

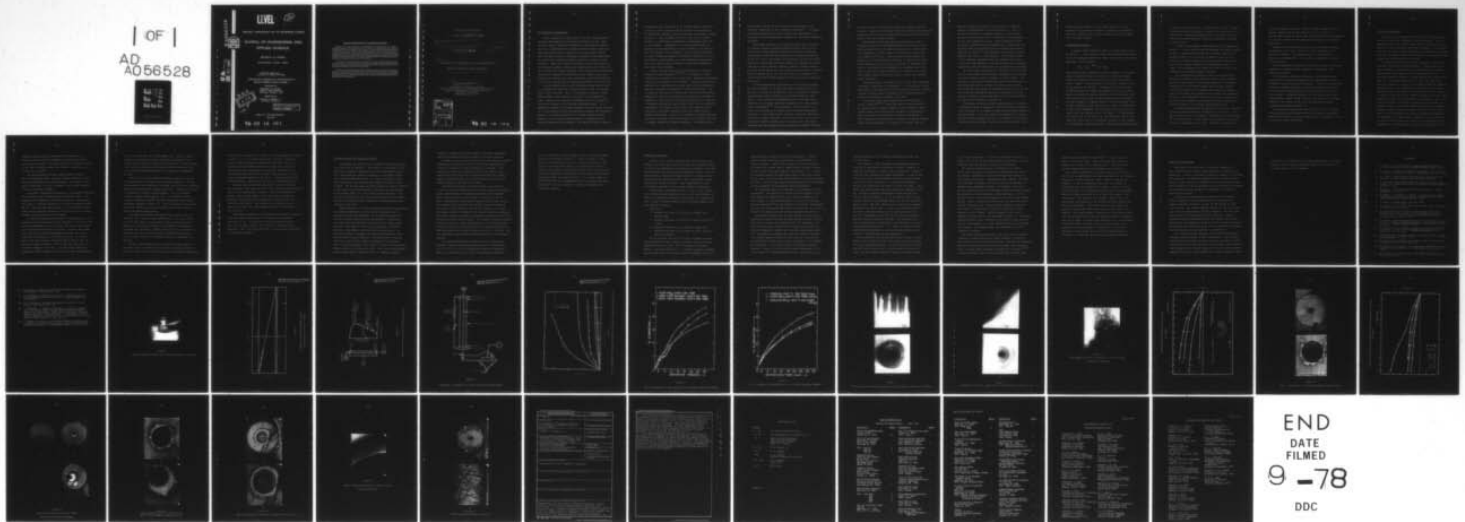
AD-A056 526

VIRGINIA UNIV CHARLOTTESVILLE DEPT OF MATERIALS SCIENCE F/G 11/5
INVESTIGATION OF ELONGATION AND ITS RELATIONSHIP TO RESIDUAL ST--ETC(U)
JUN 78 F E WAWNER
UVA/525322/MS78/101
N00014-76-C-0694
NL

UNCLASSIFIED

| OF |

AD
A056526



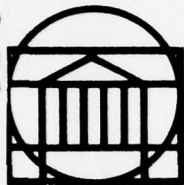
END

DATE
FILMED

9 -78

DDC

AD A 056528



LEVEL

12

RESEARCH LABORATORIES FOR THE ENGINEERING SCIENCES

SCHOOL OF ENGINEERING AND
APPLIED SCIENCE

UNIVERSITY OF VIRGINIA

Charlottesville, Virginia 22901

Technical Report No. 1
Contract No. N00014-76-C-0694

INVESTIGATION OF ELONGATION AND ITS RELATIONSHIP TO
RESIDUAL STRESSES IN BORON FILAMENTS

Submitted to:

Department of the Navy
Office of Naval Research
Arlington, Virginia 22217

Submitted by:

Franklin E. Wawner, Jr.
Principal Scientist

This document has been approved
for public release and sale; its
distribution is unlimited.

Report No. UVA/525322/MS78/101

June 1978

78 07 10 101

AD No. _____
DDC FILE COPY



RESEARCH LABORATORIES FOR THE ENGINEERING SCIENCES

Members of the faculty who teach at the undergraduate and graduate levels and a number of professional engineers and scientists whose primary activity is research generate and conduct the investigations that make up the school's research program. The School of Engineering and Applied Science of the University of Virginia believes that research goes hand in hand with teaching. Early in the development of its graduate training program, the School recognized that men and women engaged in research should be as free as possible of the administrative duties involved in sponsored research. In 1959, therefore, the Research Laboratories for the Engineering Sciences (RLES) was established and assigned the administrative responsibility for such research within the School.

The director of RLES—himself a faculty member and researcher—maintains familiarity with the support requirements of the research under way. He is aided by an Academic Advisory Committee made up of a faculty representative from each academic department of the School. This Committee serves to inform RLES of the needs and perspectives of the research program.

In addition to administrative support, RLES is charged with providing certain technical assistance. Because it is not practical for each department to become self-sufficient in all phases of the supporting technology essential to present-day research, RLES makes services available through the following support groups: Machine Shop, Instrumentation, Facilities Services, Publications (including photographic facilities), and Computer Terminal Maintenance.

Office of Naval Research

Contract No. N00014-76-C-0694

UVA/525322/M578/141, TR-1

Jun 78

Technical Report No. 1

46p.

INVESTIGATION OF ELONGATION AND ITS RELATIONSHIP TO
RESIDUAL STRESSES IN BORON FILAMENTS

Franklin E. Wawner, Jr.

Department of Materials Science
Research Laboratories for the Engineering Sciences
School of Engineering and Applied Science
University of Virginia
Charlottesville, VA

ADMISSION for	
NTIS	White Section ☒
DOC	Grey Section ☐
UNANNOUNCED	☐
JUSTIFICATION	
BY	
DISTRIBUTION/AVAILABILITY CODES	
Dist.	AVAIL. and/or SPECIAL
A	

78 07 10 101

401 761

act

Introduction and Background

Boron filaments are perhaps one of the most technologically important developments in the materials industry in many years. The high specific strength and modulus of this material makes it ideal as a reinforcement for organic and metal matrix composites. Many applications for the material can be envisioned, however, there has been a certain reluctance by designers and manufacturers to utilize boron composite materials primarily because of their high cost. There are limited applications today, particularly in the aerospace industry, where boron composites are cost effective. In the large part however they have been excluded from incorporation into specific hardware items because of the stigma of high cost. Conventional materials are then used without long-range considerations of cost savings due to improved performance and service life.

Several factors can be cited which would reduce the cost of the filaments and hence the ultimate composite cost, the primary one of which is volume. But it is difficult to create a volume market without first reducing the price to a cost competitive level. Based on this premise, a secondary factor to reduce the cost of the filament is to increase production speeds. It is physically possible to increase production speeds of boron filaments by 2-3 times using existing manufacturing equipment and techniques; however, the filament obtained is of inferior quality having, generally, a low tensile strength making it unacceptable for existing composite specifications. The reason for the low tensile

strength has been attributed to an internal defect called the "crack tip" mode of failure and is believed to be related to an undesirable residual stress distribution in the boron filament (Figure 1). This is based on the fact that the low tensile strength is occasionally accompanied by spontaneous splitting of the filament. Consequently, if one could understand the residual stress distribution in boron filaments, its relationship to fracture of the filaments, and what factors influence it, then it might be possible to determine techniques to alter the residual stress pattern to a more favorable configuration. This would lead to faster production speeds and considerably lower cost boron filament.

Several limited studies have been conducted on residual stresses in boron filaments^{1,2,3,4,5}. The essence of these studies was to determine the configuration, magnitude and apparent causes of the stresses in the filaments. Virtually nothing has been done to relate specific process conditions or fundamental material properties to unfavorable stress distributions. Unfortunately, this area of research was ignored when accelerated emphasis was placed on fabricating and studying the filament in composites. The results of the above studies were all basically in agreement showing the outer surface layers being in residual compression, the layers of boron next to the tungsten boride core being in residual tension and the core itself being in residual compression. Figure 2 is a schematic diagram depicting the typical residual stress configuration in the boron layer for a filament produced on a carbon substrate. The magnitudes for

the residual stresses in this figure were determined by two different techniques and gave remarkable agreement⁶. In general, the reported magnitudes for the stresses vary depending on the techniques used for measurement, however, all are within reasonable agreement.

The primary causes of the residual stresses were attributed to: thermal expansion mismatch between deposited boron and the boride core; volume expansion within the core due to diffusion and reaction to form borides; quenching in the mercury electrode at the exit end of the reactor; and elongation in the boron during deposition. Both boron filaments produced on tungsten and carbon substrates contain residual stresses, however, filament produced on carbon do not appear to give as high values as boron on tungsten. This is probably due to the fact that there is no diffusion and reaction and hence volume expansion in the core region eliminating this cause.

Of the aforementioned contributors to the residual stresses in boron filaments, it is felt that boron elongation during deposition is perhaps the predominant cause of unfavorable residual stress patterns when attempting to increase production speed. Talley⁷ first detected the phenomena when he noted that boron deposited on a tungsten substrate elongated by 10%. More recently other investigators^{8,9} have conducted a broader study of the effect while attempting to deposit boron on carbon monofilament substrate. It was observed that the boron elongated sufficiently to break the carbon substrate. This is due to the fact that the boron layer formed a sufficiently strong bond with the carbon substrate and the elongation during deposition exceeded the strain

to failure of the non-elongating carbon monofilament, causing fracture. Fracture of the carbon substrate created local electrical discontinuities and hence hot spots which gave rise to crystalline boron of very low tensile strength.

Measurements showed that boron elongation was primarily dependent on deposition temperature being the greatest for the low temperature end of the deposition range (i.e. approximately 2.5% elongation at 1000°C versus 1% elongation at 1200-1300°C at a diameter of 2 mils). Other factors such as reactant gas composition, selected impurity additives or tension of the substrate appeared to have little or no effect. A technique was devised to circumvent this phenomenon by pre-depositing a thin layer of pyrolytic graphite which did not bond with the carbon monofilament thereby allowing the boron to slide and rearrange during elongation.

Boron elongation, in general, is one of the least understood fundamental properties of the material. It is certainly a prime contributor to the residual stress distribution in the as produced filament and this stress distribution has a strong bearing on tensile and transverse strengths (splitting).

