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R92-918246-4

INTERFACIAL STUDIES OF REFRACTORY GLASS-CERAMIC MATRIX/ADVANCED SiC FIBER REINFORCED COMPOSITES

Prepared by
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ANNUAL REPORT

Contract N00014-87-C-0699

for

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

April 30, 1992

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East Hartford, Connecticut 06108

REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
30 April 1992

3. REPORT TYPE AND DATES COVERED
Annual Report 2/1/91 - 2/1/92

4. TITLE AND SUBTITLE
INTERFACIAL STUDIES OF REFRACTORY GLASS-CERAMIC MATRIX/ADVANCED SiC FIBER REINFORCED COMPOSITES

5. FUNDING NUMBERS
F33615-89-C-5628

6. AUTHOR(S)
J. J. Brennan

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
United Technologies Research Center
East Hartford, CT 06108

8. PERFORMING ORGANIZATION REPORT NUMBER
R92-918246-4

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
Arlington, VA 22209

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Unlimited Distribution

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The main objective of this program is to characterize the chemistry and structure of new advanced small diameter silicon based fibers and how these factors influence the nature of the fiber/matrix interface in refractory glass-ceramic matrix composites. It is the nature of this interface that then determines to a great degree the composite thermal, environmental, and mechanical properties. The fibers under investigation during the second year of this program included the new experimental polymer derived crystalline SiC fibers from Dow Corning Corp., the Si-N-C-O "Black" fibers from Textron Specialty Materials, as well as the new low oxygen radiation cured Nicalon SiC type fibers from Nippon Carbon Co. Since the availability of all of these fibers was extremely limited, emphasis was placed on the mechanical, chemical, and microstructural characterization of the fibers through tensile testing, SEM of fiber fracture characteristics, scanning Auger depth profiling of fiber surfaces, and TEM of fiber thin sections, as well as their fracture behavior, bonding characteristics, and interfacial compatibility with various glass-ceramic matrix materials. Results of these analyses are discussed.

14. SUBJECT TERMS
Crystalline SiC fibers, Textron "Black" fibers, low oxygen Nicalon fibers, SiC fiber/glass-ceramic matrix interfaces, TEM fiber analyses

15. NUMBER OF PAGES
72

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT
Unclassified

18. SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

19. SECURITY CLASSIFICATION OF ABSTRACT
Unclassified

20. LIMITATION OF ABSTRACT
SAR

UNITED TECHNOLOGIES RESEARCH CENTER
East Hartford, Connecticut 06108

R92-918246-4

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Interfacial Studies of Refractory Glass-Ceramic Matrix/ Advanced SiC Fiber Reinforced Composites

ANNUAL REPORT

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DATE 4/30/92

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INTERFACIAL STUDIES OF REFRACTORY GLASS-CERAMIC MATRIX/ADVANCED FIBER REINFORCED COMPOSITES

SUMMARY

The main objective of this program is to characterize the chemistry and structure of new advanced small diameter silicon based fibers and how these factors influence the nature of the fiber/matrix interface in refractory glass-ceramic matrix composites. It is the nature of this interface that then determines to a great degree the composite thermal, environmental, and mechanical properties. The fibers under investigation during the second year of this program included the new experimental polymer derived crystalline SiC fibers from Dow Corning Corp., the Si-N-C-O "Black" fibers from Textron Specialty Materials, as well as the new low oxygen radiation cured Nicalon SiC type fibers from Nippon Carbon Co. Since the availability of all of these fibers was extremely limited, emphasis was placed on the mechanical, chemical, and microstructural characterization of the fibers through tensile testing, SEM of fiber fracture characteristics, scanning Auger depth profiling of fiber surfaces, and TEM of fiber thin sections, as well as their fracture behavior, bonding characteristics, and interfacial compatibility with various glass-ceramic matrix materials.

In regard to the Dow Corning crystalline SiC fibers, no new fibers were received by UTRC during the past year, reflective of the difficulty that Dow Corning has had in scaling up the processing of these fibers to the multifilament tow stage. Of the four small lots of fiber evaluated at UTRC during the past year, all of them exhibited differences in chemistry and structure to one degree or another. From TEM and scanning Auger analyses, certain regions of all of the fiber lots were found to be relatively close to stoichiometric SiC in overall chemistry, although other regions (especially the center of the fibers) contained areas that consisted of mixtures of β-SiC grains and pockets of relatively pure graphite. Three of the fiber lots that were gold or brown in color exhibited a surface region that contained boron and nitrogen, the color of which became much darker when the surface region had been sputtered away. The other fiber lot exhibited a very carbon rich surface.

Boron was found to be present in all but the near-surface region of all the Dow Corning fibers in small quantities (2-3 at%), and, from PEELS analysis, may exist in discrete boride inclusions. Boron is evidently incorporated into the starting polymer precursor to act as a sintering aide and/or a grain growth inhibitor. The β-SiC grain size of the fibers, as determined from TEM as well as SEM

analysis, varied from an average of ~150nm for some fibers to a more prevalent dual grain size morphology that consisted of rather large grains (300-400nm) near the fiber surface to medium sized (100-150nm) grains surrounded by the extremely fine grained (<10nm) graphitic structure near the center of the fibers. This graphitic phase was identified from HRTEM thin foil analysis. The tensile strength of most of the fiber lots was quite low, with many of the fractures occurring at "kinks" in the fiber or from gross fiber flaws.

HRTEM conducted on a small LAS matrix composite with Dow Corning SiC fibers verified previous SAM results that a very thin (~14nm) graphitic carbon rich layer had formed at the fiber/matrix interface during composite processing. This layer may not have formed coherently around all of the fibers in a composite, since some fibers debonded from the matrix while others did not, but was found to form on at least some fibers in each composite, whether or not those fibers originally exhibited a carbon rich surface or a surface high in boron and nitrogen. Utilizing a very high temperature BAS matrix (that crystallizes to celsian) in conjunction with the Dow Corning SiC fibers, resulted in a fiber/matrix interface that did not appear to contain a carbon rich layer. The particular lot of fibers utilized for this composite exhibited an internal interface that contained either graphite or hexagonal BN. Positive identification, even through the use of HRTEM, was not able to be done. This composite, while exhibiting limited debonding at both the fiber/matrix and internal fiber interfaces, did show that the Dow Corning SiC fibers do have potential as reinforcement for advanced refractory glass-ceramic matrices. However, their interfacial bonding characteristics and their overall lack of reproducible chemistry, morphology, and strength, suggest that a great deal of further development is needed in areas such as fiber processing and fiber coating systems before these fibers can be seriously considered for use in high temperature ceramic matrix composites.

The small quantity of Textron "Black" fibers evaluated during the past year were found from SAM and TEM analyses to be very similar to Dow Corning's HPZ fibers in their chemistry and reactivity with glass-ceramic matrices. The near-surface region of the fibers is oxygen rich, while the bulk of the fiber consists of ~39 at% Si, 30% N, 27% C, and 4% O. The main difference between these fibers and HPZ is that the bulk composition of HPZ contains ~19% C. From TEM analysis of a small composite made with the Textron fibers and a BMAS matrix, it was found that a rather extensive reaction zone of Si_2N_2O formed at the fiber/matrix interface during composite fabrication. This reaction zone was bonded very strongly to both the fiber and the matrix. A similar reaction zone was previously found for HPZ fibers in both BMAS and LAS matrices. Future work with the Textron fibers, if available in large enough quantities, would have to focus on applying diffusion barrier, weakly bonded, fiber coatings in order to prevent fiber/matrix reactions and to achieve an interface that could deflect matrix cracks and thus produce a fracture tough ceramic matrix composite.

Studies of the new electron beam radiation cured low oxygen Nicalon SiC fiber have shown that this fiber is ~38% stronger and 42% stiffer than the commercial ceramic grade Nicalon fiber. The composition of the fiber is similar to ceramic grade Nicalon, in that the fiber is carbon rich (~56 at% C, 44% Si), except it contains very little oxygen (<1%). From TEM thin foil analysis, it was apparent that the low oxygen Nicalon fiber has a significantly larger β-SiC grain size (~8nm) than the ceramic grade Nicalon (~2nm). After thermal exposure to 1300°C for 30 min in both flowing Ar and 10^{-3} torr vacuum, the low oxygen Nicalon fiber retained ~70% of its original strength, compared to the ceramic grade Nicalon fiber that retained only 40-45% of its strength. A small BMAS matrix "psuedo-composite" fabricated with the low oxygen Nicalon fibers resulted in a very thin high carbon content interfacial layer being formed at the fiber/matrix interface during composite fabrication. This layer should act as a weakly bonded, crack deflecting interface, yielding a composite that is both strong and fracture tough. However, questions concerning the oxidative stability of such an interface remain to be answered.

