffe, L. D., and Jepson, J. O., "High-Temperature Tensile Properties of Graphites," *Proceedings of Third Conference on Carbon,* Pergamon Press (1959), p. 529.
2. Martens, H. E., Button, D. D., Fischbach, D. B., and Jaffe, L. D., "Tensile and Creep Behavior of Graphites Above 3000°F," *Proceedings of Fourth Conference on Carbon,* Pergamon Press (1960), p. 511.
3. Martens, H. E., Jaffe, L. D., Button, D. D., "High-Temperature Short-Time Creep of Graphite," *Transactions of The Metallurgical Society of AIME,* vol. 218, October 1960, pp. 782–87.
4. Kennedy, A. J., "Dislocations and Twinning in Graphite," *Proceedings of the Physical Society,* vol. LXXV, 1960, pp. 607–11.
5. Klug, H. P. and Alexander, L. E., *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials,* New York, John Wiley and Sons, 1954.
6. Bradshaw, F. J., and Wheeler, C., "Deformation of Deposited Carbon," *Journal of Less-Common Metals,* vol. 1 (2), 1959, pp. 101–05.
7. Martens, H. E., and Kotlensky, W. V., "Tensile Behavior of Pyrolytic Graphite at 2750°C," *Nature,* vol. 186 (4729), June 18, 1960, pp. 960–62.
8. Bacon, G. E., "The Interlayer Spacing of Graphite," *Acta Crystallographica,* vol. 4, 1951, pp. 558–61.
9. Stover, E. R., "Effects of Annealing on the Structure of Pyrolytic Graphite." Paper presented at the AIME Meeting in Dallas, Texas, October 17, 1960.



PYROLYTIC GRAPHITE
(POLARIZED LIGHT)

PITCH-COKE GRAPHITE

Figure 1. Microstructure of pyrolytic graphite and pitch-coke graphite; top block 14801, bottom block 0106 (unetched)

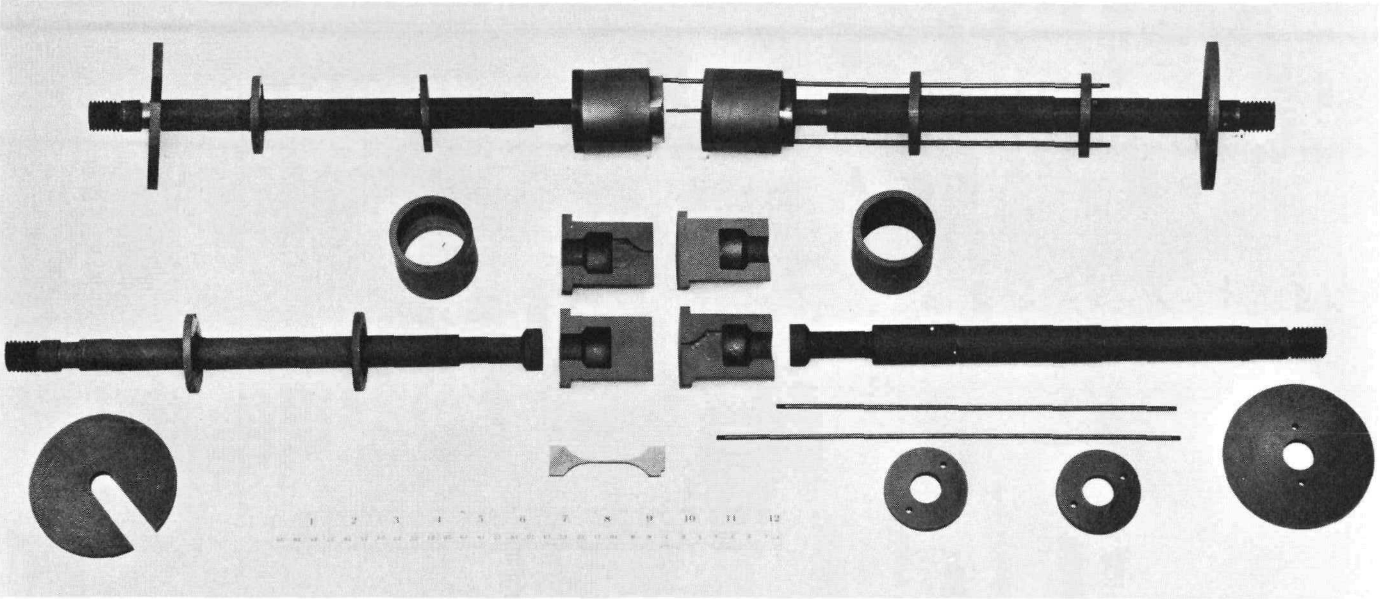


Figure 2. Specimen, holders, load-transmission rods, and extensometer rods for high-temperature testing of pyrolytic graphite

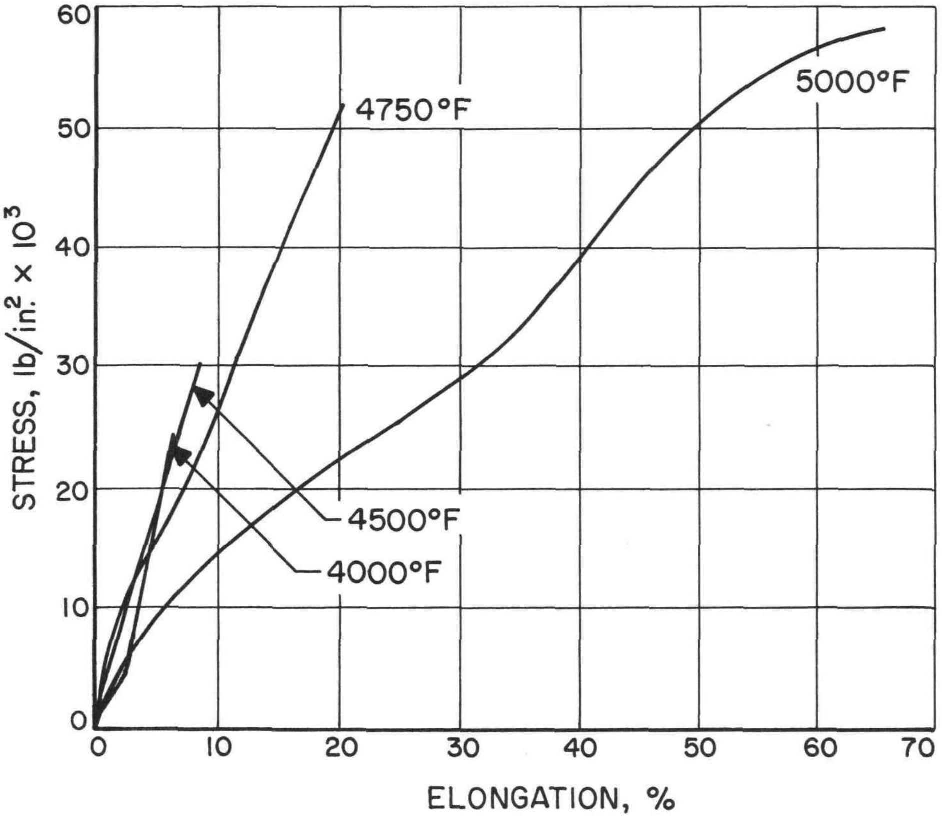


Figure 3. Typical engineering stress–strain curves for pyrolytic graphite; stress parallel to basal planes, strain rate 21 x 10^{-5} sec^{-1}; block 14601