Along these same lines, observations have been made by Soviet scientists^{10,11,12} which may also be strongly related to elongation and residual stresses in boron filaments. These studies showed that annealing the filaments at approximately 300°C for short times increased the tensile strength by 12%. This increase was accompanied by a decrease in flexural strength which was not understood. Of interest is the fact that the

material displays an internal friction peak (a relaxation maximum) at approximately the same temperature. Also, it was noted that there is anomalous behavior in the thermal expansion characteristics and in resistance in the filaments in this same temperature region. These observations along with boron elongation may be influenced by or related to the anelastic behavior displayed by boron filaments and recently described by DiCarlo¹³. Some evidence in the present program suggests that there is a relationship. All of these appear to be fundamental phenomena which are probably controlled by a structural rearrangement in the material and have a possible relationship with the elongation and residual stress phenomena.

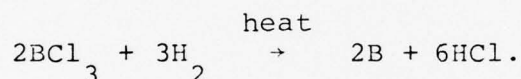
The steps taken to minimize the influence of boron elongation on carbon substrate were really circumventing or ignoring the basic problem in order to achieve a viable product. The procedure to pre-deposit the PG layer while successful has its limitations and adds to the cost of producing the filament. This emphasizes the purpose of the proposed work that if we can understand the fundamental property of elongation and hence residual stresses in boron then there may be certain measures one can take to eliminate or control it.

The primary objective of this investigation is to perform a fundamental study on elongation in boron produced by chemical vapor deposition in an attempt to understand the basic nature of this phenomenon. It is then planned to determine what factors influence boron elongation and how it is related to the elastic properties and the ultimate residual stress distribution in as

produced boron filaments. Using these results it will be possible to investigate techniques to minimize the elongation which will possibly lead to faster filament production speeds and lower cost filament.

Experimental Procedure

A typical boron production reactor is schematically shown in Figure 3. The reaction to form boron filaments is carried out by the hydrogen reduction of boron trichloride in the manner described by the equation



The substrate wire, typically 13 micron tungsten, or 36 micron carbon is pulled through the chamber by a substrate takeup motor and is heated electrically to the desired temperature (1000 - 1300°C). Mercury serves as electrical contacts as well as gas seals in the chamber. A mixture of the reactant gas is passed through the deposition chamber at positive pressure where it contacts the heated substrate wire and deposits boron. Also shown in this figure is the temperature profile assumed by boron filament on tungsten while it is being produced. The highest temperature along the profile is called the deposition or "hot spot" temperature and is normally located just a few inches below the entrance end of the reactor. The temperature at the exit end of the reactor is 200-300°C lower than at the "hot spot" and is due to a resistance decrease in the filament as the diameter increases (current is maintained constant through

a filament during production). Hence one can see that "normal" as produced boron (on tungsten) filaments are deposited over a rather severe temperature gradient which considering the contribution of boron elongation leads to a complicated residual stress situation.

In spite of the apparent undesirability of the temperature profile, it is this profile that has produced the highest quality filament. Speeding the process up by creating a uniform temperature profile in the reactor by means of auxiliary VHF heating or by other techniques (of a proprietary nature) have lead to poor quality filament that predominately fail as a result of the characteristic "crack tip" mode of failure, representative of abnormal residual stresses.

The program being conducted at UVA is to produce boron filament by chemical vapor deposition using a static reactor. Using this type reactor will eliminate many of the variables encountered in a continuous process and allow much greater control over growth of the filament and consequently greater ease of observation and recording of the growth and elongation process. A very important factor using this type reactor will be the ability to achieve and maintain a uniform temperature along the length of the filament during boron growth.

Elongation measurements are made using the device constructed during the program and shown schematically in Figure 4. The basic concept is one of a change in inductance of a coil located in a bridge circuit. A small steel rod is attached to the substrate and positioned in the coil. The meter is then set at

zero by a balancing resistor. As the filament elongates during growth, readings can be taken from the meter or traced by a recorder for a permanent record. The substrate is heated resistively by a DC power supply and the temperature measured by a Milletron Ratioscope.

Substrates used to date in this study have included tungsten of diameters 5, 13, 18, 33 38 and 43 microns and carbon of 36 microns in diameter. The carbon substrate was coated with a thin laver (approximately 1 μ) of pyrolytic graphite to minimize "light bulbing".

Primary deposition variables investigated have been deposition temperature, filament tension, substrate diameter and doping (impurity addition).

In addition to elongation measurements the filaments were subjected to a series of characterization experiments to define structural and microstructural phenomena. A Philips 400 analytical electron microscope was used to obtain electron micrographs and electron diffraction patterns from inner and outer portions of the filaments. Filaments subjected to electron microscopy were appropriately thinned (either from the outer surface to the inner surface or vice versa) using an ion micromilling instrument (Commonwealth Scientific Model III).

Experiments to measure the anelastic effect in the filaments were made using the previously described elongation measurement device while heating to various temperatures in a hydrogen, helium nitrogen and argon atmospheres.

Results and Discussion

The initial CVD experiments were designed to generate data to define a model for elongation in boron filaments. Initial emphasis was on using tungsten substrates of various sizes. The results of these experiments are shown in Figure 5. It was noted that with the large tungsten substrates, the elongation was linear with time; whereas the smaller the diameter of the substrate, the greater was the deviation from linearity.

The shape of these curves can be explained by the growth mechanism of boron on tungsten filament. During growth of the boron filaments, a boron sheath is formed around the tungsten substrate and simultaneously boron diffuses into the wire. It has been shown that different tungsten borides are formed in the core due to this boron diffusion (i.e. W_2B , δWB , W_2B_5 , WB_4). The rapid increase in length, for the smaller diameter tungsten substrates (up to 18μ) signified the boriding of the tungsten, whereby diffusion and reaction is such that all of the tungsten is depleted resulting in only tungsten borides in the core. This leads to a rather large volume change (approximately 30%) in the core region which is partially transmitted axially within the filament leading to the large elongations observed in filaments produced on small diameter tungsten substrates. This implies that the deposited boron must undergo considerable deformation to accommodate the large strains imparted to it. At least part of this deformation has been reported to be anelastic¹³ and is recoverable. Experiments were attempted to determine if the

filaments undergo plastic deformation under application of tensile forces at elevated temperature (approximately 1000°C) in an argon environment. All tests resulted in premature failure of the boron filaments without any evidence of plastic yielding as previously reported¹⁴.

The large diameter substrate samples shown in Figure 5 have a considerable amount unreacted tungsten remaining in the core which constrains the axial expansion. This leads to much lower elongations ($\approx 2\%$) but in general a more highly stressed (brittle) and weaker filament.

In general, elongation measurements on the tungsten substrates are meaningless when considering boron elongation alone. The expanding core dominates, distorting the results. Consequently, this makes it virtually impossible to define an elongation model per se. These are real data though, in a real system and when combined with anelastic effects in boron lead to a very complex internal stress situation in the filament.

To obtain the most meaningful data on boron elongation, the influence from the substrate must be minimized. This can be most closely accomplished by using a carbon substrate in which there is no diffusion and reaction in the core. Figure 6 shows some data taken using a carbon monofilament substrate (PG coated) under static conditions in a production reactor. Of interest here is the lower ultimate elongation than evident in the use with the tungsten substrate. This is expected since there is no volume expansion in the core. Also the higher deposition temperature samples elongate less and do not have the pronounced

dip in the curve that the 1200°C samples have. That the higher deposition temperatures produce filaments that elongate less is a fact already reported by Mehals and Diefendorf⁹. (The substrate used in earlier experiments and used in present production have a different thermal history which may influence any comparisons of data.)

The dip in the lower temperature samples occurs as a result of "light bulbing" or fracture of the carbon substrate. The more this occurs the less constraint the carbon core has on the elongating boron and the greater the recorded elongation. Typically the amount of elongation at 1250°C was approximately 3.5% in 30 seconds (filament diameter approximately 130 μ). In filament produced at lower temperature (1200°C) and which exhibited "light bulbing" elongation extended to above 4.5%. Use of deposition temperatures lower than 1200°C led to profuse "light bulbing" which tended to distort elongation measurements.

The carbon monofilament substrate used in these studies is routinely heat treated to above 2000°C prior to its usage. This leads to lower creep in the substrate than previously reported⁸. Applying a load of 12gm (15,000 psi) and heating the substrate to deposition temperature (1250°C) produced only 0.16% elongation. Substrate used in the previous studies exhibited approximately 3% creep with a tension of 30,000 psi applied at deposition temperature.

Figure 7 gives additional data obtained on carbon substrate. The upper curve is elongation data produced on substrate that had been prestressed (in the creep studies) and then used for deposition

of boron while subjected to a greater load (approximately 10 times). It can be seen that tension does appear to have an influence on the filament elongation (compare with the other curves). No noticeable "light bulbing" occurred in these runs. Since the substrate had been prestressed at deposition temperature prior to deposition and there was no obvious "light bulbing" then the greater elongation appears to be due to a tension effect on the elongating boron. This is contrary to previous observations^{8,9}.

Reactant gas history does not appear to have an influence on elongation. The curves in Figure 7 for plant BCl_3 and "depleted" BCl_3 are not significantly different. The primary difference between these reactant gases is that the plant BCl_3 contains diborane (approximately, 4%) whereas the "depleted" BCl_3 is of relatively high purity. The presence of this species in the reactant gas leads to a faster deposition rate than obtained in the pure BCl_3 .

Preliminary experiments to determine the influence of impurity additions indicate that there is no influence on elongation properties at all. Silicon from SiCl_4 and tungsten from WF_6 were added in small amounts (less than 2%) to the BCl_3 for co-deposition onto the carbon substrate. No significant difference in elongation was noted.

Elongation Model and Structural Studies

A mechanism for boron filament elongation has been suggested in earlier work by Mehalso¹⁵. The essence of this model is that each layer of boron is deposited with less than maximum density (i.e. many vacancies, partial icosahedra and individual atoms). With continued deposition there is a radial diffusion of boron atoms towards the core and vacancies toward the surface of the filament. The driving force for this diffusion is overall lowering of the energy of the system whereby the boron atoms are seeking a more ordered state (i.e. their lowest energy position). The diffusion of atoms into the interior portions of the boron mantle creates a net volume increase resulting in elongation and densification of the boron.