While it appears that all of the fibers studied during the past year may have eventual potential as reinforcement for advanced refractory glass-ceramic matrices, the low oxygen Nicalon fiber appears to offer the most potential for the near future. While this fiber is not yet available in commercial quantities, it should be available during the coming year in enough quantity for further composite evaluation. Plans are in place to utilize the fibers that are in-house in a refractory BAS matrix for fiber/matrix interaction studies. Additional low oxygen Nicalon fibers anticipated to be received during the coming year will then be incorporated into either BMAS or BAS matices for composite thermomechanical studies. If other fibers of interest become available during the coming year, they will also be incorporated into the program.

I. INTRODUCTION

During the past decade, the interest in ceramic matrix composites for high temperature structural applications, especially for use in heat engines, has increased to the point that a large number of industrial organizations as well as universities and government laboratories throughout the world are actively performing research into a myriad of different systems and different processing procedures for these materials. Among the types of ceramic matrix composites under investigation are whisker reinforced glasses and glass-ceramics[1-4] as well as whisker reinforced crystalline ceramics[5-34], and continuous fiber reinforced ceramics produced by methods that include hot-pressing of glasses and glass-ceramics[35-50], sol-gel infiltration and pyrolysis of ceramics[51], polymer precursor infiltration and pyrolysis[52], reactive oxidation of metals[53], reactive sintering[54], and chemical vapor infiltration (CVI) of silicon based ceramics[55-66].

It has been found in all of the above-mentioned ceramic composites that in order to achieve high strength and, in particular, high toughness, the bonding at the fiber/matrix interface must be controlled such that bonding is strong enough to allow load transfer from the matrix to the fibers under stress but weak enough so that an advancing matrix crack can be deflected by the fibers. In addition, the nature of the fiber/matrix interface must include resistance to oxidation at elevated temperature as well as resistance to other environmental effects.

For the past thirteen years, research at United Technologies Research Center (UTRC) in the area of ceramic matrix composites has centered on systems based on the reinforcement of glass and glass-ceramic matrices with Nicalon polymer derived SiC fibers. In the past few years, this research has concentrated on the study of the fiber/matrix interface and the relationship of the interfacial chemistry and morphology to the composite mechanical and thermal properties[44,47,50,67]. The characterization of the interfaces in these composites has been accomplished primarily by a combination of scanning electron microscope (SEM) observations of composite fracture surfaces, transmission electron microscope (TEM) replica and thin foil analysis, and scanning Auger microprobe (SAM) analysis of composite fracture surfaces. This work has enabled a greater understanding to be reached of the reactions that occur and the phases formed in these systems and has led to the successful development of strong, tough, and oxidatively stable glass-ceramic matrix/Nicalon fiber composite systems for use to temperatures approaching 1000°C.

While the attainment of much higher use temperature glass-ceramic matrices than 1000°C has been demonstrated at UTRC, the inherent formation of a carbon rich interfacial layer between the Nicalon fibers and the glass-ceramic matrices during fabrication makes the oxidative stability of these composites difficult to achieve in the temperature range of 1000-1300°C. In addition, the high fabrication temperatures necessary to densify such glass-ceramic matrices as the barium-magnesium aluminosilicates (BMAS) and the barium aluminosilicates (BAS) can lead to severe fiber degradation for fibers such as Nicalon and Ube's Tyranno. More recently developed fibers such as Dow Corning's HPZ, and new experimental fibers such as Textron's "Black" Si-N-C fiber and Dow Corning's crystalline SiC fiber may have the temperature capability to withstand the higher processing temperatures. These new fibers may also require tailoring of the fiber/matrix interfacial chemistry in order to prevent strong bonding or reaction at the fiber matrix interface. Preliminary work in the area of interface tailoring has been initiated at UTRC utilizing Nicalon fibers, primarily through the application of fiber coatings prior to composite fabrication[68]. These coatings must act as weakly bonded crack deflecting media and also be effective as diffusion barriers and be resistant to oxidation.

The approach offered in the current program is building upon the successfully incorporated technology, as discussed above, and other efforts currently ongoing in the area of high temperature (1100-1400°C) glass-ceramic matrix composite systems. The emphasis of the program is concerned with the interfacial chemistry, bonding, and reactions that occur between various new fibers under development and advanced glass-ceramic matrices, and the relationship of the interface to the resultant composite thermal and mechanical properties. The fibers under investigation include, but are not limited to, new experimental fibers from Dow Corning such as their polymer derived crystalline SiC fiber, Textron's "Black" (Si-C-N-O) small diameter fiber, as well as the new low oxygen radiation cured Nicalon SiC fibers from Nippon Carbon Co. During the first year of the program, a small effort was also expended studying the new low oxygen "Lox M" Tyranno SiC type fibers from Ube Industries, Ltd., Japan. Other new fibers under development that were considered for investigation, but that could not be obtained, were the sintered SiC fibers from Carborundum and DuPont. The glass-ceramic matrices utilized or scheduled to be utilized include LAS, BMAS, CAS, and BAS based compositions.

This report discusses the results of research activities at UTRC during the second year (Feb. 1, 1991 - Feb. 1, 1992) of support under this program.

II. BACKGROUND

As discussed in the Introduction, UTRC has been active in the area of ceramic matrix composites for over a decade. Most of this work has concentrated on glass and glass-ceramic matrix composites reinforced with SiC, graphite, and oxide fibers. More recently, ceramic matrix composites fabricated by other means such as CVI and polymer infiltration have come under investigation. In the area of glass-ceramic matrix composites, Nicalon fiber reinforced lithium aluminosilicate (LAS) and barium/magnesium aluminosilicate (BMAS) matrices have been shown to possess excellent strength in inert (argon) environment to 1300°C. Other glass-ceramic matrices based on calcium and barium aluminosilicate (CAS and BAS) have the potential to yield high strength composites to temperatures of 1400°C (2550°F) or higher. However, from results of interfacial characterization of these composites, work that was partially supported under ONR Contract N00014-82-C-0096[67], a carbon rich fiber/matrix interface is formed that acts as an excellent matrix crack deflecting medium but that is oxidatively unstable at temperatures above ~500°C. The result is weak and brittle composite behavior in oxidizing environments compared to strong and tough behavior in inert environments. Other fibers and whiskers, such as the oxide based Nextel 440 from 3M or Fiber FP from DuPont, the high nitrogen content HPZ fiber being developed at Dow Corning, and stoichiometric SiC whiskers from various suppliers, do not form the carbon interfacial zone when incorporated into glass-ceramic matrices but instead bond very strongly, and in some cases react with the matrices, resulting in weak and brittle composites[50].

While UTRC has overcome to a large degree the oxidative instability of LAS matrix/Nicalon fiber composites by incorporating a lower melting glass forming addition that acts as a oxygen diffusion barrier "plug" at the carbon rich interfacial zone[67], this addition lowers the effective use temperature of the composite to less than 1000°C (UTRC-100 and 200 matrices). In order to take advantage of the inherent refractory nature of the aforementioned glass-ceramic matrices, reinforcing fibers will have to be used that can withstand the higher processing temperatures necessary for these matrices and yet also possess an oxidatively stable fiber/matrix interface.

Dow Corning Corp. is developing a family of SiC type small diameter fibers, partly under in-house funding and partly under a NASA-Lewis program (Contract NAS 3-25641), that may very well have greater thermal stability than the currently available Nicalon and Tyranno fibers. As reported by Dow Corning[69], the 10µm diameter stoichiometric SiC fibers exhibit tensile strengths to 360 ksi (2500 MPa) and elastic moduli to 65 Msi (450 GPa), and retain up to 87% of their tensile strength after 1800°C, 12 hr, argon exposure. The increased thermal stability is reportedly due to the nature of the chemistry of these new fibers. Analysis of one of these fiber types in the scanning Auger at UTRC indicated that the fiber consisted only of Si and C, with no oxygen present. It has been well documented that the inherent thermal instability of Nicalon fibers above 1200°C or so is a result of oxygen in the fiber combining with excess carbon forming CO, which comes out of the fiber with a concurrent increase in SiC grain size, leading to severely reduced fiber strength. It was thus decided, with Dow Corning's approval and assistance, to evaluate these new SiC fibers in refractory glass-ceramic matrix composites, with the ultimate goal being the development of a fiber reinforced glass-ceramic composite system capable of use under stress at temperatures in excess of 1300°C. During the first year of the program emphasis was placed on the characterization of the fibers themselves (UTS, SEM, scanning Auger, TEM), as well as their fracture behavior, bonding characteristics, and interfacial compatibility with various glass-ceramic matrix materials[70].