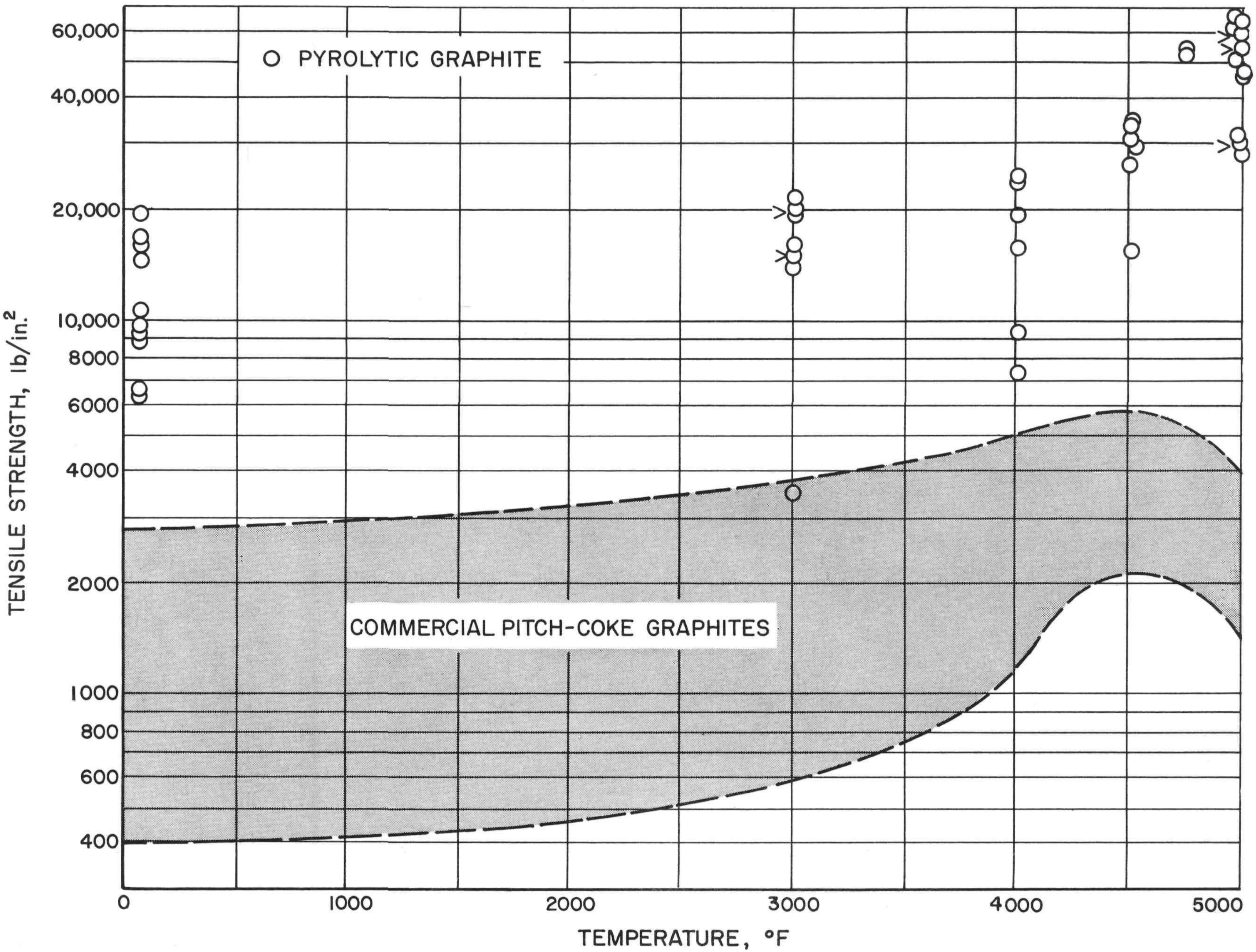


Figure 4. Ultimate tensile strength vs test temperature