Atomic mobility is of course temperature dependent consequently the elongation behavior as a function of temperature can be rationalized from this phenomena. At the high deposition temperature, surface mobility of the boron atoms is sufficiently great that they can immediately migrate to their lowest energy position. This leads to little or no elongation in filament prepared at temperatures such that they are crystalline. On the other extreme at extremely low deposition temperature (for example 1000°C) surface mobility of the boron atoms is minimal resulting in their being trapped by deposition of subsequent layers of deposited boron. This leads to a less than theoretically maximum density in the deposited boron. With time, bulk diffusion of boron atoms inward towards the core and vacancies outward

towards the surface creates the observed elongation phenomenon and densification of the inner regions of the boron filament.

Evidence for this model is given by the fact that the greatest elongations are observed at the low deposition temperature decreasing in magnitude as the temperature is increased. Also, supporting evidence was given by DiCarlo¹⁶ who recently made measurements which allow one to suggest that there is a radial density variation whereby the surface layers are less than the average density in the bulk of the fiber.

Assuming the validity of the above model for elongation it was felt that one should be able to detect localized structural and/or microstructural variations between the first deposited boron layers and those on the surface. In order to test for this, longitudinally split boron filaments with the core removed were thinned (with an ion milling machine) from the outside in (to study the bulk material) and from the inside out (to study the surface layers). Figures 8 and 9 depict transmission electron micrographs along with electron diffraction patterns from the inner and outer portions of the filament. The primary difference observed between the inner and outer microstructure is a regularly spaced rod-like appearance approximately $1000 \text{ \AA}$ in diameter separated by less dense areas for the outer surface (Figure 3). The inner surface exhibited a rather uniform microstructure with no pronounced features.

The electron diffraction patterns from both regions were basically identical, being the normal pattern of diffuse halos at $4.3 \text{ \AA}$, $2.5 \text{ \AA}$, $1.7 \text{ \AA}$, $1.4 \text{ \AA}$ previously shown for "amorphous" boron. No difference in line width or spacings was noted for

the two regions nor was the presence of other crystalline phases detected as previously reported¹⁷. Figure 10 shows a region near the surface between two of the rod-like structures. What appears to be small dense areas or particles (up to 100 Å in diameter) are present in the material between the rods. Electron diffraction patterns of these areas did not yield any additional information other than reported above. If, in fact, these are microcrystallites of β -rhombohedral boron as has been previously suggested¹⁷ they do not appear to produce a characteristic diffraction pattern.

Anelastic Deformation

DiCarlo¹³ has recently suggested that all non-elastic deformation in boron fibers can be explained by an anelastic model. In other words deformation in the boron is recoverable with time and temperature upon removal of the deforming stress. This was demonstrated by applying a bending stress to a filament while heating and then allowing to cool. After cooling the filament retained the imposed curvature. Upon reapplication of heat, the filament returned to its original straight configuration.

To determine if anelasticity was, in fact, active axially in the filaments experiments were made to heat the filaments at 900°C while measuring elongation (contraction) as a function of time. Figure 11 depicts these results for boron filaments with four different histories.

There were:

1. standard production 4 mil boron on tungsten (B/W) recently made
2. standard production 4 mil boron on tungsten stored for 4 years
3. standard production 4.2 mil boron on carbon (B/C)
4. standard production 4.2 mil boron on carbon etched on 2.95 mils diameter.

The figure shows that all of the boron filaments contract upon application of heat (thermal expansion effects have been subtracted from the data). After 10 minutes the standard production B/W contracted by 1.7%. Standard production filament that had been stored for 4 years contracted somewhat less (1.4%)

indicating some recovery even at room temperature. Boron on carbon filament exhibited a contraction of approximately 1% after 10 minutes. Similar B/C filament that had been reduced in diameter by etching thereby redistributing residual stresses in the filament contracted only by approximately 0.3%. Etching the filament removed the compressive layer on the outer surface of the fiber letting the high tensile forces in the inner portion to relax. This in itself permits some contraction in the filament thereby lessening the contribution from the annealing.

The surprising factor in these data is the magnitude of the contraction. The magnitude of contraction from etching is 0.17%. This places the tungsten boride core, which is bonded to the boron sheath, in very high compression (a value of -163,000 psi has been calculated¹⁸ for the change in core stress). Consequently with the core constraining the boron it is difficult to see how the filament can contract further without debonding from the core.

In addition filament that had been annealed in the various atmospheres exhibited slight curviness and was extremely brittle. There was no evidence of crystallization. To determine if, in fact, there was some internal factor leading to the large contractions measured, filament that had been annealed was cleaved (i.e. scratched with diamond paste and then flexed to fracture the filament smoothly across the cross section. This presents an undisturbed surface such as would be obtained if the filament were polished). It was then examined in a scanning electron microscope. Figure 12 is a scanning electron micrograph of the cross section of a filament annealed in H₂. Large voids can be

detected around the core interface separating the core from the bulk boron.

To determine if this phenomenon was atmosphere sensitive a series of experiment was conducted to anneal filaments at 900°C for 10 minutes in various inert environments. Figure 13 shows the data obtained from these experiments. It can be seen that in H_2 , N_2 and Ar environments contraction ranged between 1.0 and 1.7% after 10 minutes. In the helium environment, however, the contraction was nearly 4% after 10 minutes. Filaments from each of these runs were cleaved and examined in the SEM. Figure 14 depicts representative cross sections from each of these environments. It can be observed that in every instance there are voids formed around the core and separation from the core. The most dramatic case is that of the filament annealed in He (Figure 14d). A very large void has formed in the center allowing separation of the tungsten boride core. The core is displaced to one side of the void and probably is buckling along the length of filament. The buckling of the core and hence lack of constraint on the bulk boron allows the large contraction observed ($\approx 4\%$). Figure 15 presents higher magnification micrographs of the core region showing various stages of void formation and core separation.

The presence of the voids around the core allows the boron sheath to be released from the constraining core which permits the large contraction observed. By this separation, the large residual tensile stresses in the boron sheath are allowed to relax plus any anelastic effect is allowed to recover leading

to the large contraction. It might be noted that there is not radial crack in any of the cross sections implying that the void formation relieved residual stresses in the filament.

The immediate question that is suggested by the above observations is where did the boron go which formed the voids. One possible explanation is further diffusion and reaction in the tungsten boride core. Measurements show, however, that there is no increase in diameter of the core as would be expected if further boride formation occurred. To determine if the core had any influence on the void formation a boron on carbon filament was annealed in Ar and subjected to SEM examination. In this type of filament there is no reaction in the core to form boride phases. Figure 16 shows the cross section of a boron on carbon filament annealed in Ar. Extensive void formation around the core region is obvious and is similar in magnitude to those observed in B/W filament. Carbide formation in the core is minimal as can be seen in the micrograph in Figure 17. The boron carbide diffusion layer (indicated by an arrow) is only slightly thicker (approximately 1μ total thickness) than in as produced B/C filament. This suggests that core influence on the void formation is minimal.

The above observations indicate that there is a net outward diffusion of boron atoms and an inward diffusion of vacancies which coalesce to form the internal voids. This type of phenomenon has been previously observed in boron filaments when fabricated into a titanium matrix composite at 1000°C for 10 minutes.^{19,20} It was also noted in one of these studies that the boron fiber

diameter does not change significantly²⁰. This is also the case in the present study. There is no detectable change in diameter as a result of the annealing step. Also no obvious surface change occurred in the filaments after annealing.

As a further experiment B/W filament was heated in vacuum (10^{-7} Torr) to approximately the same temperature as the annealing temperature (900°C) previously used. Figure 18 depicts this filament. It can be immediately seen that the filament has crystallized at this temperature in vacuum. However it can be noted that there is no pronounced void formation as was detected when the filament was annealed in an inert environment. This information, along with the core evidence, implies that the boron atoms are diffusing to the surface and being removed from there in some manner. This could occur for trace amounts of residual oxygen in the inert gases forming boron oxide at the surface. Since the annealing temperature is considerably higher than the melting point of B_2O_3 this species would be transported away in the vapor. The only other possibility for an explanation of where the boron is going would be a densification of the remainder of the boron sheath. Although this is obviously occurring to some extent (due to the net inward diffusion of vacancies) it is not felt that this is the primary mechanism.

Summary and Conclusions

Measurements have been made to determine elongation in boron filaments while they are being produced by chemical vapor deposition. To date the primary variable that appears to influence the elongation is deposition temperature which verifies earlier results. Small amounts of additives of silicon and tungsten have been incorporated into the filaments via the gas phase to determine if this approach would minimize the elongation. No positive results were obtained.

Structural and microstructural studies on the filaments using transmission electron microscopy and diffraction have shown an apparent difference in boron at the surface and that near the core. The surface material appears to grow in a column type structure approximately $1000 \text{ \AA}$ in diameter. The inner surface presents no significant structural features. Electron diffraction studies show consistently the characteristic broad halo pattern for "amorphous" boron with little apparent deviation. No evidence of microcrystals of one of the crystalline polymorphs has been obtained (as was reported in reference 17).

Very interesting and important results were obtained while annealing boron filaments in inert environments. The filaments were observed to contract by almost 2% after 10 minutes at 900°C . Examination of the cross section of these filaments show extensive void formation in the region adjacent to the core. The experiments suggest that boron is being removed by a surface reaction of some

sort but at the present time must remain unspecified. The large amount of recovery during annealing suggests that anelasticity is active axially in the filaments.

References

1. F. Wawner, "Boron Filaments", Modern Composite Materials, ed. by Broutman and Krock, Addison and Wesley, 1967, p. 244.
2. H. Rogers, "Research on Improved High Modulus, High Strength Filaments and Composites Therof", AFML-TDR-65-319, Sept. 1965.
3. R. Witucki, "High Modulus High Strength Filaments and Composites", Technical Report AFML-TR-66-187, May 1967.
4. K. Faughnan, "Longitudinal Residual Stresses in Boron Filaments", 29th Annual Tech. Cong., Reinforced Plastics/Composites Institute, 1974.
5. G. Layden, "Fracture Behavior of Boron Filaments", J. Mat. Science 8, 1581 (1973).
6. H. DeBolt, V. Krukonis, J. McKee, R. Prescott and F. Wawner, "Development and Demonstration of a Low Cost Boron Filament Formation Process", AFML-TR-72-271, 1972.
7. C. Talley, J. Appl. Phys., 30, 114, 1959.
8. H. DeBolt, et al., "Lower Cost High Strength Boron Filament", AFML-TR-70-287, June 1971.
9. R. Diefendorf and R. Mehalso, "Vapor Deposition of High Strength-High Modulus Boron on a Mono-Filament Substrate", 3rd Intl. Conf. on Chemical Vapor Deposition, Salt Lake City, Utah, Apr. 1972, p. 552.
10. F. Tavazde, "Low Temperature Internal Friction Peaks in Boron Fibers", Mekhanizmy Vnutrennego Treniya v poluprovodnikurykh I. Met. Mat., AKH 9103, 1972, p. 24.
11. G. Gunyaev, et al., "Effect of Temperature on the Mechanical Properties of Boron Fibers", Mekhanika Polimerou, No. 2, Mar.-Apr., 1971, p. 329.
12. F. Tavazde and G. Tsagaireshuili, "Crystalline Boron", Soviet Science Review, No. 1972, p. 357.
13. J. DiCarlo, NASA Technical Memorandum, NASA TM X-71907 May 1976 and NASA TM X-71710 March 1977.
14. E. Ellison and D. Boone, "Some Mechanical Properties of Boron-Tungsten Boride Filaments", J. Less-Common Metals, 13, 103 (1967).
15. R. Mehalso, Ph.D. Dissertation, Rensselaer Polytechnic Inst. Troy, NY, Nov. 1973.