Since during the first year of this program the availability of the Dow Corning SiC fibers was rather limited, an attempt was made to procure other newly developed fibers to incorporate into the program. Both DuPont and, in particular, Carborundum Corp. have been investigating the processing of SiC fibers by the sintering of extruded SiC fine powder/binder mixes. Requests to evaluate small amounts of these fibers under this program were, unfortunately, denied. However, a new SiC type fiber from Ube Industries, Ltd. in Japan, known as Lox M Tyranno, was obtained in continuous tow form and incorporated into the program. Previous studies under ONR Contract N00014-86-C-0649[71,72] utilizing earlier type TRN-M401 Tyranno fiber resulted in very low strength LAS matrix composites, when compared to Nicalon fiber composite properties. The reason for this was determined to be the very high oxygen content (~20 at%) of the fibers leading to severe fiber degradation due to a large amount of matrix element (Al) diffusion into the fibers and/or strong interfacial bonding during composite processing. Others[73,74] have also found the high oxygen Tyranno fiber to be less stable and more reactive than Nicalon fiber. The newer Lox M Tyranno fibers reportedly contained 10-12 at% oxygen, which is on the order of that for ceramic grade NICALON fiber. It was thus decided to devote a relatively small effort towards the evaluation of the interfacial chemistry and morphology, as well as composite properties, of the Lox M Tyranno fiber in glass-ceramic matrices.

During the first year of the program, Lox M Tyranno fibers were incorporated into both lithium aluminosilicate (LAS) and the more refractory barium magnesium aluminosilicate (BMAS) glass-ceramic matrices. The chemistry and microstructure of the Tyranno fiber/matrix interfaces were studied by means of scanning Auger and TEM, respectively, with the composite strength as a function of temperature being evaluated and compared to previous data obtained for both Nicalon fiber and earlier high oxygen Tyranno fiber composites.

It was found that the mechanical properties of Lox M Tyranno fiber/glass-ceramic matrix composites were much improved over similar composites fabricated with the older higher oxygen Tyranno fibers. The tough fracture behavior of composites fabricated with the Lox M Tyranno fibers was due to the formation of an ~50nm thick carbon layer at the fiber/matrix interface during composite fabrication. This carbon rich interfacial layer formation was essentially identical to that formed in Nicalon fiber/glass-ceramic matrix composites, except for the additional formation of titanium rich crystalline particles within or near the carbon rich interfacial layer. The formation of these particles is evidently due to a reaction between the small amount of titanium in the Tyranno fibers with certain matrix and/or fiber constituents. The thermal and mechanical properties of both UTRC-200 LAS and BMAS matrix composites were very similar for either Lox M Tyranno or Nicalon fiber reinforcement. Overall, it appears that, while the Lox M Tyranno SiC type fiber does not exhibit any distinct advantages over Nicalon fiber (except possibly its somewhat smaller diameter), it certainly can be considered to be as good as Nicalon as a reinforcement for glass-ceramic matrix composites and a candidate as a second source of fiber.

Of the seven small lots of Dow Corning SiC fiber evaluated at UTRC during the first year of the program, all of them exhibited differences in chemistry to one degree or another. Although they all could be considered to be relatively close to stoichiometric SiC in overall chemistry, three of the fiber lots exhibited a surface region that contained boron and nitrogen, while the others exhibited carbon rich surfaces to varying degrees. Boron was found to be present in most of the fiber lots in small quantities (3-5 at%) and is evidently utilized as a grain growth inhibitor. The grain size of the fibers, as determined from TEM as well as SEM analysis, varied from an average of ~150nm for some fibers to a dual grain size morphology that consisted of rather large grains (300-400nm) near the fiber surface to medium sized (100-150nm) grains surrounded by an extremely fine grained (<10nm) structure near the center of the fibers. Electron diffraction analysis of the medium to large grains indicated that they consisted almost exclusively of β-SiC. The fine grained structure has been the subject of investigation during the second year's efforts under this program, and will be discussed in later sections of this report. The tensile strength of most of the fiber lots was quite low, with many of the fractures occurring at "kinks" in the fiber or from gross fiber flaws.

Small pseudo-composites were fabricated with two of the crystalline SiC fiber lots; one that indicated from scanning Auger (SAM) analysis to have a carbon rich surface and one that exhibited a surface rich in boron plus nitrogen. Both lithium aluminosilicate (LAS) and barium magnesium aluminosilicate (BMAS) glass-ceramic matrices were utilized in these samples. From these small pseudo-composites, indications of reaction and bonding at the fiber/matrix interface and the chemistry and structure of the interfacial regions could be determined from subsequent SEM analysis of fracture surfaces, SAM depth profiling of fractured fiber surfaces and matrix troughs, and TEM replica and thin foil studies.

The results of the above analyses were not particularly definitive. The SEM analysis of fracture surfaces indicated that debonding between the fibers and the matrix occurred for many of the fiber/matrix combinations, indicative of relatively weak fiber/matrix bonding and thus potentially tough composite behavior. However, within the same sample, examples of very strong bonding between fiber and matrix could generally be found. SAM depth profiles of fiber/matrix interfacial regions showed that a very thin (<20nm) carbon rich layer formed at the fiber/matrix interface during composite processing for some composites, thus leading to the observed fiber/matrix debonding, but did not form in all cases. TEM thin foil analysis of the fiber/matrix interfacial regions did not delineate the formation of a distinct carbon interfacial layer, but indications were seen that an extremely thin interfacial layer of some type might be present at some of the fiber/matrix interfaces. High resolution TEM (HRTEM) was deemed to be necessary to characterize the exceedingly fine structure observed, and was pursued during the second year of the program.

III. TECHNICAL DISCUSSION

A. Materials

The fibers utilized during the second year of the program consisted of the same small quantities of several different lots of crystalline SiC fiber from Dow Corning Corp., Midland, MI, that were used for the previous year's work, a small amount of Textron's "Black" Si-N-C-O fiber that was obtained through Pratt & Whitney, W. Palm Beach, Fla., and a three meter section of 500 filament tow of Nippon Carbon Co. low oxygen Nicalon fiber, that was obtained from Dow Corning. No additional samples of crystalline SiC fiber were supplied to UTRC by Dow Corning during the past year. As mentioned in the Background section of this report, sintered SiC fibers from both DuPont and Carborundum were attempted to be obtained for evaluation under this program, without success.

The glass-ceramic matrix materials used during the second year of this program consisted of a barium-magnesium aluminosilicate (BMAS) matrix and a barium aluminosilicate (BAS) matrix. The BMAS matrix, when ceramed at 1200°C for 24 hrs, crystallized to the barium osumilite phase, while the BAS matrix crystallized to celsian.

B. Dow Corning SiC Fibers and Composites

1. Fiber Characterization

As detailed in the previous annual report on this contract[70], during the first year of the program seven different lots of Dow Corning crystalline SiC fibers were received at UTRC, only four of which were large enough to perform any significant experiments. Figure 1 shows these four mats of fiber and their lot numbers. From this figure, it can be seen that lots 53C1 and 41C tended to be rather gold in color, while lots 50C and 57C1 ranged in color from brown to black.

a. Scanning Auger Analyses

Previous scanning Auger depth profiles into the fiber surfaces to a depth of 400-600nm indicated that the compositions of three of these fiber lots were quite similar, with the near-surface regions (0-50nm) of lots 41C, 53C1, and 50C exhibiting quite high amounts of both boron and nitrogen. At a depth of ~300nm into the fiber, both lots 50C and 53C1 became slightly carbon rich, while lot 41C remained very close to stoichiometric SiC. No boron was detected in the bulk of any of these fibers.

The last lot of Dow Corning SiC fibers that was received was from NASA-Lewis (#9217-57C1) and ranged in color from brown to black. Scanning Auger depth profiles were obtained previously on a typical brown fiber and a typical black fiber. The brown fiber showed very trace amounts of boron and nitrogen on the very surface, along with very small amounts of oxygen to a depth of 100nm, with 4-5% boron beginning to appear at a depth of 400nm. The surface of this fiber was also somewhat carbon rich. In contrast, the black fiber from this lot was very stoichiometric SiC with a quite carbon rich surface with a trace of N and B, but no boron was detected in the bulk of the fiber.