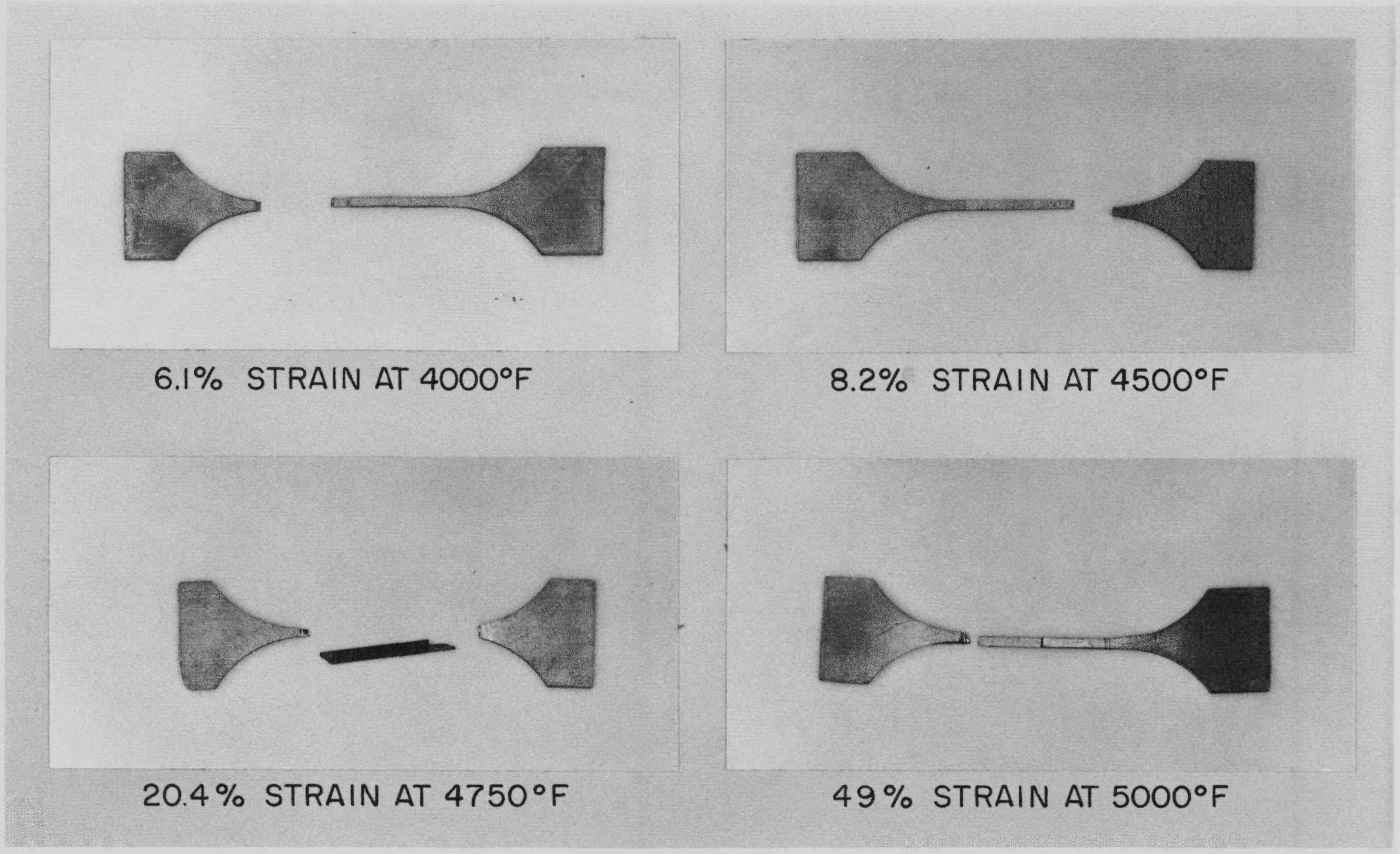
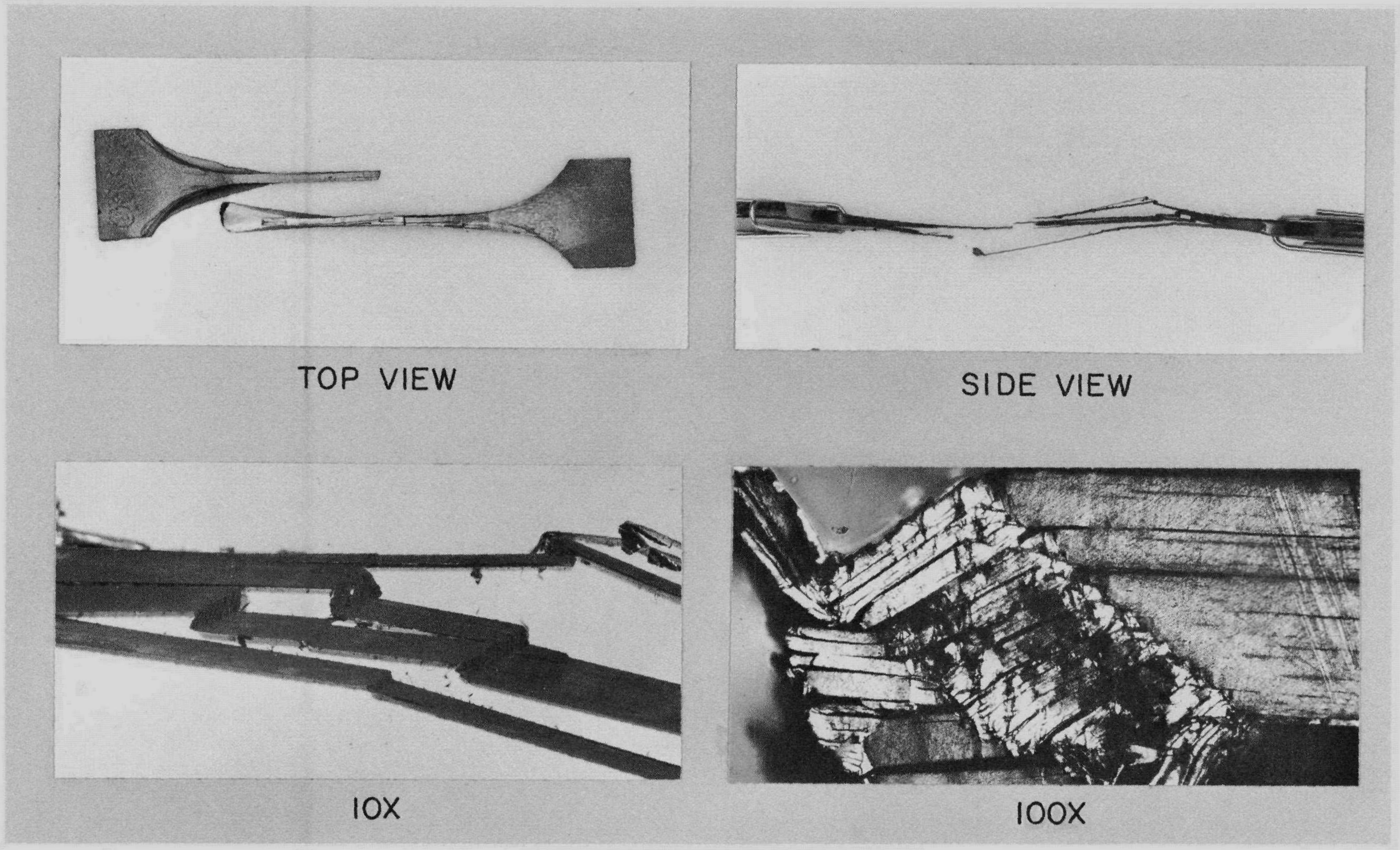