16. J. DiCarlo, "Mechanical and Physical Properties of Modern Boron Fibers", NASA TM73882, 1978
17. P. Lindquest, M. Hammond and R. Bragg, "Crystal Structure of Vapor-Deposited Boron Filaments", J. Appl. Physics, 39 5152 (1968).
18. D. R. Behrendt, "Longitudinal Residual Stresses in Boron Fibers", NASA TM X-73402, 1977.
19. L. Blackburn, J. Herzog, W. Meyerer, J. Snide, W. Stuhrke, and A. Brisbane, "MAMS Internal Research on Metal Matrix Composites", MAM-TM-66-3 (1966) from A. Metcalfe, "Physical Chemical Aspects of the Interface", in Interfaces in Metal Matrix Composites, Volume 1, Ed. by L. Broutman and R. Krock, Academic Press, New York, 1974, pg. 65.
20. J. Thebault, R. Pailler, G. Bontemps-Moley, M. Bourdeau and R. Naslain, "Chemical Compatibility in Boron Fiber-Titanium Composite Materials", J. Less-Common Metals, 47, 221 (1976).



Figure 1
Typical Fracture Surface for a "Crack Tip" Mode of Failure

THIS PAGE IS BEST QUALITY PRACTICABLE
FROM COPY FURNISHED TO DDC

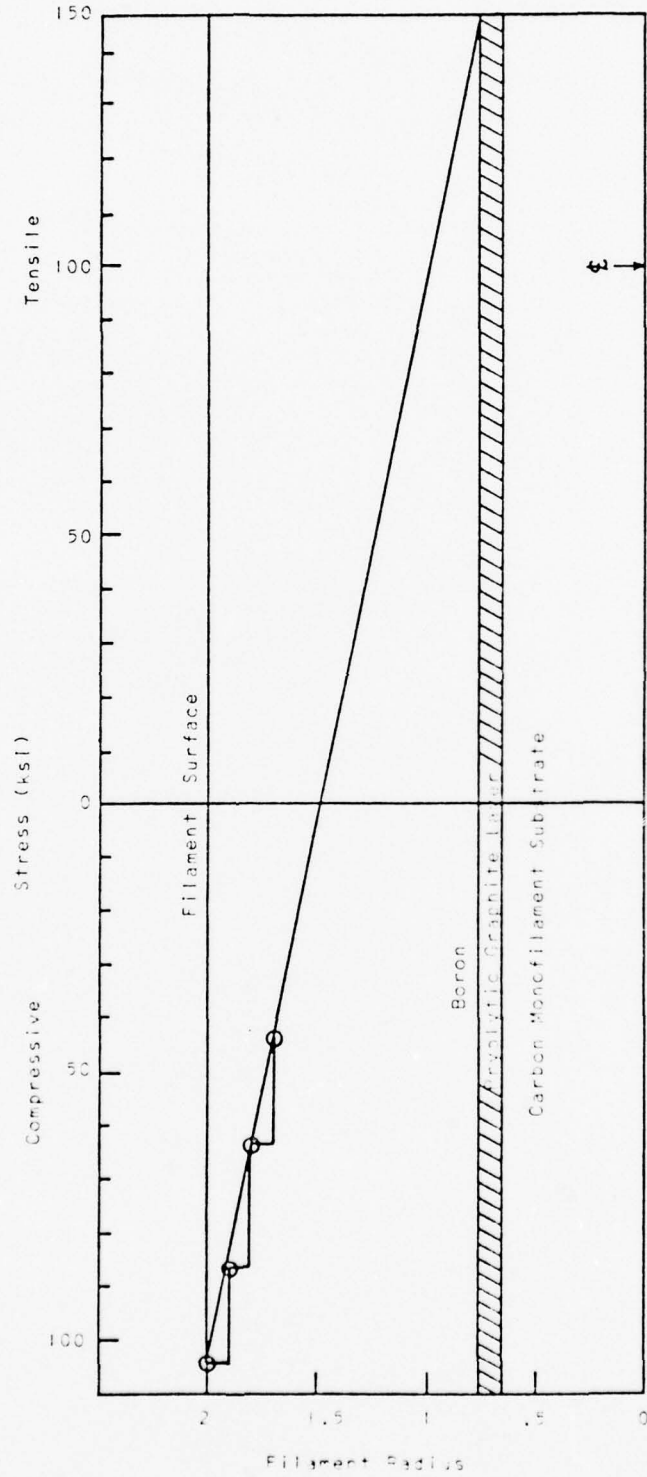


Figure 2
Schematic Diagram of Residual Stress
Configuration in Boron Filament

THIS PAGE IS BEST QUALITY PRACTICABLE
FROM COPY FURNISHED TO DDC

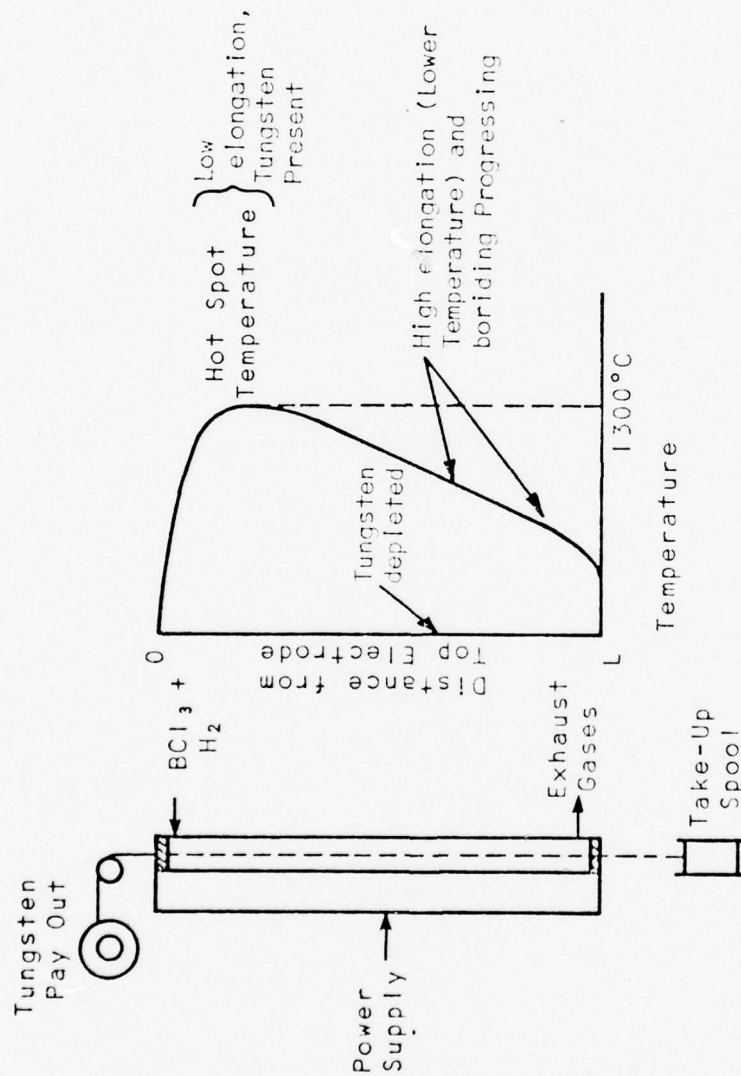


Figure 3

Temperature Profile Within Production Reactor

THIS PAGE IS BEST QUALITY PRACTICABLE
FROM COPY FURNISHED TO DDC

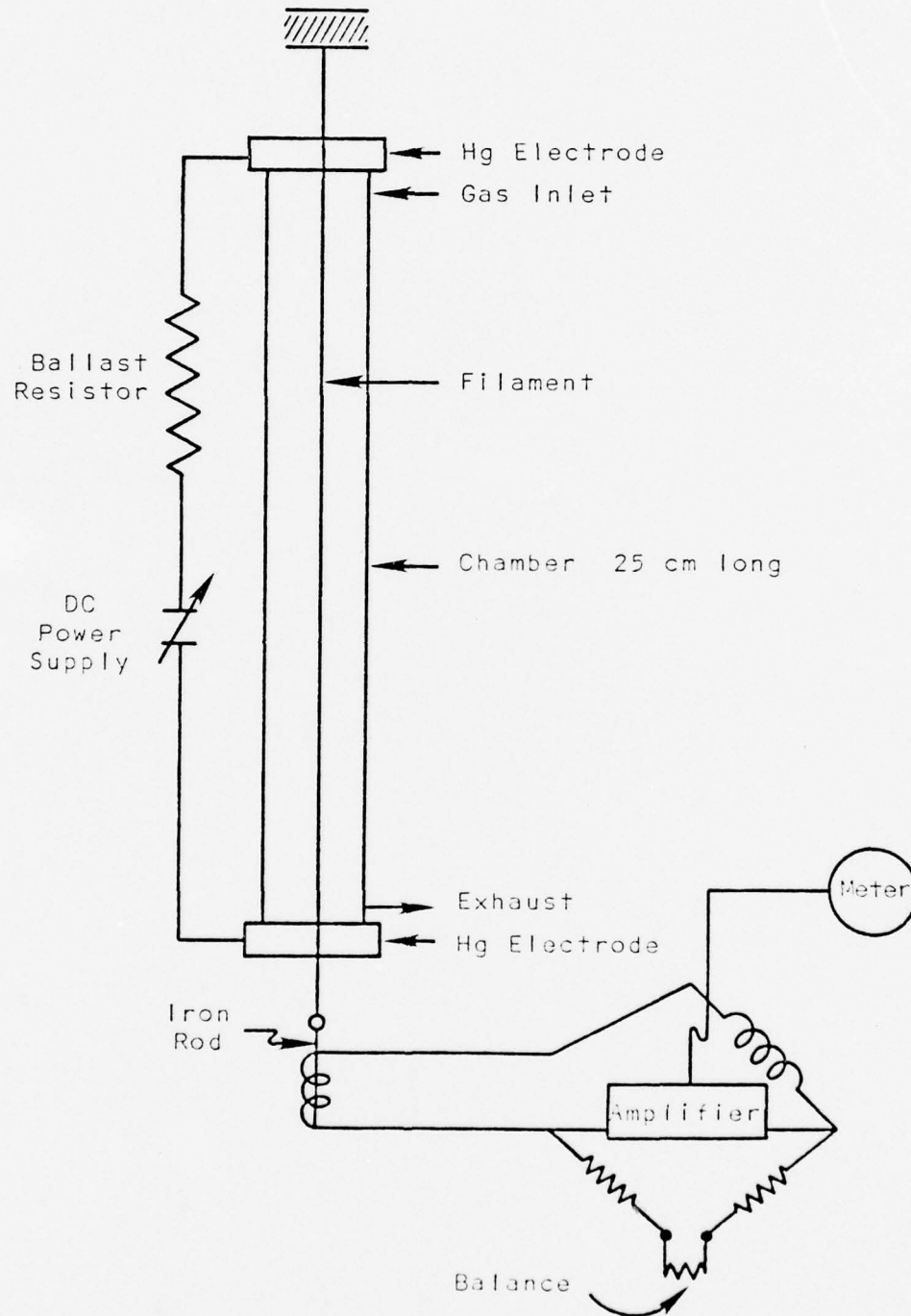


Figure 4

Schematic of Apparatus for Static Elongation Measurements

THIS PAGE IS BEST QUALITY PRACTICABLE
FROM COPY FURNISHED TO DDC

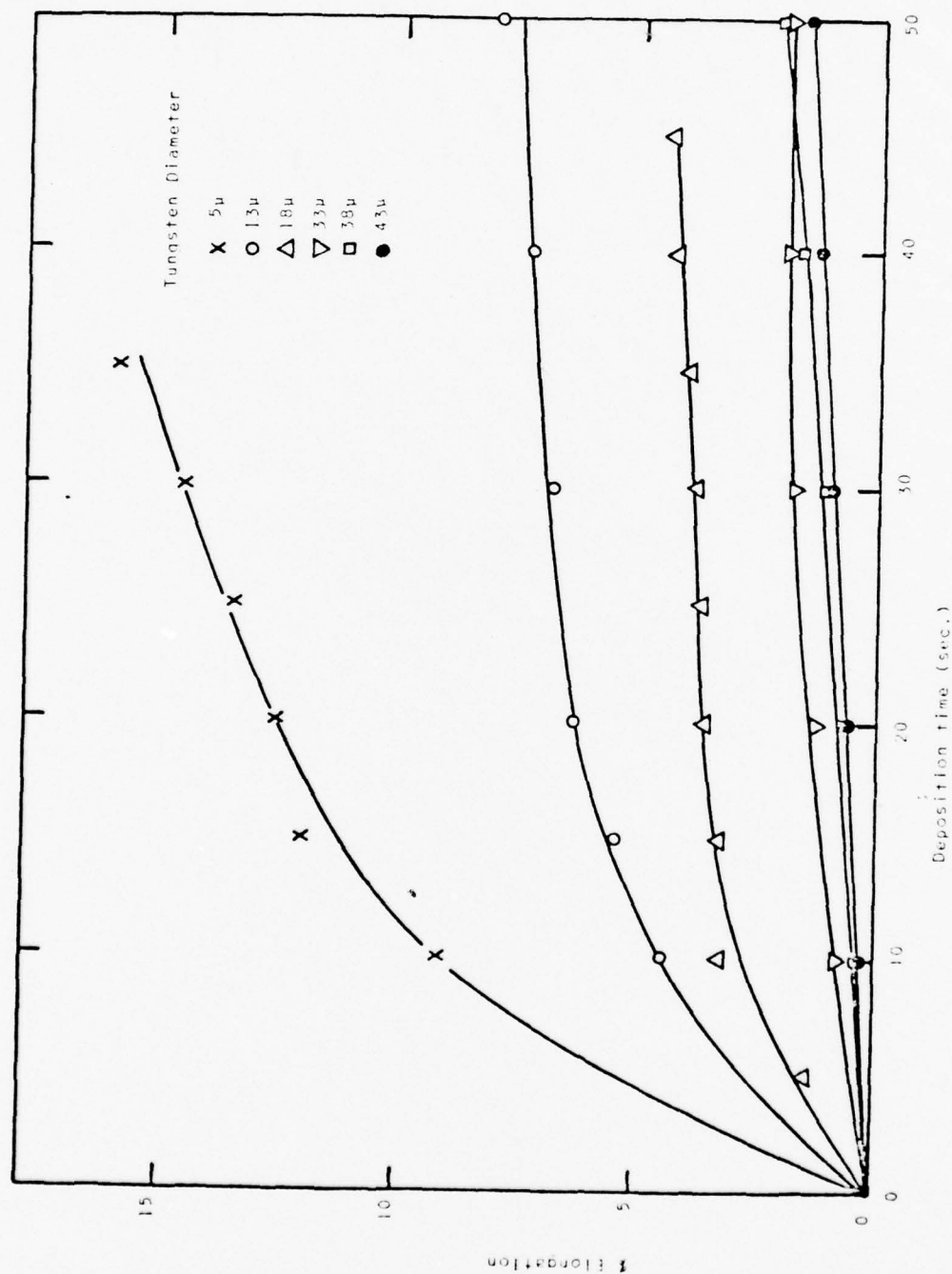