During the past year, calibration experiments conducted on high purity stoichiometric SiC platelets in the scanning Auger revealed that, depending on the mode of measurement of the Auger electron intensity, ie, analog (V/F) or pulse count (PC), different sensitivity factors would have to be utilized for the Si and C peaks to calculate the corresponding atomic percents. Since the measurement of electron intensity was not kept in a specific mode during the previous analyses of the Dow Corning SiC fibers, it was decided to repeat the analyses of two of the fiber lots (41C and 57C1) utilizing only the V/F mode. All scanning Auger analyses conducted during the past six months and in the future will utilize only the V/F electron intensity mode.

Figure 2 shows the scanning Auger depth profile of a typical black fiber from the lot 57C1 SiC fibers. As was found previously, the surface and near-surface region of this fiber lot is very carbon rich. Very small amounts of nitrogen and boron were detected on the fiber surface. Within the fiber, only a trace of oxygen was detected, with ~2% boron appearing at a depth into the fiber of ~500nm. At this depth, the fiber is close to stoichiometric SiC, with a carbon content of 49% and a silicon content of 48%. As will be shown in a later section of this report, from high resolution TEM (HRTEM) studies it has been found that this lot of fiber is primarily β-SiC in the region within ~2μm of the fiber surface, but contains significant excess carbon towards the center of the fiber.

Figure 3 shows the latest scanning Auger depth profile for one of the gold colored fibers from lot 41C. In contrast to the black 57C1 fiber, the gold fibers contain more boron and nitrogen on the fiber surface, and do not have a carbon rich surface layer. The overall composition of the lot 41C fiber is ~50% C, 47% Si, and 3% B. An interesting effect noted for the gold colored fibers is that after argon ion sputtering to 500nm during the Auger depth profiling, the fibers became much darker in color, as shown in Fig. 4. The gold color of these fibers may be related to their surface nitrogen and boron content.

b. Tensile and SEM Analyses

In the previous Annual Report on this program[70], it was reported that the single filament tensile strengths measured at UTRC on the Dow Corning SiC fibers were much lower than that reported by Dow Corning. During 1991, UTRC obtained a new single filament tensile tester that allowed fiber modulus values to be obtained, as well as UTS. Two of the fiber lots that gave very low UTS values in the past (50C and 53C1) were remeasured on this new equipment. The average UTS of lot 50C was 223±92 ksi (1540±635 MPa), while lot 53C1 was 206±107 ksi (1420±735 MPa). Both fiber lots gave average elastic modulus values of 53 Msi (365 GPa). These UTS values are significantly higher than that reported previously, but still less than Dow Corning reports. The very high standard deviation reflects that some fibers were very weak (<700 MPa), with failure occurring at kinks in the fiber or at large internal flaws.

Figures 5-8 show typical SEM micrographs of fractured fiber ends for the Dow Corning SiC fibers from lots 57C1, 41C, 53C1, and 50C, respectively. From Fig. 5, the dual grain size nature of the 57C1 fibers can be seen clearly. The outer 1.5-2.0μm region of the fibers consists of rather large grains of SiC (up to 500nm) with a significant amount of porosity. The inner region of the fibers consists of much smaller grain size material. As will be shown later, from HRTEM analysis this inner region of the fibers consists of a mixture of β-SiC and graphite. The gold colored fibers from lot 41C, as shown in Fig. 6, exhibit a more uniform grain size than lot 57C1. A flaw in one of the fibers is shown in Fig. 6B, and represents one of the fibers from this lot that failed at a rather low stress. The gold colored fibers from lot 53C1, as shown in Fig. 7, appear to be a cross between the two previous lots, in that overall the grain size is relatively small, but the very near surface region (~0.5μm) does contain some larger grains. As can be seen in Fig. 7B, the surface of these fibers is not particularly smooth, but rather grainy in appearance. This is true of all lots of the Dow Corning SiC fibers.

The lot 50C fibers shown in Fig. 8 indicate a rather unusual morphology. It appears that a distinct interface exists between the outer 1μm and the rest of the fiber. The grain size appears to be relatively uniform except in the very center of the fiber, where it appears to be quite small. This particular fiber lot will be investigated in more detail in a later section of this report dealing with the TEM analysis of a BAS matrix composite made with these fibers.

c. TEM Analyses

As was discussed in the previous annual report on this program, TEM thin foil analysis of lot 57C1 SiC fibers that were incorporated in an LAS matrix (Composite #414-90) showed that the outer region of the fibers consisted of quite large β-SiC grains (~300-400nm), while the inner fiber region consisted of medium sized SiC grains (~100-150nm) surrounded by an extremely fine grained structure. This was shown in Fig. 36 of the previous report and reproduced in Fig. 9 of this report. At the time, this fine grained structure was unable to be identified.

Additional TEM analysis of the lot 57C1 fibers themselves was performed during the past year. Figure 10 shows the transistion region between the larger grain size outer region and the smaller grain size inner region. The interface between these two regions appears to be rather abrupt. Figure 11 shows a bright field/dark field pair and the selected area electron diffraction (SAED) pattern for an inner region of the lot 57C1 fibers that clearly indicates the presence of graphitic carbon in the light colored regions between β-SiC grains. In Fig. 12, the energy dispersive X-ray (EDX) patterns are shown for the light colored regions (A) and the SiC grains (B), with the high amount of carbon present in area A quite evident. The graphitic nature of the intergranular phase can be seen using high resolution TEM (HRTEM), as shown by the lattice fringe images of 0.336nm spacing in Fig. 13. Studies done by Dow Corning on similar fibers verified that a graphitic phase existed between SiC grains[69].

TEM thin foil analysis was also done on one of the gold colored SiC fiber lots (53C1). From SEM of fractured fibers (Fig. 7), these fibers appeared to have a much more uniform grain size compared to lot 57C1 fibers. From the TEM thin foil shown in Fig. 14, however, it can be seen that the region very close to the fiber edge appears to have larger SiC grains than the bulk of the fiber. Although from SAM analysis of these and similar gold colored fibers (Fig. 3), boron and nitrogen were found to be present on the fiber surface, no evidence of a surface BN layer was found from TEM analysis. From SAED analysis of the smaller grain size region of the fiber (Fig. 15), and comparing this figure to that for the lot 57C1 fiber shown in Fig. 11, it can be seen that the amount of graphitic carbon between SiC grains is much less for the lot 53C1 fibers. However, as seen in Fig. 16, there does exist some of the light colored intergranular regions that were found to contain free graphitic carbon in the previous fibers. Only upon HRTEM analysis, as shown in Fig. 17, were these regions in the lot 53C1 fibers indentified to contain graphitic carbon "ribbons". The lattice fringe images for the graphitic carbon in the intergranular phase, as well as the β-SiC images can be seen clearly in Fig. 17.

2. Dow Corning SiC Fiber/Glass-Ceramic Matrix Composite Characterization

As discussed in the last annual report on this program[70], small psuedo-composites were fabricated for fiber/matrix compatibility studies utilizing both black (57C1) and gold (41C) fibers in LAS and BMAS matrices. During this past year, these composites were studied in more detail and a very refractory BAS matrix composite was fabricated with the remaining lot 50C fibers.

a. LAS and BMAS Matrix/SiC Fiber Composites

From scanning Auger depth profiling studies on fractured composite surfaces performed last year, it was found that in three of the four composite samples, a carbon rich interfacial layer formed between the fiber and matrix, similar to but considerably thinner than that found previously for glass-ceramic matrix composites with either Nicalon or Tyranno SiC type fibers[67]. The formation of this carbon interfacial layer may result from the carbon-condensed oxidation displacement reaction of the fiber with free oxygen during composite processing:

$$(1)\ SiC + O_2 \Rightarrow SiO_2 + C$$

as described for NICALON fibers in glass-ceramic matrices by Cooper, et al[49,75]. For the lot 41C fibers in an LAS matrix, no trace of the nitrogen or boron that was in the surface region of the fiber could be found in either the LAS or BMAS matrix composites. The surface B and N in these fibers probably diffused out into the matrix during composite fabrication.

From TEM thin foil analysis of the LAS matrix composite #1-91 with lot #9217-41C SiC fibers, an extremely thin interfacial layer of some sort could be rather indistinctly seen, but was too thin to identify. A TEM replica and thin foil, with associated SAED patterns of the fiber and glassy matrix, for composite #1-91 is shown in Fig. 18. HRTEM analysis at 1,574,000X of the interfacial structure in this composite, as shown in Fig. 19, does, however, show distinct lattice fringe images at the fiber/matrix interface that are indicative of graphitic carbon. The width of the graphitic region appears to be on the order of 12nm, which is close to the thickness of the high carbon interfacial region seen from previous scanning Auger analyses.