Figure 5. Pyrolytic graphite specimens after fracture; block 14601



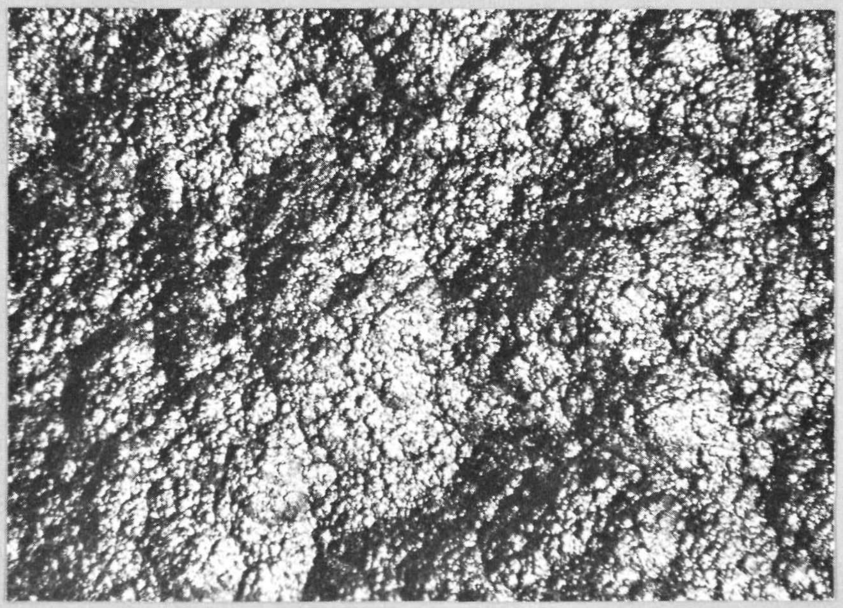
TOP VIEW

SIDE VIEW

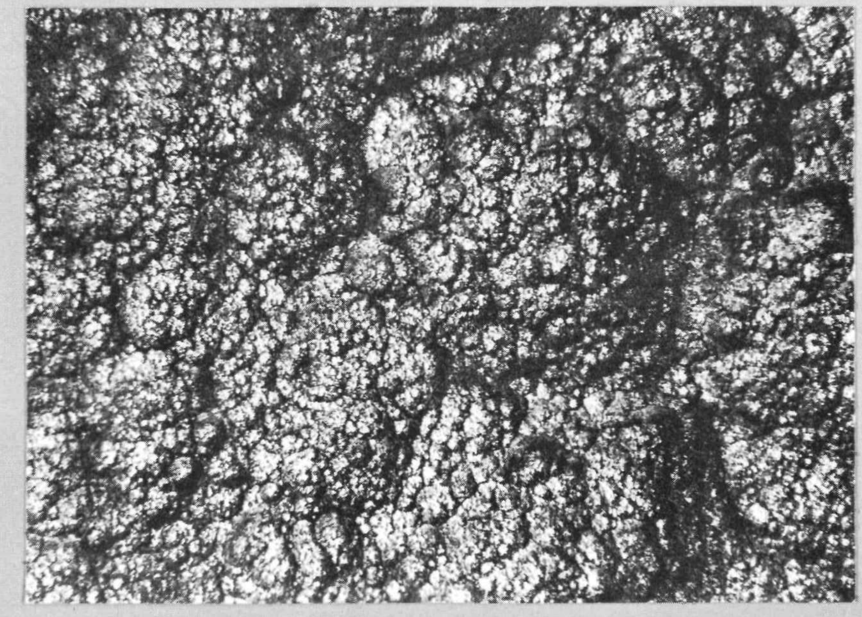
IOX

IOOX

Figure 6. Fractured pyrolytic graphite specimen showing kinked region; specimen 14601–2590; 58 % deformation at 5000°F



AS DEPOSITED



HEATED TO 5000°F
(PHOTOGRAPHED AT 100X)

Figure 7. Microstructure of pyrolytic graphite looking perpendicular to basal planes; block 14124 (unetched)