Figure 5

Plot of Elongation vs Deposition Time for Different Tungsten Substrate Sizes

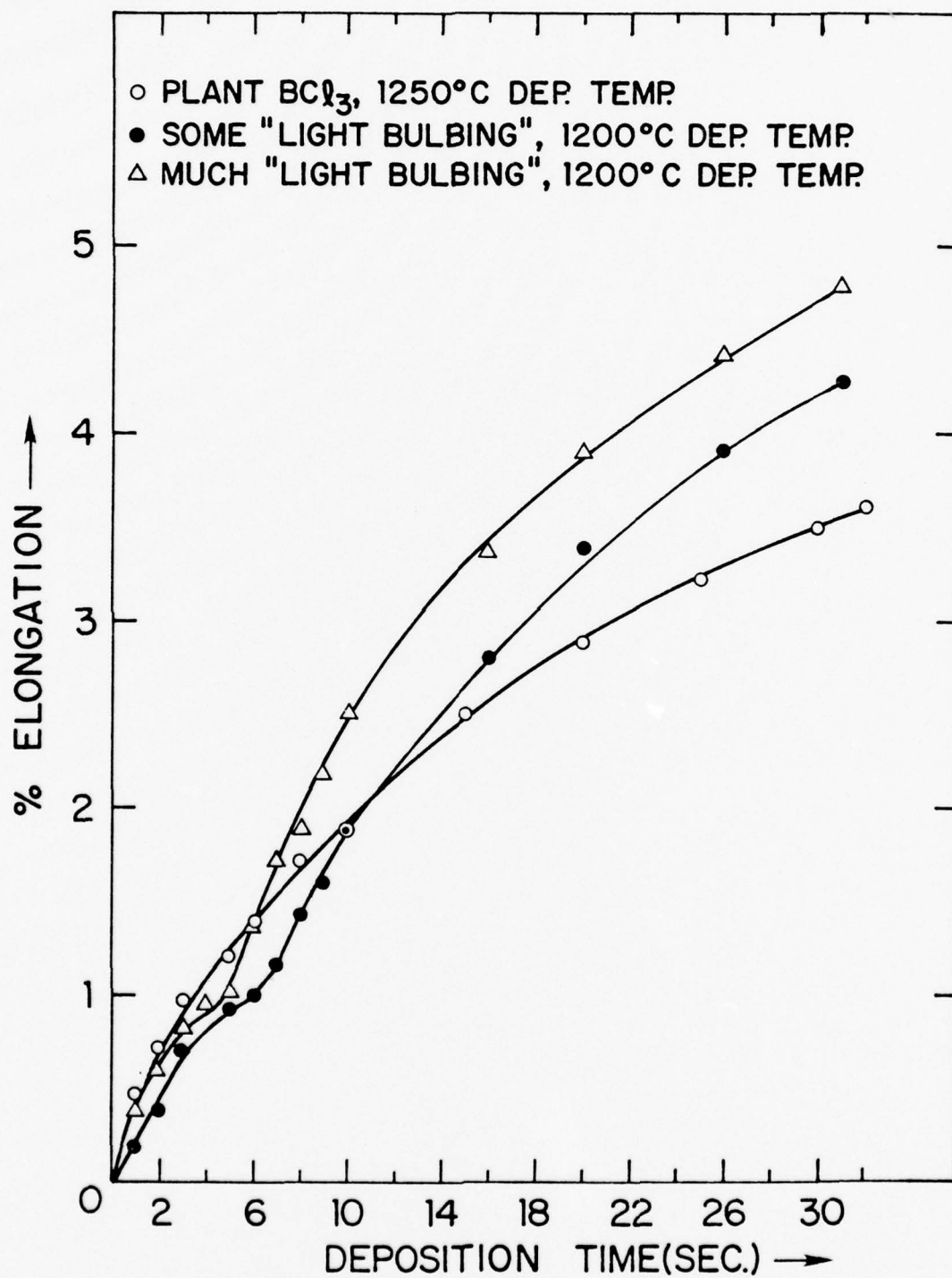


Figure 6

Plot of Elongation vs Deposition Time for Carbon Substrate Filament

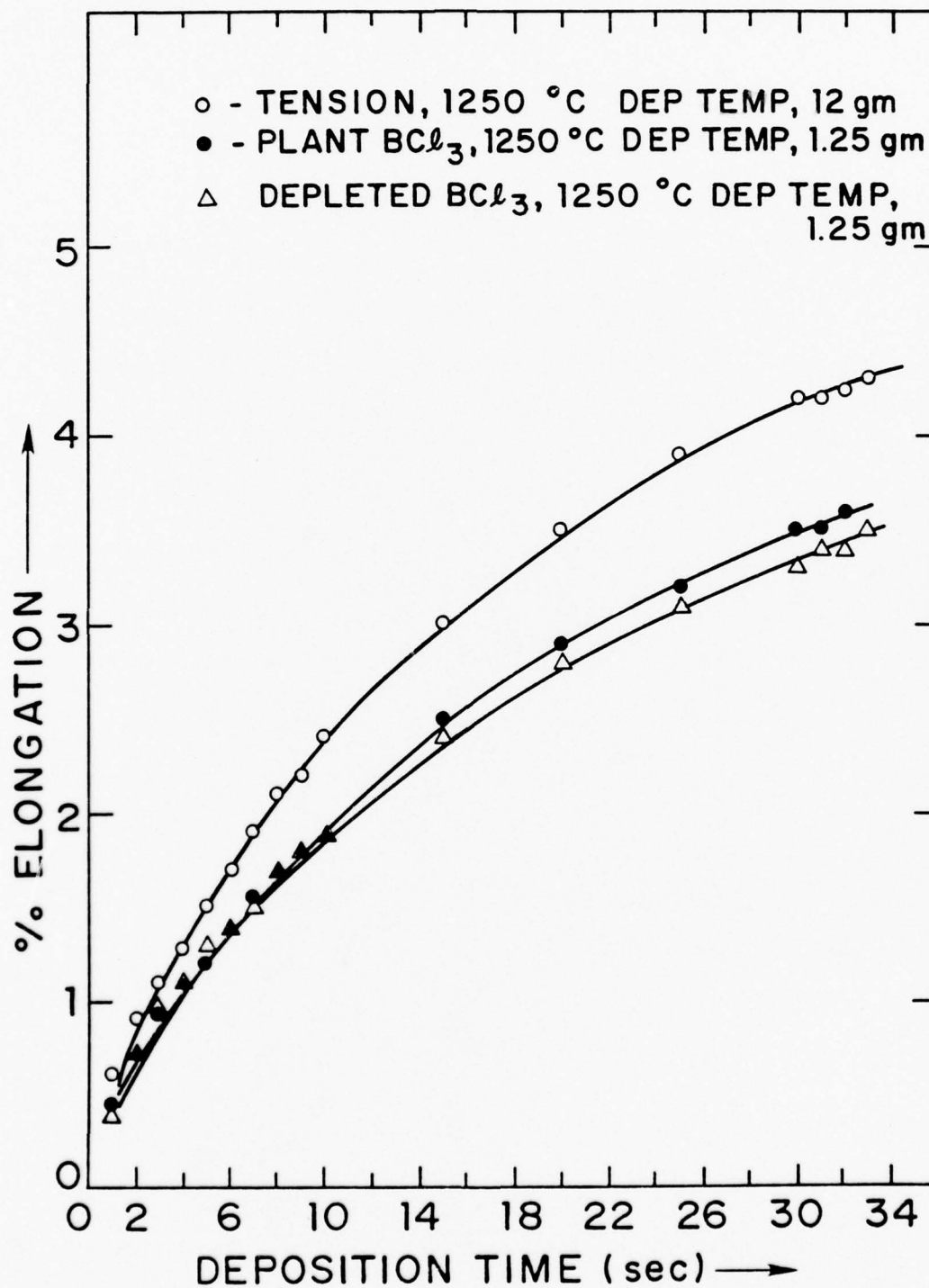


Figure 7

Plot of Elongation vs Deposition Time for Carbon Substrate Filament



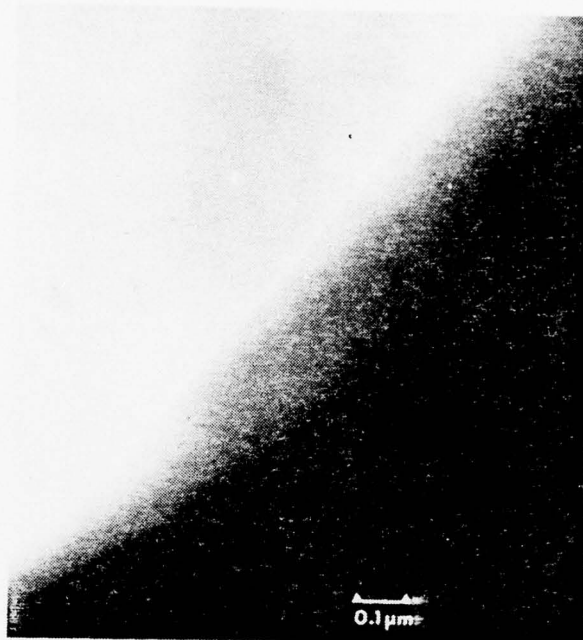
A



B

Figure 8

Transmission Electron Micrographs of Boron Filament (outside of filament)



A



B

Figure 9
Transmission Electron Micrographs of Boron Filament (inside of filament)



Figure 10
Transmission Electron Micrographs of Boron Filament
(outside of filament)

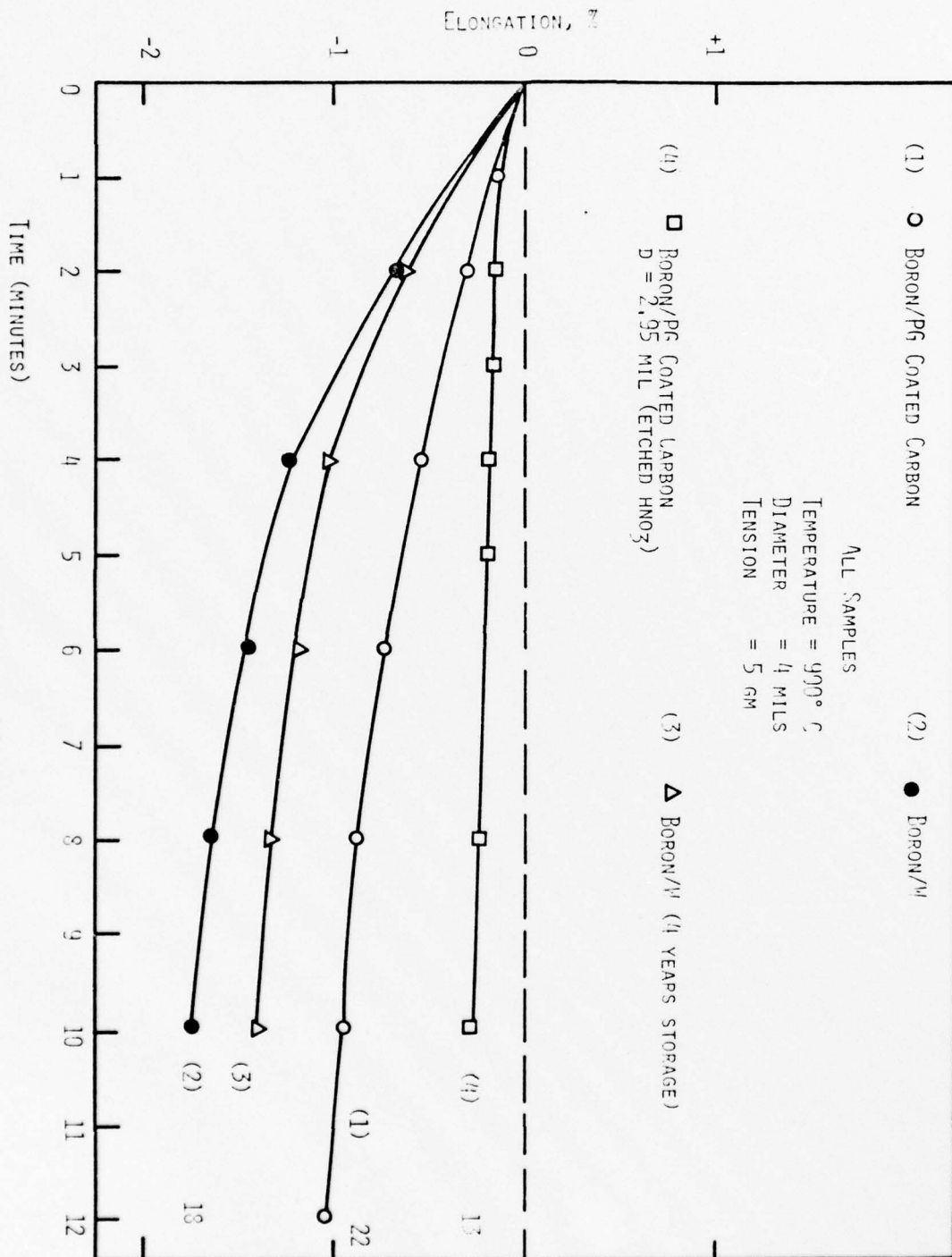
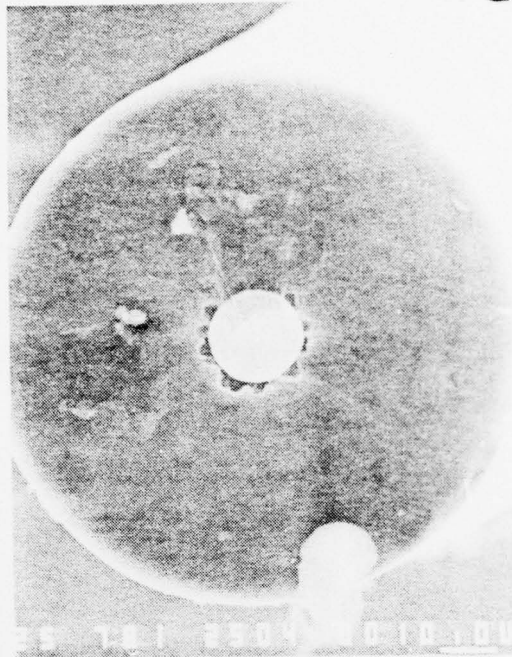
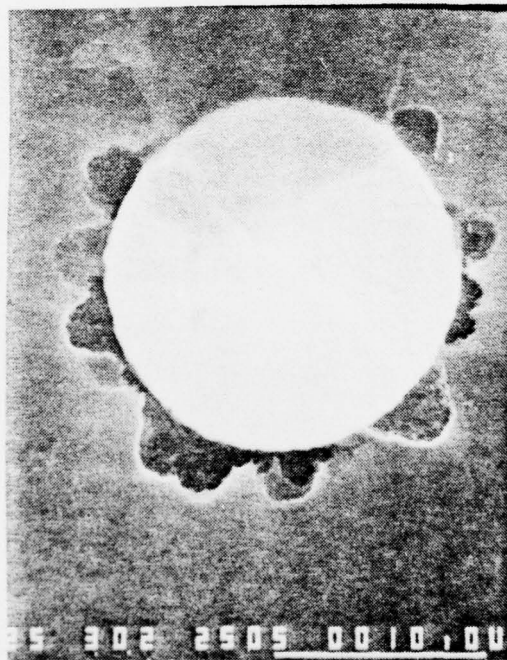