One of the questions concerning the Dow Corning SiC fiber microstructure is the location of the boron that is known to be present in the fibers from the scanning Auger depth profile studies. It was decided to analyze a lot 57C1 SiC fiber that had previously been fabricated into composite form (LAS matrix composite #414-90) and ion beam thinned for TEM analysis, by parallel electron energy loss spectroscopy (PEELS). The PEELS technique is very sensitive to small amounts of low atomic number elements.

The particular region of the lot 57C1 fiber analyzed is shown in bright field TEM in Fig. 20A, and consists predominantly of equiaxed, faulted β-SiC grains. However, a reversed-contrast, digitally-processed annular dark field STEM image of this same region contained a distinctive population of smaller grains, which appeared to be revealed primarily by their difference in electron scattering factor (the darker grains in Fig. 20B). Careful examination of the bright field image revealed that some, but not all, of these grains could be distinguished by their uniformly bright contrast, which suggests a lower absorption cross section, and thus a lower average atomic number. Silicon-Kα X-ray mapping of this region (Fig. 20C) showed that most of these grains were deficient in silicon. (A carbon X-ray map showed no enhancement of carbon in these grains, and a boron X-ray map was unable to be obtained due to boron X-ray absorbtion by the Si.)

The upper edge of this thin foil region was sufficiently thin to permit analysis by PEELS. Portions of the PEELS spectra from one of the dark contrast grains (locations "ES6" and "ES7") are shown in Fig. 21. Although the ~10nm beam spot size probably accessed part of the adjacent SiC grain in each case, the presence of boron within one of the dark contrast grains is clearly revealed by the boron-K edge at 188 eV in Fig. 21. Although the composition of the other dark grains in Fig. 20B could not be directly confirmed by PEELS (due to excessive foil thickness) or by EDX (due to the high absorption cross section for boron Kα X-rays), the results that were obtained suggest that the boron in these fibers is concentrated in certain individual grains, probably as a boron carbide. Boron may still exist, however, in grain boundary regions or triple points, but this could not be verified from the HRTEM analyses done.

b. BAS Matrix/SiC Fiber Composites

In order to assess the capability of the Dow Corning crystalline SiC fibers for the reinforcement of very refractory glass-ceramic matrices, the remaining fibers from lot 50C were utilized to fabricate a small psuedo-composite with a BAS glass-ceramic for fiber/matrix compatibility studies. The BAS system, when properly crystallized to monoclinic celsian ($BaO \bullet Al_2O_3 \bullet 2SiO_2$), has a high melting point (1760°C), low thermal expansion (2.29×10^{-6}/°C), and relatively low density (3.39 g/cc). The formation of hexacelsian, which undergoes a phase transformation at ~300°C that is accompanied by a rather large volume change, has been a problem in the past for utilizing BAS as a matrix material. However, it has been shown recently[76,77] that additions of SrO to the BAS composition stabilizes the celsian phase.

The fabrication of the BAS matrix/lot 50C SiC fiber composite was accomplished by hot-pressing a mixture of the matrix powder (with small amounts of SrO additive) with the lot 50C fibers at a temperature in excess of 1500°C and a pressure of 14 MPa. Other small diameter SiC fibers, such as Nicalon or Tyranno, would not survive these composite processing parameters without severe microstructural and strength degradation. Figure 22 shows the microstructure of the BAS matrix/SiC fiber composite #212-91. From this figure, it can be seen that the BAS matrix is essentially fully dense and crystalline. The X-ray diffraction analysis of this composite, as shown in Fig. 23, confirms that the as-pressed matrix has crystallized upon cooling to the celsian phase, as represented by the vertical line overlays in Fig. 23. The peaks in the X-ray pattern not identified as celsian are primarily β-SiC from the fibers. No hexacelsiam peaks were found in the X-ray pattern.

Other features to note in Fig. 22 are that most of the fibers exhibit a different grain structure in the center than around the fiber edge, except for the "pac-man" appearing split fibers that do not exhibit the inner structure. Also, all of the fibers in this composite exhibit a ring around the fiber approximately 1μm from the fiber edge. This ring, or internal fiber interface, was observed in the SEM analysis of fractured lot 50C fibers, as was shown in Fig. 8, so it is not a result of the composite processing, but rather a feature introduced during fiber processing.

Figure 24 shows the TEM thin foil characterization of composite #212-91 from a region between the outer surfaces of two fibers with BAS matrix in between, and from the center region of a fiber. It can be seen that the outer fiber edge appears very similar to that for the as-received lot 53C1 fiber that was shown in Fig. 14, in that the very near surface region consists of relatively large (~300nm) SiC grains that transistion quite abruptly to a smaller grain size region within ~100nm of the fiber surface. The center region, or core of the fiber appears to consist of a mixture of small SiC grains and free graphitic carbon, much like the center of the lot 57C1 SiC fibers shown in Figs. 11 and 12. No discernable reaction could be detected between the lot 50C SiC fibers and the BAS matrix.

Figure 25 shows a TEM thin foil of two longitudinal fibers with the BAS matrix in between. The internal fiber interface in both of the fibers can be seen quite clearly in this figure. HRTEM analysis of this interface appears to indicate that it consists of a mixture of small SiC grains and graphitic carbon, as shown in Fig. 26. The measured lattice fringes in Fig. 26 are 0.33nm in width, which is very close to the graphite lattice spacing of 0.336nm. However, hexagonal BN also has a lattice spacing of 0.332nm, and, as found from scanning Auger depth profiling of this composite (Fig. 27), may be present at this internal fiber interface. The SAM depth profile shown in Fig. 27 was done for the matrix trough, outer fiber surface, and inner fiber surface as shown in the actual SEM photo of the region subjected to the SAM analysis. The outer fiber surface/BAS matrix interface does not indicate any carbon layer formation, and the B and N found on the as-received lot 50C fibers from SAM analysis done last year (Fig. 8 of the last annual report[70]) appears to have diffused into the matrix during composite fabrication. Oxygen, aluminum, and barium diffusion into the outer fiber surface has occurred, as well as some carbon diffusion into the matrix. The inner fiber surface indicates that a considerable amount of boron and nitrogen are present, as well as oxygen and a trace of barium. The boron and nitrogen were undoubtedly present in the as-received fibers at this internal interface, and may be present as hexagonal BN. Verification of this would require PEELS analysis, but this was not attempted.

From the results of the analyses conducted under this program on the Dow Corning crystalline SiC fibers, it would appear that they have potential as reinforcement for advanced refractory glass-ceramic matrices. The observation that they apparently do not react significantly with matrices such as BAS after a >1500°C composite fabrication lends credence to this conclusion. However, their interfacial bonding characteristices and their overall lack of reproducible chemistry, morphology, and strength, suggest that a great deal of further development is needed in areas such as fiber processing and fiber coating systems. Since Dow Corning has not supplied any new fibers to this program during the past year and does not appear to be particularly successful in scaling up to multifilament production, it was decided to suspend further research pertaining to interfacial studies of these fibers in refractory glass-ceramic matrices. Two other new fibers that were supplied to UTRC in very small quantities during the past year, one of which appears to have great potential as a high temperature reinforcement, were integrated into the program in place of the Dow Corning SiC fibers.

C. Textron "Black" Si-N-C-O Fiber and Composites

A small quantity (four, thirty cm lengths of ~500 filament tow) of Textron Specialty Materials "Black" fiber was received from Pratt & Whitney-GESP, W. Palm Beach, Fla., for analysis under this program. This polymer derived fiber is being developed at Textron under in-house and Air Force funding.

1. Fiber Characterization

From previous characterization at P&W, it was determined that the Texton fiber was essentially amorphous to X-rays, had an average filament diameter of 9.8µm, and an average single filament UTS of 226 ± 59 ksi (1560 ± 407 MPa) and elastic modulus of 21.9 ± 0.5 msi (151 ± 3.5 GPa). A scanning Auger depth profile was run at UTRC on the Textron fiber, as shown in Fig. 28. The near-surface region of the Textron fiber is oxygen rich at the expense of nitrogen. The bulk chemistry of the fiber is reached at a a sputter depth of 200-300nm, and consists of ~39 at% Si, 30% N, 27% C, and 4% O. The chemistry of these fibers is similar to that found for recent HPZ fibers from Dow Corning, as shown for comparison in Fig. 29. The difference between the two fibers lies mainly in the overall carbon content and the chemistry of the oxygen rich surface layer. While the oxygen content of the Textron fiber gradually decreases from ~35% on the surface to ~4% in the bulk of the fiber, the oxygen content of the HPZ fiber remains relatively constant in the near-surface region at ~34% until at a depth of 100-200nm, it rather abruptly drops to the bulk level of ~4%. The carbon content of the Textron fiber remains relatively constant at ~27%, while the HPZ carbon content increases gradually from ~8% on the surface to ~19% in the bulk of the fiber.