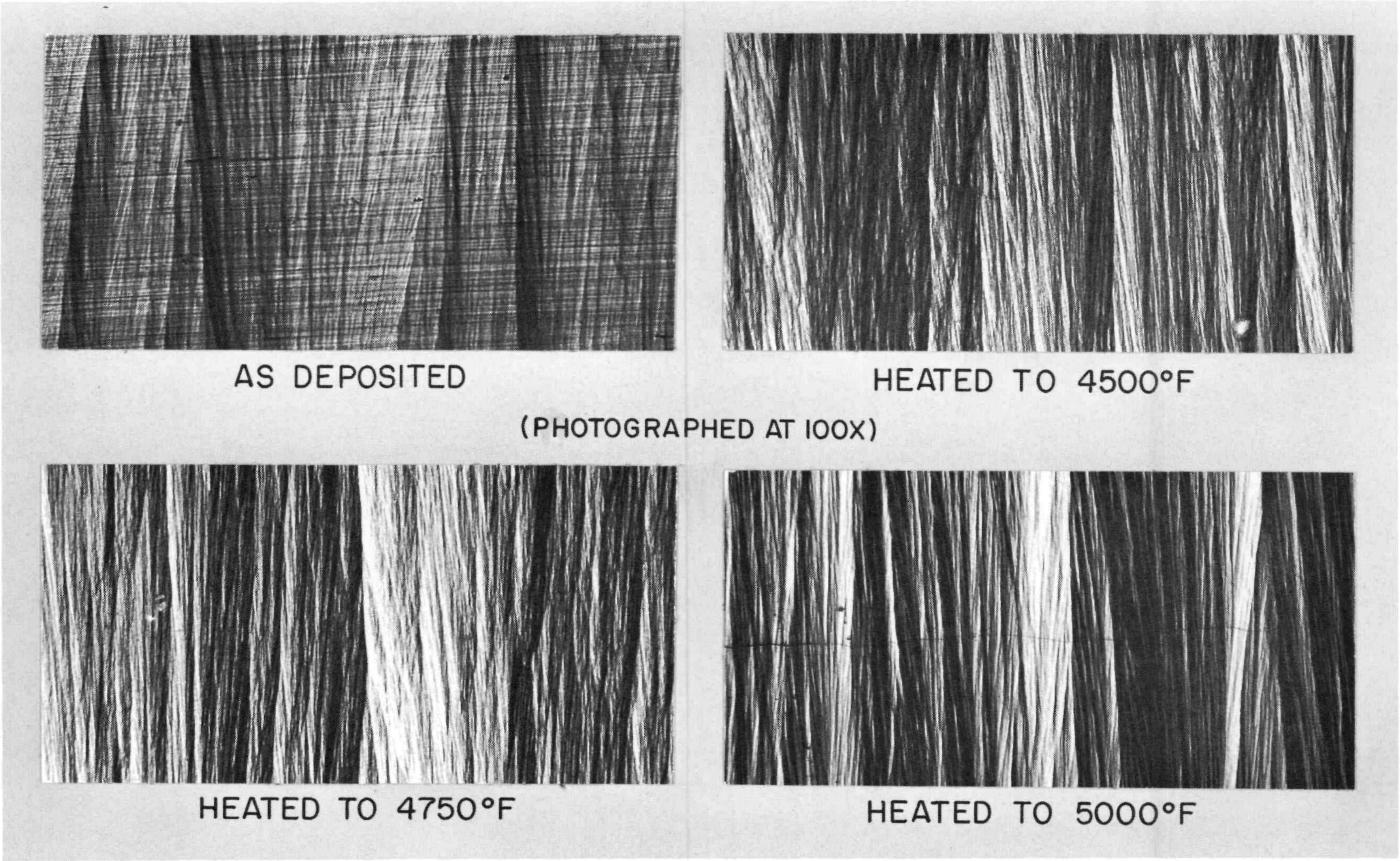


Figure 8. Microstructure of pyrolytic graphite looking parallel to basal planes; block 14601 (polarized light, unetched)

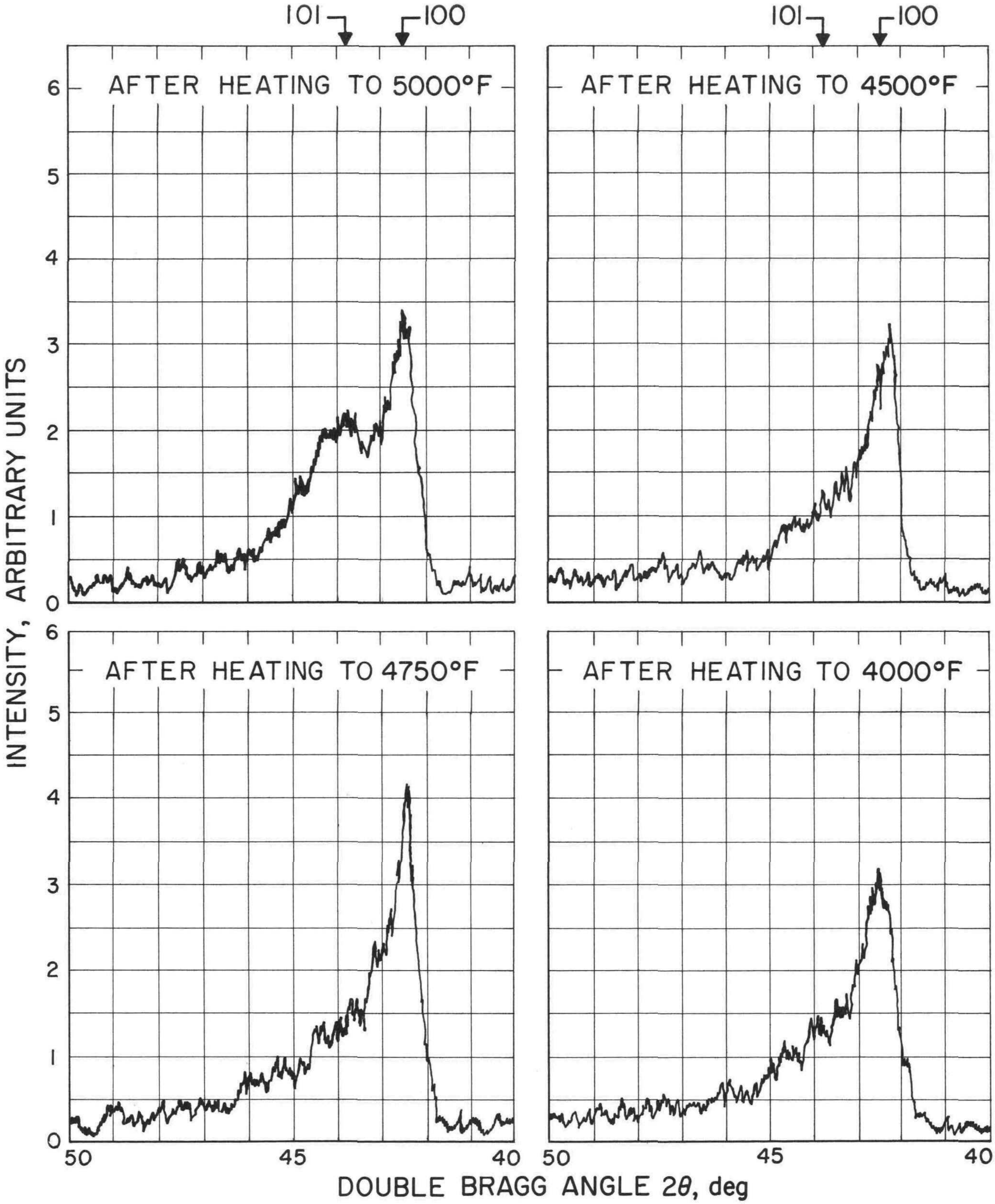
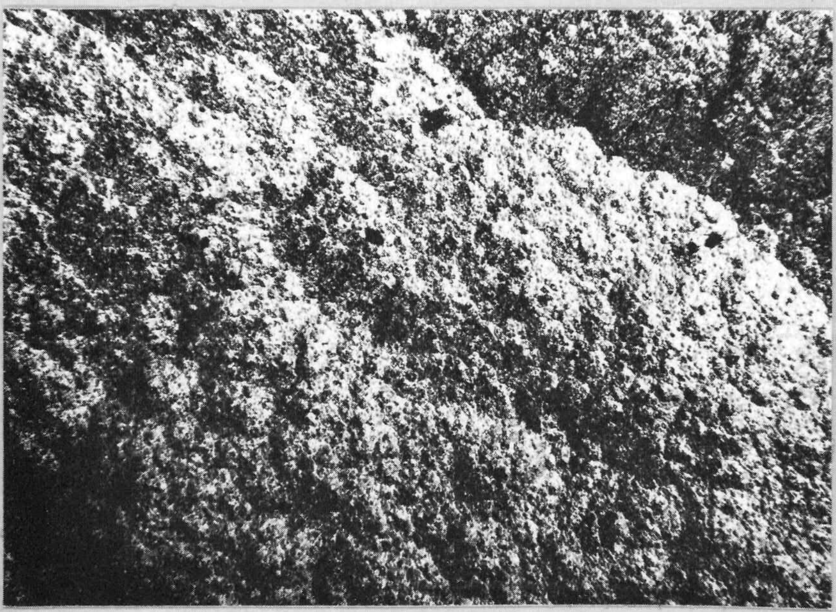
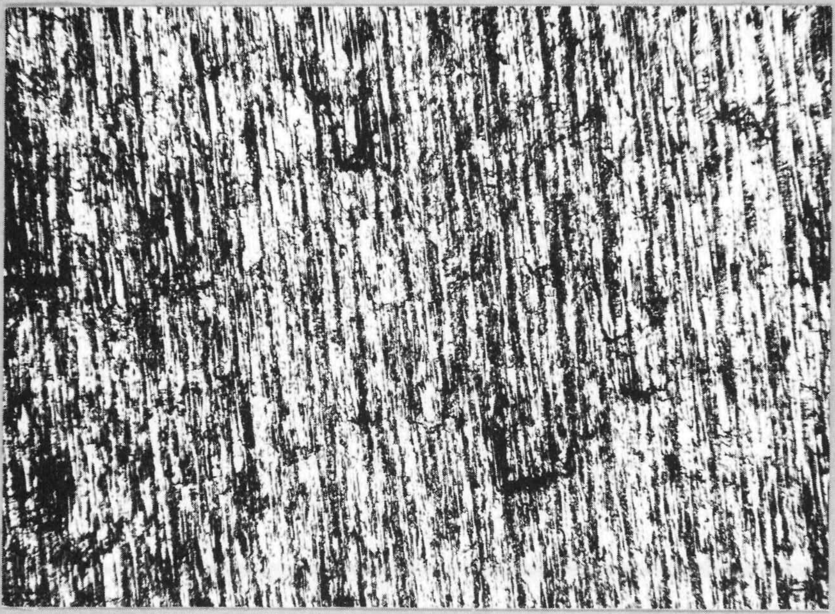