Figure 11

Effect of Heat Treating Boron Filament



A



B

Figure 12

SEM of Cross Section of Annealed Filament Showing Voids

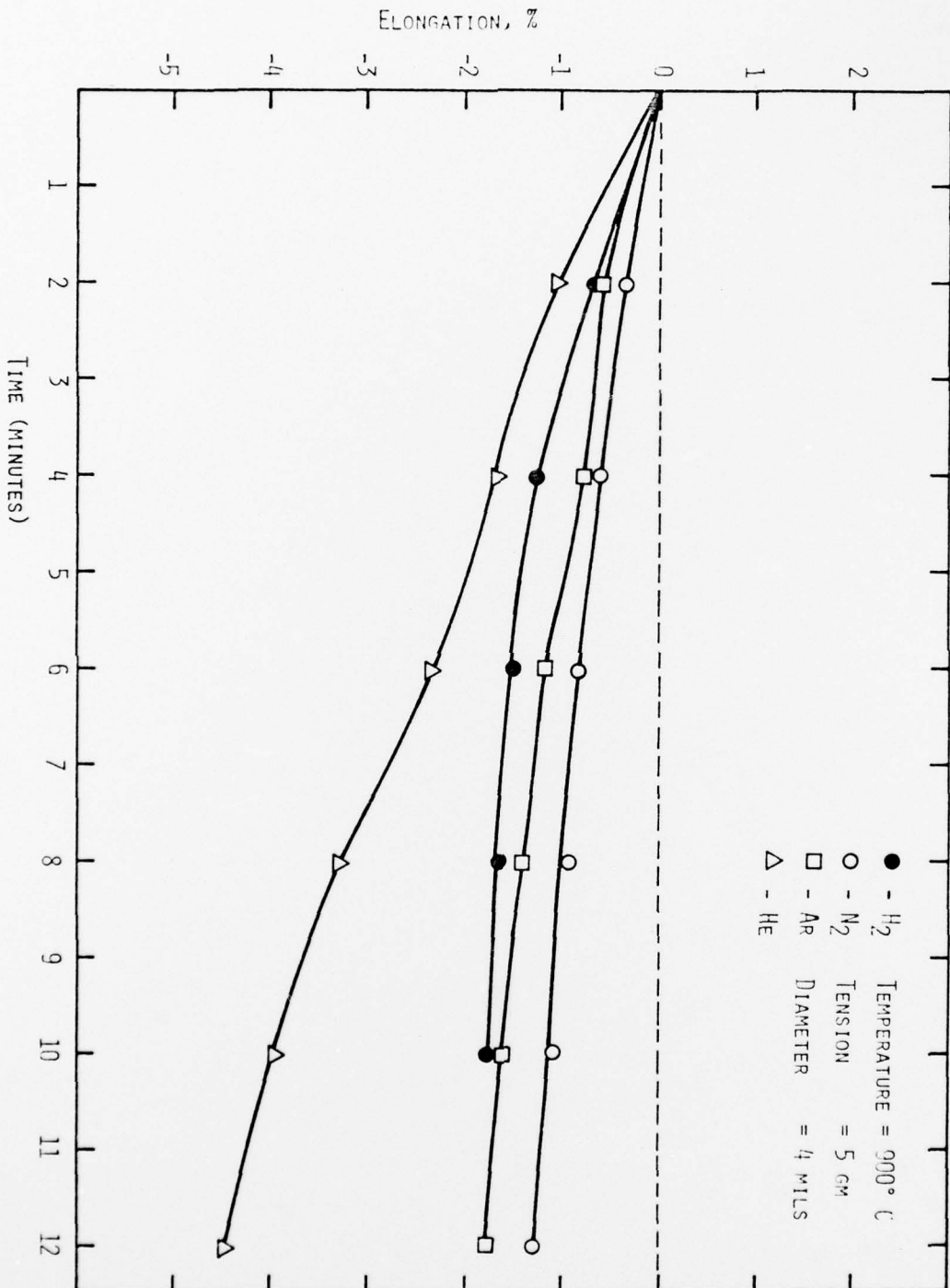
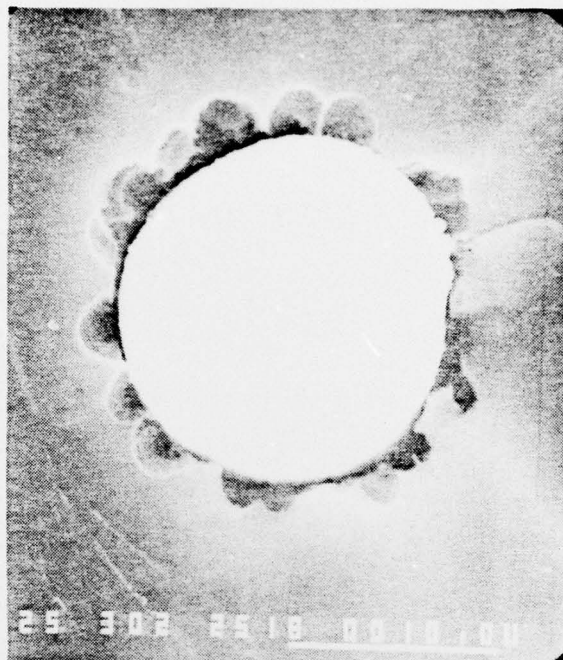


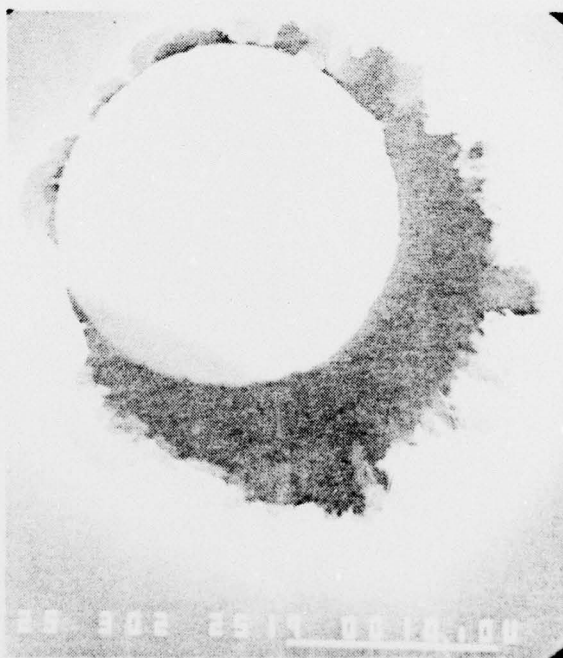
Figure 13
Effect of Heat Treating Boron Filament in Various Environments



Figure 14
SEM of Cross Sections of Boron Fibers
Annealed in Various Environment

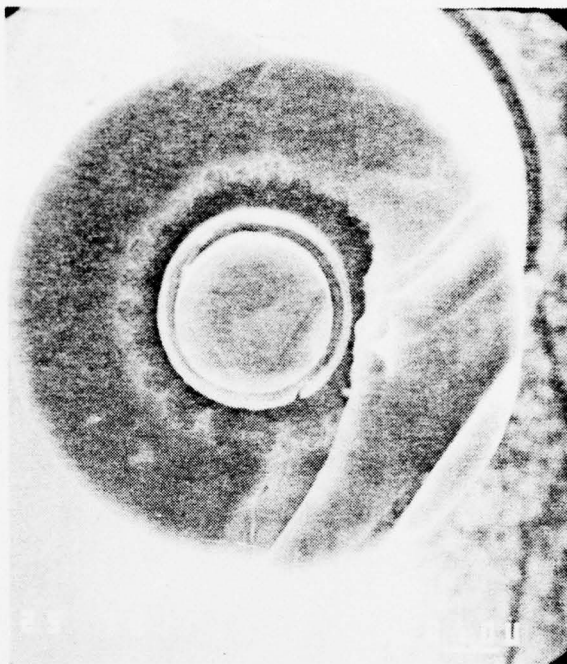


A



B

Figure 15
SEM of Cross Sections of Boron Fibers
Showing Void Formation (Annealed in Ar)



A



B

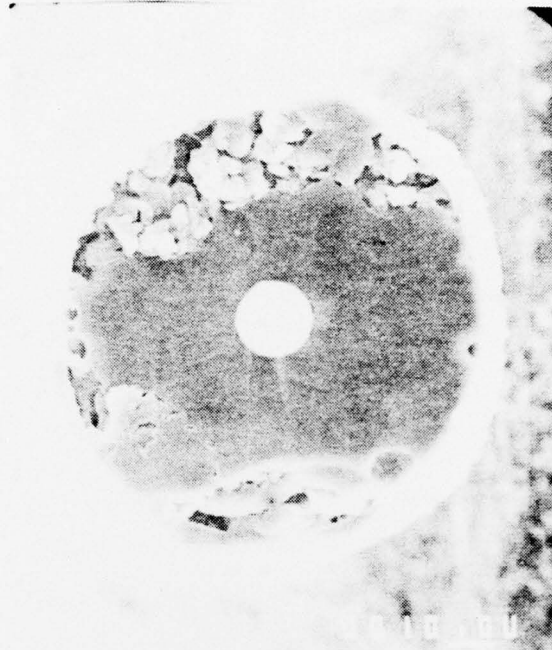
Figure 16

SEM of Cross Section of Boron on Carbon Fiber Annealed in Ar



Figure 17

SEM of Interfacial Region in Annealed Boron
on Carbon Filament



A



B

Figure 18
SEM of Filament Annealed in Vacuum

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER No. 1	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Investigation of Elongation and its Relationship to Residual Stresses in Boron Filaments		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Franklin E. Wawner, Jr.		8. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0694
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Materials Science, SEAS University of Virginia, Thornton Hall Charlottesville, Virginia 22901		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Office of Naval Research Research Arlington, Virginia 22217		12. REPORT DATE July, 1978
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Distribution of this document is unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Measurements have been made to determine elongation in boron filaments while they are being produced by chemical vapor deposition. To date the primary variable that appears to influence the elongation is deposition temperature which verifies earlier results. Small amounts of additives of silicon and tungsten have been incorporated into the filaments via the gas phase to determine if this approach would minimize the elongation. No		

positive results were obtained.