2. Textron "Black" Fiber/BMAS Glass-Ceramic Matrix Compatibility Studies

With the limited amount of Textron fiber available, it was decided to fabricate a small BMAS matrix "psuedo-composite" for TEM analyses. Figure 30 shows the microstructure of this composite (#239-91) utilizing both optical light microscopy and TEM replica analysis. From this figure, it can be seen that the matrix, while primarily glassy, appears to contain more crystalline phases in regions with low fiber concentrations. It is also evident that a reaction has occurred during composite processing between fibers and matrix, forming a rather non-uniform reaction product around the fiber periphery. A thin foil was made of the fiber/matrix interfacial region for this composite in order to determine the composition and structure of the reaction product. Figure 31 shows the microstructure of the fiber/reaction/matrix interface and the associated EDX spectra of the BMAS matrix (A), larger grains of reaction product (B), fine grained reaction layer (C), and the underlying fiber (D). While not definitive due to the spot size for the EDX analyses being large enough to undoubtedly pick up signals from adjacent matrix, the larger grains (B) appear to consist of a silicon oxynitride with possible Al and Mg constituents, as does the smaller grained reaction region (C). SAED analysis of the reaction product, as seen in Fig. 32, identifies it as Si_2N_2O, which has been found previously at UTRC as a reaction product between Dow Corning HPZ fibers and glass-ceramic matrices[50].

HRTEM analysis of the reaction layer was conducted, both in the small grained region and in the larger grains that protrude out into the BMAS matrix. Figure 33 shows the lattice fringes observed in the smaller grained region of the reaction product. These rather randomly distributed grains give lattice spacings of predominantly 0.468nm in width (A), with some being 0.336nm (B). The former is representative of the (110) spacing for Si_2N_2O, while the latter is equivalent to the (111) lattice of this compound. The latter could also be that for graphitic carbon, but there is no indication of carbon in the EDX spectra for this region (Fig. 31C), nor do the fringes exhibit the usual wavy or "ribbon-like" nature of graphite. Figure 34 shows one of the larger grains of reaction product that is growing out of the fiber surface into the BMAS matrix. Like the smaller grains, the lattice fringes visible for this grain exhibited the 0.468nm spacing of the (110) plane of silicon oxynitride.

With the limited supply of the Textron "Black" fibers and the results that indicate that they behave similar to HPZ fibers when incorporated into glass-ceramic matrices, no further work under this program is planned utilizing these fibers. If at some time in the future they become available in larger quantities, additional research could be done in the areas of fiber thermal stability and diffusion barrier, weakly bonded, fiber coatings in order to prevent fiber/matrix reactions and to achieve an interface that could deflect matrix cracks and thus produce a fracture tough ceramic matrix composite.

D. Nippon Carbon Co. Low Oxygen Nicalon SiC Fiber

Nippon Carbon Co., Yokohama, Japan, has recently developed a polycarbosilane polymer precursor SiC fiber that has been reported to contain very low oxygen content (<0.5 wt%), processed by electron beam radiation curing followed by inert gas pyrolyzation[78]. Due to the low oxygen content, the thermal stability of these fibers has been found to be much better than currently available "ceramic grade" Nicalon fiber[78]. Currently, this fiber is only available in very small research quantities, but is scheduled to be produced in larger quantities beginning in 1993 or 1994. UTRC recently received a 3 meter length of 500 filament, 14µm diameter, low oxygen Nicalon from Dow Corning Corp., the US distributor of Nicalon fiber, for investigation under this program. To date, the as-received fiber has been subjected to SEM, scanning Auger, and TEM analyses, as well as tensile and thermal stability testing. A small psuedo-composite was fabricated with a BMAS glass-ceramic matrix for fiber/matrix compatibility studies. More recently, another 3 meter length of low oxygen Nicalon fiber was received from Dow Corning.

1. Fiber Characterization

The RT tensile strength and elastic modulus of the low oxygen Nicalon fibers was determined for 15 fibers utilizing a 2.54 cm gage length. The average single filament UTS was 498 ± 125 ksi (3435 ±860 MPa), with an average modulus of 41 ± 5.1 msi (282 ± 35 GPa). These values are somewhat higher than that reported by Nippon Carbon Co. using a resin impregnated strand method. Comparable values for commercial "ceramic grade" Nicalon fiber measured in an identical fashion at UTRC are an average UTS of 361 ± 103 ksi (2490 ± 710 MPa) and a modulus of 28.9 ±2.1 msi (199 ± 14.5 GPa). Thus, low oxygen Nicalon fiber is 38% stronger and 42% stiffer than current commercially available Nicalon fiber.

The fracture surface of a low oxygen Nicalon fiber is shown in Fig. 35. Most of the fracture surfaces of these fibers appeared somewhat more granular, or rough, than that seen for ceramic grade Nicalon fibers. The fracture origin appears to be surface related, but the source of failure cannot be identified. The surface of these fibers appears relatively smooth, but some fine scale texturing is noted.

Figure 36 shows the scanning Auger depth profile obtained for the low oxygen Nicalon fiber. A trace of nitrogen was found on the very surface, and 1-2% oxygen was seen to a sputter depth of 100nm into the fiber. Sputtering deeper into the fiber revealed only a trace of oxygen (<1%). On the fiber surface, the carbon content was quite high and the silicon quite low, but by a depth of ~10nm the carbon stabilized at ~56 at% and the silicon at ~44 at%. Thus, while the oxygen content is very low compared to the commercial "ceramic grade" Nicalon (~10 at% O), the relative amounts of Si and C remain similar. It would appear that this fiber contains SiC plus residual carbon. The higher amount of carbon seen on the fiber surface may be a result of the fiber pyrolysis, or it may be adsorbed carbon from the atmosphere. No attempt was made to clean or heat-treat the fiber surface, since they came with no sizing. Some surface debris was noted on the fibers, and, from scanning Auger analysis, appeared to contain considerable aluminum and oxygen.

TEM thin foil analyses of both ceramic grade and low oxygen Nicalon fibers were performed, with the results shown in Figs. 37 and 38, respectively. From Fig. 37, it can be seen that the ceramic grade Nicalon fiber exhibits a very diffuse diffraction pattern for β-SiC, with the average grain size estimated from the dark field analysis to be ~2nm. A considerable amount of oxygen can be seen in the EDX spectra for the ceramic grade fiber. In contrast, the low oxygen Nicalon fiber (Fig. 38) has a much sharper electron diffraction pattern for β-SiC, which is indicative of a larger grain size. From the bright field/dark field images, it can be seen that the grain size is indeed larger, with the average estimated to be ~8nm. The EDX spectra for the low oxygen fiber shows very little oxygen signal. In fact, the signal for Mo, which is a trace impurity on all of the thin foil specimens due to contamination from the Mo holder used during ion beam thinning, is stronger than the oxygen signal. The low oxygen Nicalon fiber thin foil sample is scheduled for HRTEM analysis in the near future in order to determine the fine structure of the SiC grains and the excess carbon in the fiber.

Both low oxygen and ceramic grade Nicalon fibers were subjected to high temperature thermal exposure inside the hot press used to fabricate glass-ceramic matrix composites. The exposure conditions were 1300°C for 30 min in both gently flowing argon and 10^{-3} torr vacuum. The heating rate and cooling rate was 10°C/min. After exposure, 25 fibers from each run were subjected to tensile testing. The results of these exposure tests are presented in Table I.

From Table I, it can be seen that ceramic grade Nicalon fiber degrades considerably in strength after heat-treatment at 1300°C, losing 53% of its strength in argon and 63% in vacuum. The vacuum heat-treatment also lowered the modulus of the fiber. In contrast, the low oxygen Nicalon fiber after argon and vacuum exposure lost only 27% and 31% of its original strength, respectively. The strength of the low oxygen fiber after the 1300°C exposures is approximately that of the ceramic grade fiber before thermal exposure. The modulus of the low oxygen fiber did not change significantly after either of the thermal exposures.