Figure 9. Development of modulations in the (10) x-ray reflections of pyrolytic graphite with heating; block 14601, CuKα radiation

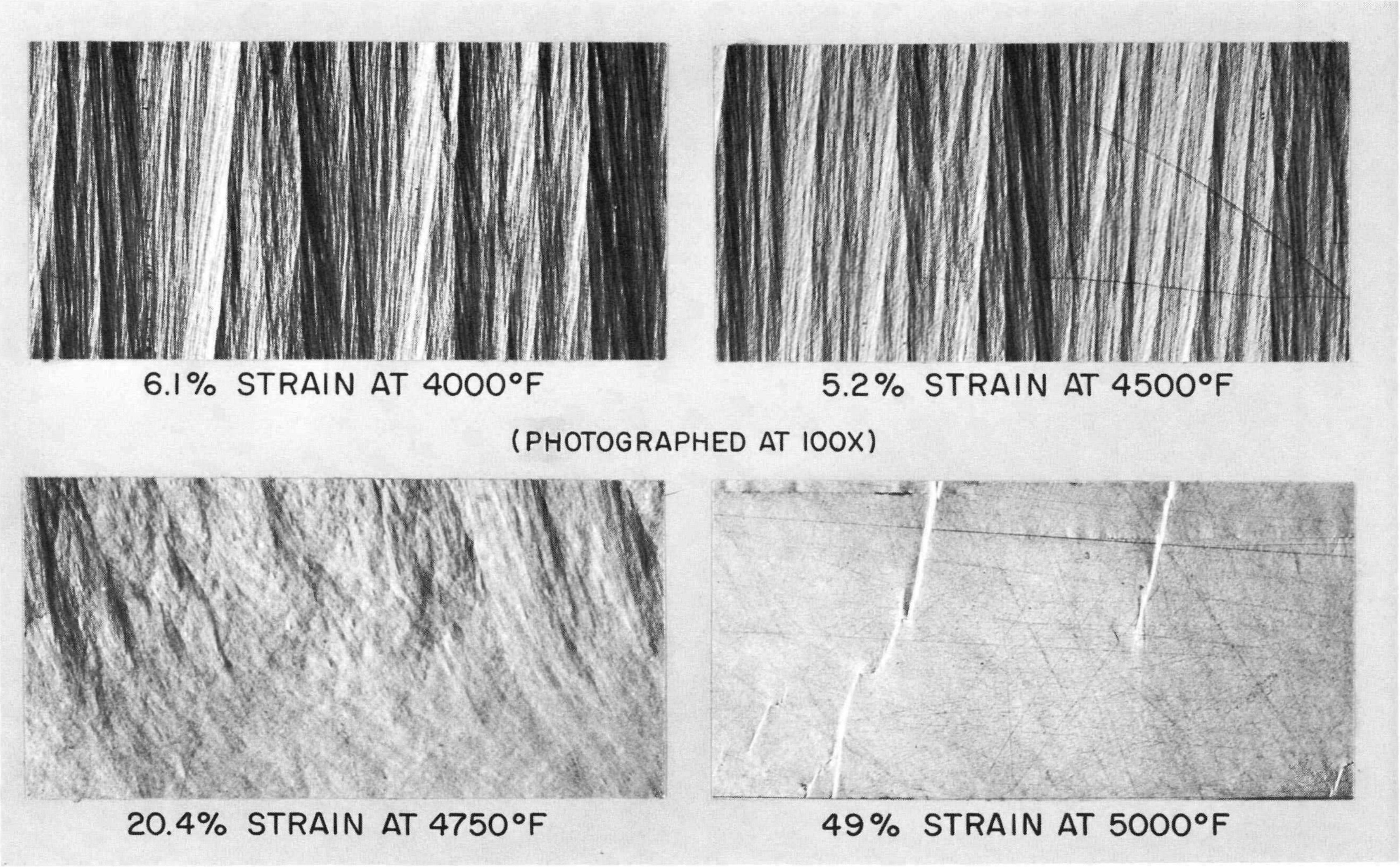


0.1% STRAIN AT ROOM TEMPERATURE



56% STRAIN AT 5000°F
(PHOTOGRAPHED AT 100X)

Figure 10. Microstructure of pyrolytic graphite after heating and straining, looking perpendicular to basal planes; top block 14104, bottom block 14124 (unetched)



6.1% STRAIN AT 4000°F

5.2% STRAIN AT 4500°F

(PHOTOGRAPHED AT 100X)

20.4% STRAIN AT 4750°F

49% STRAIN AT 5000°F

Figure 11. Microstructure of pyrolytic graphite after heating and straining, looking parallel to basal planes; block 14601 (polarized light, unetched)