Structural and microstructural studies on the filaments using transmission electron microscopy and diffraction have shown an apparent difference in boron at the surface and that near the core. The surface material appears to grow in a column type structure approximately 1000 Å in diameter. The inner surface presents no significant structural features. Electron diffraction studies show consistently the characteristic broad halo pattern for "amorphous" boron with little apparent deviation. No evidence of microcrystals of one of the crystalline polymorphs has been obtained. (as was reported in reference 17).

Very interesting and important results were obtained while annealing boron filaments in inert environments. The filaments were observed to contract by almost 2% after 10 minutes at 900°C. Examination of the cross section of these filaments show extensive void formation in the region adjacent to the core. The experiments suggest that boron is being removed by a surface reaction, of some sort but at the present time must remain unspecified. The large amount of recovery during annealing suggests that anelasticity is active axially in the filaments.

DISTRIBUTION LIST

Copies

1 - 56	See Basic Distribution List
57 - 90	See Supplementary Distribution List
91	Johns Hopkins University 34th and Charles Streets Baltimore, MD 21218 Attn: C. R. Main
92 - 120	F. E. Wawner, Jr.
121	K. R. Lawless
122	I. A. Fischer Office of Sponsored Programs
123 - 124	E. H. Pancake Clark Hall
125	RLES Files

9328:hfc

BASIC DISTRIBUTION LIST

Technical and Summary Reports

April 1978

<u>Organization</u>	<u>Copies</u>	<u>Organization</u>	<u>Copies</u>
Defense Documentation Center Cameron Station Alexandria, VA 22314	12	Naval Air Propulsion Test Center Trenton, NJ 08628 ATTN: Library	1
Office of Naval Research Department of the Navy 800 N. Quincy Street Arlington, VA 22217		Naval Construction Battalion Civil Engineering Laboratory Port Hueneme, CA 93043 ATTN: Materials Division	1
ATTN: Code 471	1	Naval Electronics Laboratory San Diego, CA 92152 ATTN: Electron Materials Sciences Division	1
Code 102	1		
Code 470	1		
Commanding Officer Office of Naval Research Branch Office Building 114, Section D 666 Summer Street Boston, MA 02210	1	Naval Missile Center Materials Consultant Code 3312-1 Point Mugu, CA 92041	1
Commanding Officer Office of Naval Research Branch Office 536 South Clark Street Chicago, IL 60605	1	Commanding Officer Naval Surface Weapons Center White Oak Laboratory Silver Spring, MD 20910 ATTN: Library	1
Office of Naval Research San Francisco Area Office 760 Market Street, Room 447 San Francisco, CA 94102	1	David W. Taylor Naval Ship Research and Development Center Materials Department Annapolis, MD 21402	1
Naval Research Laboratory Washington, DC 20375		Naval Undersea Center San Diego, CA 92132 ATTN: Library	1
ATTN: Codes 6000	1	Naval Underwater System Center Newport, RI 02840 ATTN: Library	1
6100	1		
6300	1		
6400	1	Naval Weapons Center China Lake, CA 93555 ATTN: Library	1
2627	1		
Naval Air Development Center Code 302 Warminster, PA 18964 ATTN: Mr. F. S. Williams	1	Naval Postgraduate School Monterey, CA 93940 ATTN: Mechanical Engineering Department	1

BASIC DISTRIBUTION LIST (cont'd)

<u>Organization</u>	<u>Copies</u>	<u>Organization</u>	<u>Copies</u>
Naval Air Systems Command Washington, DC 20360 ATTN: Codes 52031 52032	1	NASA Headquarters Washington, DC 20546 ATTN: Code RRM	1
Naval Sea System Command Washington, DC 20362 ATTN: Code 035	1	NASA Lewis Research Center 21000 Brookpark Road Cleveland, OH 44135 ATTN: Library	1
Naval Facilities Engineering Command Alexandria, VA 22331 ATTN: Code 03	1	National Bureau of Standards Washington, DC 20234 ATTN: Metallurgy Division Inorganic Materials Div.	1 1
Scientific Advisor Commandant of the Marine Corps Washington, DC 20380 ATTN: Code AX	1	Director Applied Physics Laboratory University of Washington 1013 Northeast Fortthieth Street Seattle, WA 98105	1
Naval Ship Engineering Center Department of the Navy Washington, DC 20360 ATTN: Code 6101	1	Defense Metals and Ceramics Information Center Battelle Memorial Institute 505 King Avenue Columbus, OH 43201	1
Army Research Office P.O. Box 12211 Triangle Park, NC 27709 ATTN: Metallurgy & Ceramics Program	1	Metals and Ceramics Division Oak Ridge National Laboratory P.O. Box X Oak Ridge, TN 37380	1
Army Materials and Mechanics Research Center Watertown, MA 02172 ATTN: Research Programs Office	1	Los Alamos Scientific Laboratory P.O. Box 1663 Los Alamos, NM 87544 ATTN: Report Librarian	1
Air Force Office of Scientific Research Bldg. 410 Bolling Air Force Base Washington, DC 20332 ATTN: Chemical Science Directorate Electronics & Solid State Sciences Directorate	1 1	Argonne National Laboratory Metallurgy Division P.O. Box 229 Lemont, IL 60439	1
Air Force Materials Laboratory Wright-Patterson AFB Dayton, OH 45433	1	Brookhaven National Laboratory Technical Information Division Upton, Long Island New York 11973 ATTN: Research Library	1
Library Building 50, Rm 134 Lawrence Radiation Laboratory Berkeley, CA	1	Office of Naval Research Branch Office 1030 East Green Street Pasadena, CA 91106	1

M
January 1978

SUPPLEMENTARY DISTRIBUTION LIST

Technical and Summary Reports

Professor G. S. Ansell
Rensselaer Polytechnic Institute
Dept. of Metallurgical Engineering
Troy, New York 12181

Professor H. K. Birnbaum
University of Illinois
Department of Metallurgy
Urbana, Illinois 61801

Dr. E. M. Breinan
United Aircraft Corporation
United Aircraft Res. Laboratories
East Hartford, Connecticut 06108

Professor H. D. Brody
University of Pittsburgh
School of Engineering
Pittsburgh, Pennsylvania 14213

Mr. P. J. Cacciatore
General Dynamics
Electric Boat Division
Eastern Point Road
Groton, Connecticut 06340

Professor J. B. Cohen
Northwestern University
Dept. of Material Sciences
Evanston, Illinois 60201

Professor M. Cohen
Massachusetts Institute of Technology
Department of Metallurgy
Cambridge, Massachusetts 02139

Professor Thomas W. Eagar
Massachusetts Institute of Technology
Department of Materials
Science and Engineering
Cambridge, Massachusetts 02139

Professor B. C. Giessen
Northeastern University
Department of Chemistry
Boston, Massachusetts 02115

Dr. G. T. Hahn
Battelle Memorial Institute
Department of Metallurgy
505 King Avenue
Columbus, Ohio 43201

Professor D. G. Howden
Ohio State University
Dept. of Welding Engineering
190 West 19th Avenue
Columbus, Ohio 43210

Dr. C. S. Kortovich
TRW, Inc.
23555 Euclid Avenue
Cleveland, Ohio 44117

Professor D. A. Koss
Michigan Technological University
College of Engineering
Houghton, Michigan 49931

Professor A. Lawley
Drexel University
Dept. of Metallurgical Engineering
Philadelphia, Pennsylvania 19104

Professor Harris Marcus
The University of Texas at Austin
College of Engineering
Austin, Texas 78712

Dr. H. Margolin
Polytechnic Institute of New York
333 Jay Street
Brooklyn, New York 11201

Professor K. Masubuchi
Massachusetts Institute of Technology
Department of Ocean Engineering
Cambridge, Massachusetts 02139

Dr. H. I. McHenry
National Bureau of Standards
Institute for Basic Standards
Boulder, Colorado 80302

SUPPLEMENTARY DISTRIBUTION LIST (Cont'd)

Professor J. W. Morris, Jr.
University of California
College of Engineering
Berkeley, California 94720

Professor Ono
University of California
Materials Department
Los Angeles, California 90024

Dr. Neil E. Paton
Rockwell International
Science Center
1049 Camino Dos Rios
P.O. Box 1085
Thousand Oaks, California 91360

Mr. A. Pollack
Naval Ships Research & Development
Center
Annapolis, Maryland 21402

Dr. Karl M. Prewé
United Technologies Laboratories
United Technologies Corporation
East Hartford, Connecticut 06108

Professor W. F. Savage
Rensselaer Polytechnic Institute
School of Engineering
Troy, New York 12181

Professor O. D. Sherby
Stanford University
Materials Sciences Division
Stanford, California 94300

Professor J. Shyne
Stanford University
Materials Sciences Division
Stanford, California 94300

Dr. R. P. Simpson
Westinghouse Electric Corporation
Research & Development Center
Pittsburgh, Pennsylvania 15235

Dr. E. A. Starke, Jr.
Georgia Institute of Technology
School of Chemical Engineering
Atlanta, Georgia 30332

Professor David Turnbull
Harvard University
Division of Engineering and
Applied Physics
Cambridge, Massachusetts 02139

Dr. F. E. Wawner
University of Virginia
School of Engineering and Applied
Science
Charlottesville, Virginia 22901

Dr. C. R. Whitsett
McDonnell Douglas Research
McDonnell Douglas Corporation
Saint Louis, Missouri 63166

Dr. J. C. Williams
Carnegie-Mellon University
Department of Metallurgy and
Materials Sciences
Schenley Park
Pittsburgh, Pennsylvania 15213

Professor H. G. F. Wilsdorf
University of Virginia
Charlottesville, Virginia 22903

Dr. M. A. Wright
University of Tennessee
Space Institute
Tullahoma, Tennessee 37388