2. Low Oxygen Nicalon Fiber/BMAS Glass-Ceramic Matrix Composite Characterization

As mentioned previously, a small "psuedo-composite" was fabricated with a small length of the low oxygen Nicalon fiber and a BMAS glass-ceramic matrix. To date, the only analysis completed on this composite has been a scanning Auger depth profile of a fiber surface and a matrix trough from which a fiber had debonded. Figure 39 shows the SAM depth profile for the low oxygen Nicalon fiber and the BMAS matrix trough. As can be seen, a very thin high carbon content (but not pure carbon) fiber/matrix interface has formed during composite processing, similar to but much thinner than the pure carbon interface that forms in ceramic grade Nicalon fiber/BMAS matrix composites. It can also be seen that very small amounts of matrix elements, such as Al, Mg, and Ba, have diffused into the fiber to a depth of ~20nm. These elements are also found to diffuse into ceramic grade Nicalon fibers, but to a much greater depth. The oxygen content of the fiber has also increased significantly within ~40nm of the fiber surface, due to oxygen diffusion from the BMAS matrix and/or the silica created during the carbon condensed oxidation reaction, as described earlier (Equation 1). Very little carbon from the fiber was found to have diffused into the matrix during composite processing.

It thus appears that the low oxgen Nicalon fiber behaves similarly to ceramic grade Nicalon fiber when incorporated into a glass-ceramic matrix, in that a carbon rich interfacial region forms during composite processing between the fiber and matrix. Even though this layer is not pure carbon and is much thinner than that formed with ceramic grade Nicalon fibers, it should act as a weakly bonded, crack deflecting interface, resulting in a composite that is both strong and fracture tough. The oxidative stability of this interface remains to be determined, however. The fact that it is not pure carbon and is very thin may enhance its stability with respect to diffusion of oxygen. Additional TEM characterization of the BMAS matrix composite already fabricated, as well as studies of a higher temperature BAS matrix composite with the remaining low oxygen Nicalon fibers, are planned for the near future.

IV. CONCLUSIONS AND RECOMMENDATIONS

From the results of the second year's work on this program, certain conclusions and recommendations can be made. In regard to the Dow Corning crystalline SiC fibers, no new fibers were received by UTRC during the past year, reflective of the difficulty that Dow Corning has had in scaling up the processing of these fibers to the multifilament tow stage. Of the four small lots of fiber evaluated at UTRC during the past year, all of them exhibited differences in chemistry and structure to one degree or another. From TEM and scanning Auger analyses, certain regions of all of the fiber lots were found to be relatively close to stoichiometric SiC in overall chemistry, although other regions (especially the center of the fibers) contained areas that consisted of mixtures of β-SiC grains and pockets of relatively pure graphite. Three of the fiber lots that were gold or brown in color exhibited a surface region that contained boron and nitrogen, the color of which became much darker when the surface region had been sputtered away. The other fiber lot exhibited a very carbon rich surface.

Boron was found to be present in all but the near-surface region of all the Dow Corning fibers in small quantities (2-3 at%), and, from PEELS analysis, may exist in discrete boride inclusions. Boron is evidently incorporated into the starting polymer precursor to act as a sintering aide and/or a grain growth inhibitor. The β-SiC grain size of the fibers, as determined from TEM as well as SEM analysis, varied from an average of ~150nm for some fibers to a more prevalent dual grain size morphology that consisted of rather large grains (300-400nm) near the fiber surface to medium sized (100-150nm) grains surrounded by the extremely fine grained (<100Å) graphitic structure near the center of the fibers. This graphitic phase was identified from HRTEM thin foil analysis. The tensile strength of most of the fiber lots was quite low, with many of the fractures occurring at "kinks" in the fiber or from gross fiber flaws.

HRTEM conducted on a small LAS matrix composite with Dow Corning SiC fibers verified previous SAM results that a very thin (~12nm) graphitic carbon rich layer had formed at the fiber/matrix interface during composite processing. This layer may not have formed coherently around all of the fibers in a composite, since some fibers debonded from the matrix while others did not, but was found to form on at least some fibers in each composite, whether or not those fibers originally exhibited a carbon rich surface or a surface high in boron and nitrogen. Utilizing a very high temperature BAS matrix (that crystallizes to celsian) in conjunction with the Dow Corning SiC fibers, resulted in a fiber/matrix interface that did not appear to contain a carbon rich layer. The particular lot of fibers utilized for this composite exhibited an internal interface that contained either graphite or hexagonal BN. Positive identification, even through the use of HRTEM, was not able to be done. This composite, while exhibiting limited debonding at both the fiber/matrix and internal fiber interfaces, did show that the Dow Corning SiC fibers do have potential as reinforcement for advanced refractory glass-ceramic matrices. However, their interfacial bonding characteristics and their overall lack of reproducible chemistry, morphology, and strength, suggest that a great deal of further development is needed in areas such as fiber processing and fiber coating systems before these fibers can be seriously considered for use in high temperature ceramic matrix composites.

The small quantity of Textron "Black" fibers evaluated during the past year were found from SAM and TEM analyses to be very similar to Dow Corning's HPZ fibers in their chemistry and reactivity with glass-ceramic matrices. The near-surface region of the fibers is oxygen rich, while the bulk of the fiber consists of ~39 at% Si, 30% N, 27% C, and 4% O. The main difference between these fibers and HPZ is that the bulk composition of HPZ contains ~19% C. From TEM analysis of a small composite made with the Textron fibers and a BMAS matrix, it was found that a rather extensive reaction zone of Si_2N_2O formed at the fiber/matrix interface during composite fabrication. This reaction zone was bonded very strongly to both the fiber and the matrix. A similar reaction zone was previously found for HPZ fibers in both BMAS and LAS matrices[50]. Future work with the Textron fibers, if available in large enough quantities, would have to focus on applying diffusion barrier, weakly bonded, fiber coatings in order to prevent fiber/matrix reactions and to achieve an interface that could deflect matrix cracks and thus produce a fracture tough ceramic matrix composite.

Studies of the new electron beam radiation cured low oxygen Nicalon SiC fiber have shown that this fiber is ~38% stronger and 42% stiffer than the commercial ceramic grade Nicalon fiber. The composition of the fiber is similar to ceramic grade Nicalon, in that the fiber is carbon rich (~56 at% C, 44% Si), except it contains very little oxygen (<1%). From TEM thin foil analysis, it was apparent that the low oxygen Nicalon fiber has a significantly larger β-SiC grain size (~8nm) than the ceramic grade Nicalon (~2nm). After thermal exposure to 1300°C for 30 min in both flowing Ar and 10^{-3} torr vacuum, the low oxygen Nicalon fiber retained ~70% of its original strength, compared to the ceramic grade Nicalon fiber that retained only 40-45% of its strength. A small BMAS matrix "psuedo-composite" fabricated with the low oxygen Nicalon fibers resulted in a very thin high carbon content interfacial layer being formed at the fiber/matrix interface during composite fabrication. This layer should act as a weakly bonded, crack deflecting interface, yielding a composite that is both strong and fracture tough. However, questions concerning the oxidative stability of such an interface remain to be answered.

While it appears that all of the fibers studied during the past year may have eventual potential as reinforcement for advanced refractory glass-ceramic matrices, the low oxygen Nicalon fiber appears to offer the most potential for the near future. While this fiber is not yet available in commercial quantities, it should be available during the coming year in enough quantity for further composite evaluation. Plans are in place to utilize the fibers that are in-house in a refractory BAS matrix for fiber/matrix interaction studies. Additional low oxygen Nicalon fibers anticipated to be received during the coming year will then be incorporated into either BMAS or BAS matices for composite thermomechanical studies. If other fibers of interest become available during the coming year, they will also be incorporated into the program.

V. ACKNOWLEDGMENTS

The author would like to thank Mr. James Rabe and Mr. Rick Jones of Dow Corning Corp. and Ms. Janet Hurst of NASA, Lewis, for their assistance in obtaining the Dow Corning crystalline SiC fibers for use on this program, Mr. Rick Jones for his assistance in obtaining the low oxygen Nicalon fibers, Ms. Jean Horlacher of P&W, GESP for the Textron "Black" fibers, Dr. Bruce Laube and Mr. Dan Delong of UTRC for the SAM analyses, Mr. Gerald McCarthy and Dr. David Snow of UTRC for the TEM and PEELS analyses, Mr. Bernarr Jacob and Ms. Laura Austin for the fabrication of the composites, and to Dr. Steve Fishman of ONR for his sponsorship of the program.