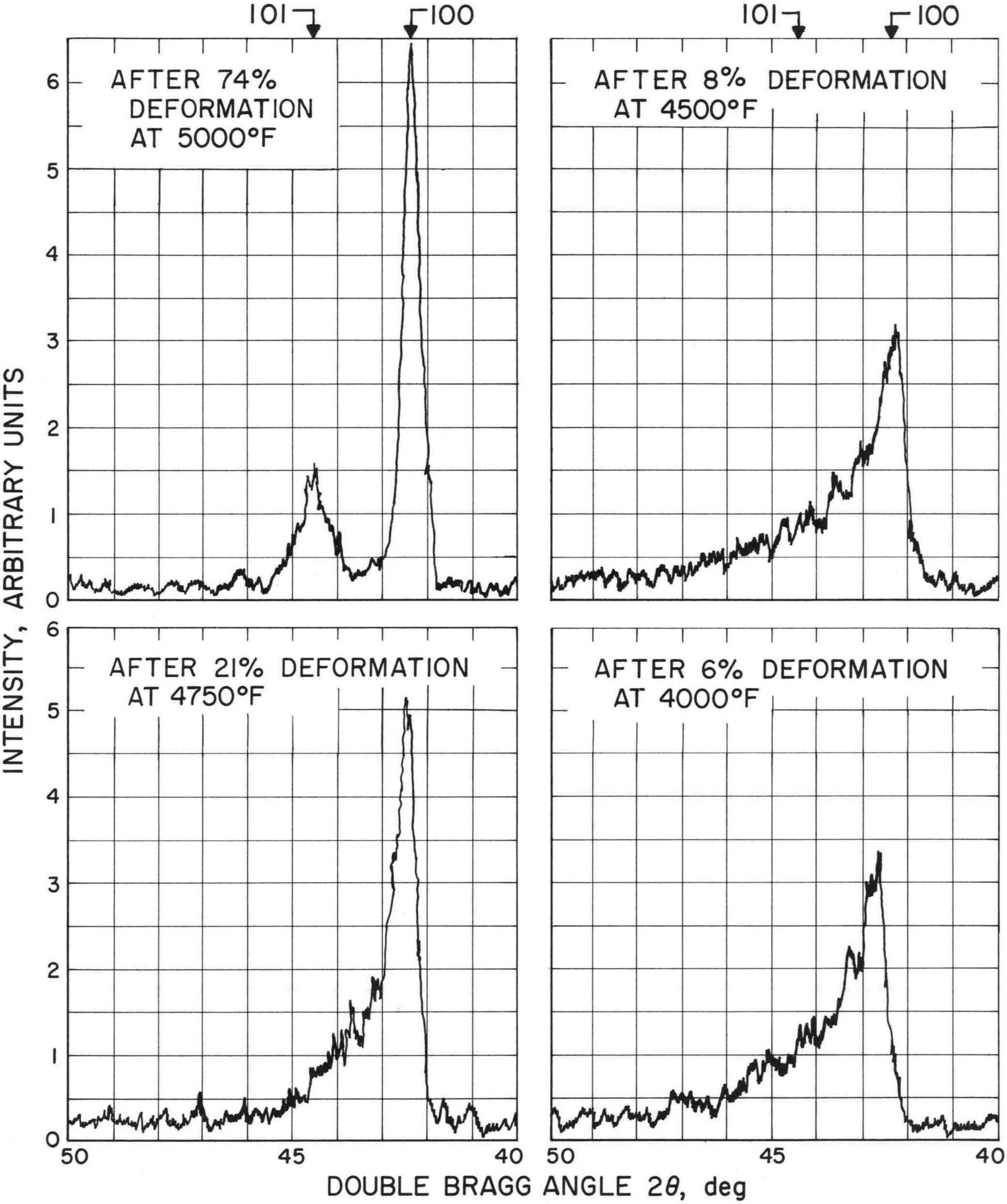


Figure 12. Development of modulations in the (10) x-ray reflections of pyrolytic graphite with heating and straining; block 14601, CuKα radiation

065 19

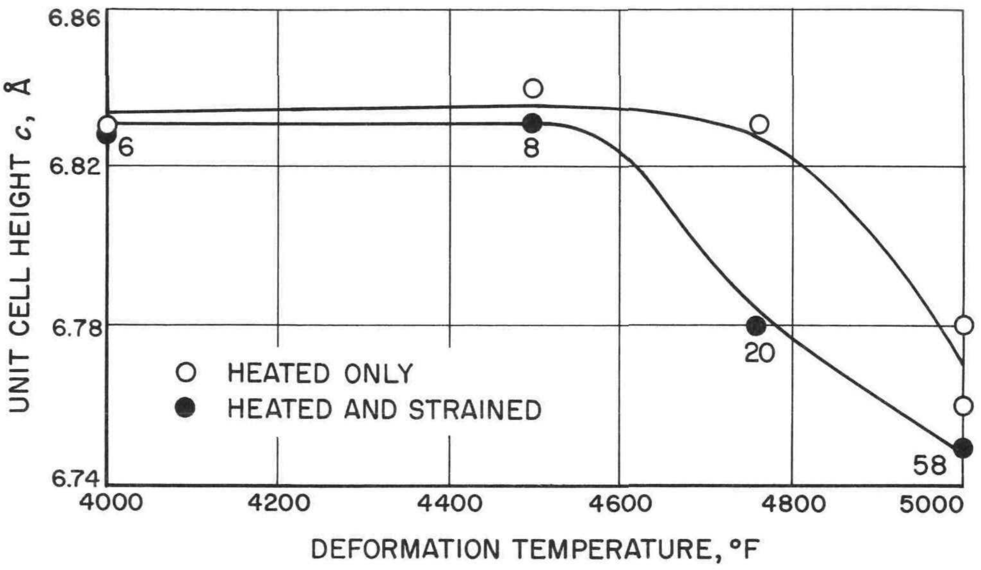


Figure 13. Change in unit cell height of pyrolytic graphite with heating and straining; block 14601, CuKα radiation (numbers by solid symbols indicate per cent deformation)

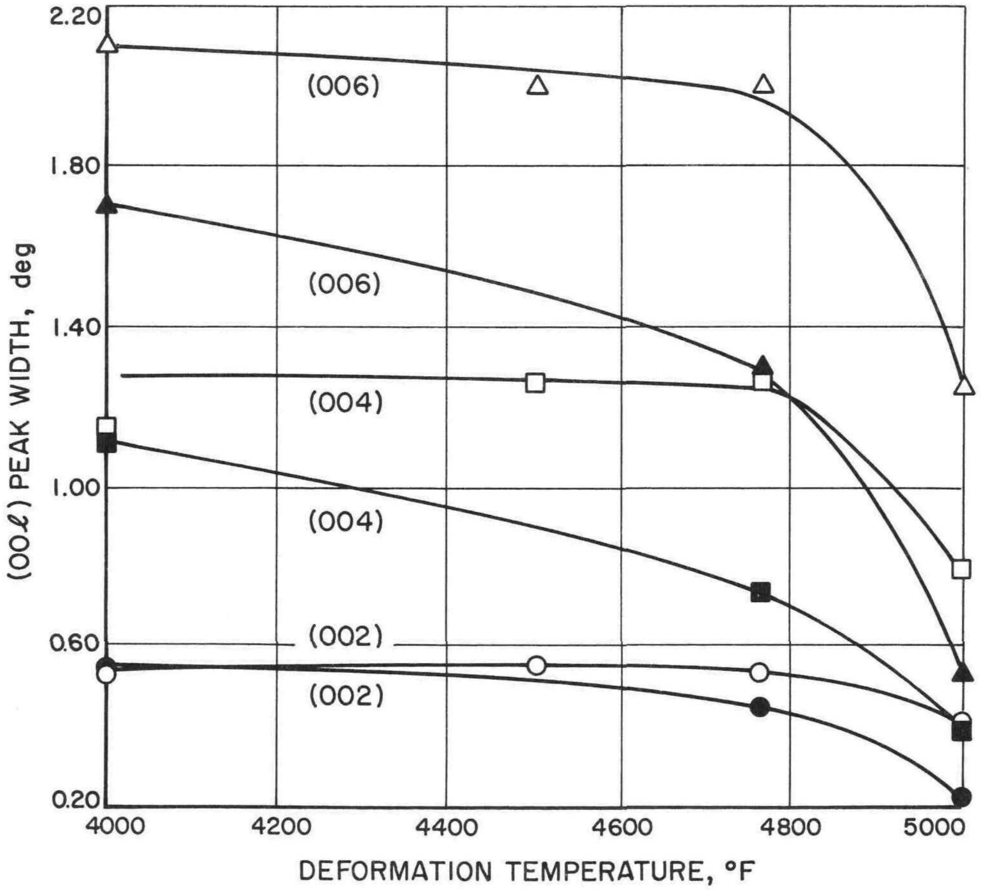


Figure 14. Change in (00*l*) x-ray peak width of pyrolytic graphite with heating and straining; block 14601, CuKα radiation (Open symbols are for heated only, solid symbols are for heated and strained. Deformations same as in Fig. 13.)

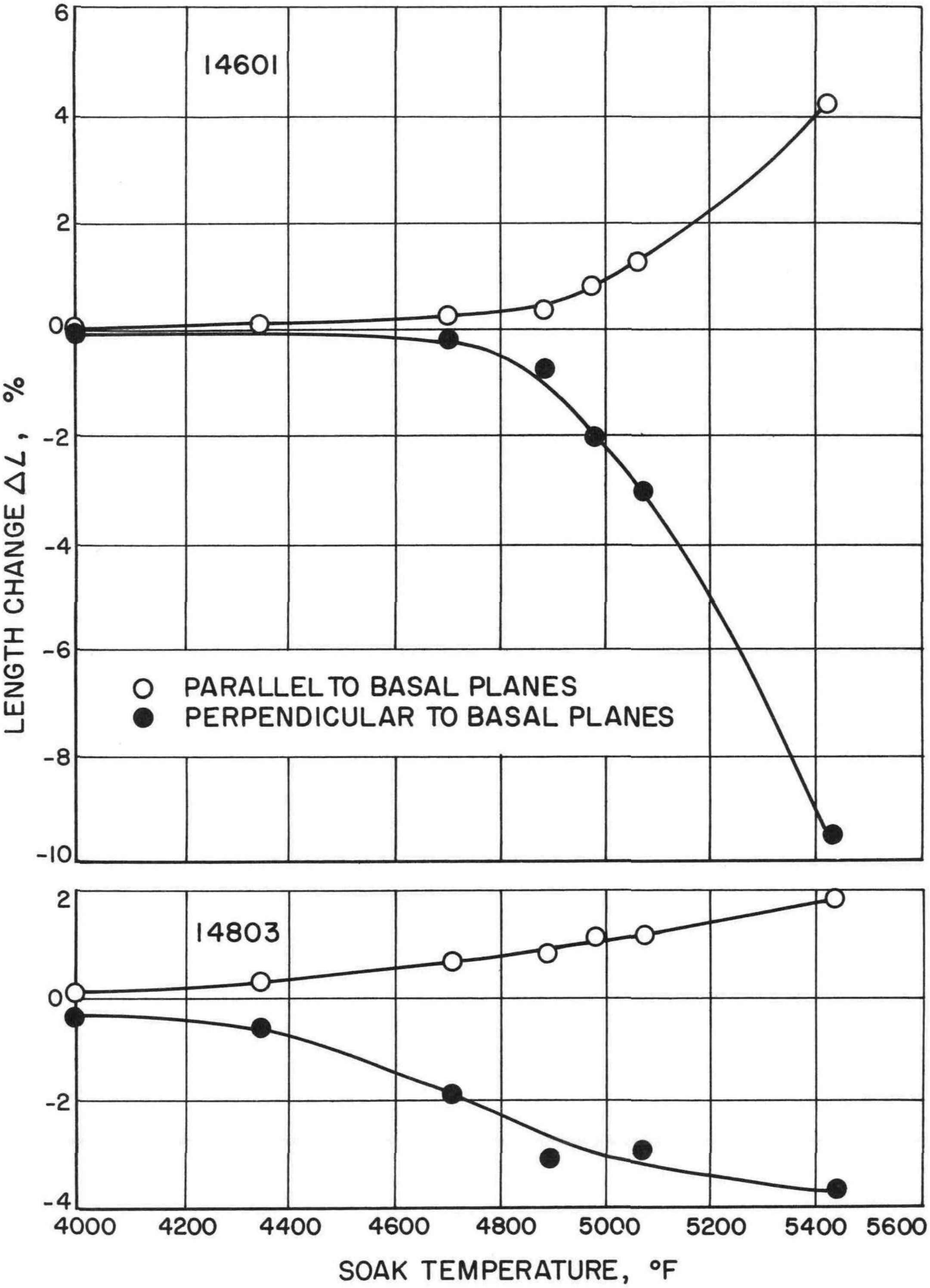


Figure 15. Change in room-temperature dimensions of pyrolytic graphite produced by heating; blocks 14601 and 14803

065 21