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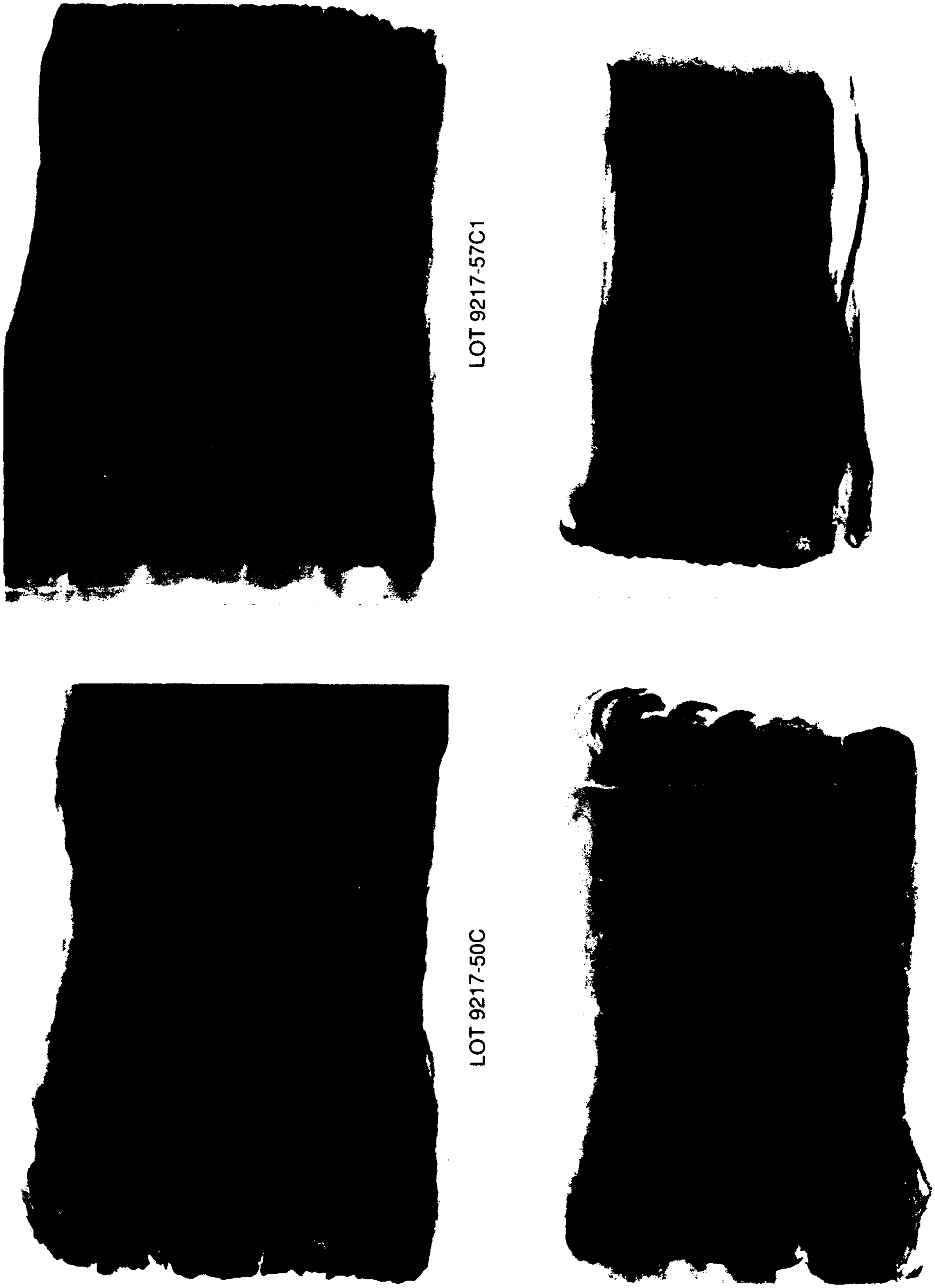
Table I

Thermal Exposure Testing of Nicalon Fibers

Fiber Type	Exposure Conditions	UTS - ksi (MPa)	E - msi (GPa)
Ceramic Grade Nicalon (Lot 168)	none	361 (2490)	28.9 (199)
"	1300°C, 30 min, Ar	171 (1180)	28.9 (199)
"	1300°C, 30 min, Vac	133 (917)	24.6 (170)
Low Oxygen Nicalon (Lot 45)	none	498 (3435)	41.0 (282)
"	1300°C, 30 min, Ar	365 (2519)	43.0 (296)
"	1300°C, 30 min, Vac	344 (2370)	39.5 (272)

FIG. 1

DOW CORNING CRYSTALLINE SiC FIBERS



91-4-52-2

FIG. 2

SAM DEPTH PROFILE
DOW CORNING SIC FIBER (#9217-57C1) BLACK

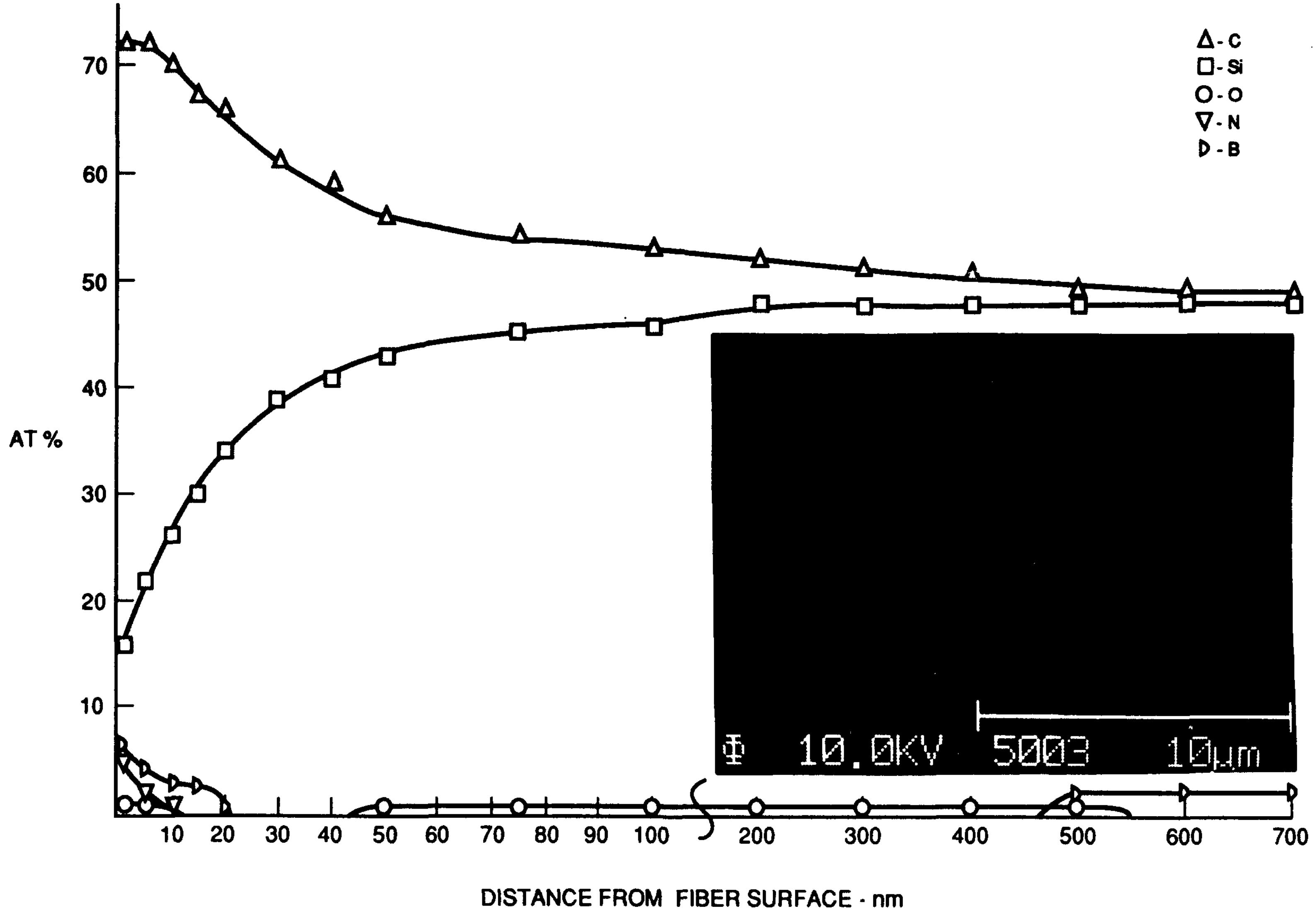


FIG.3

SAM DEPTH PROFILE
DOW CORNING SIC FIBER (#9217-41C) GOLD

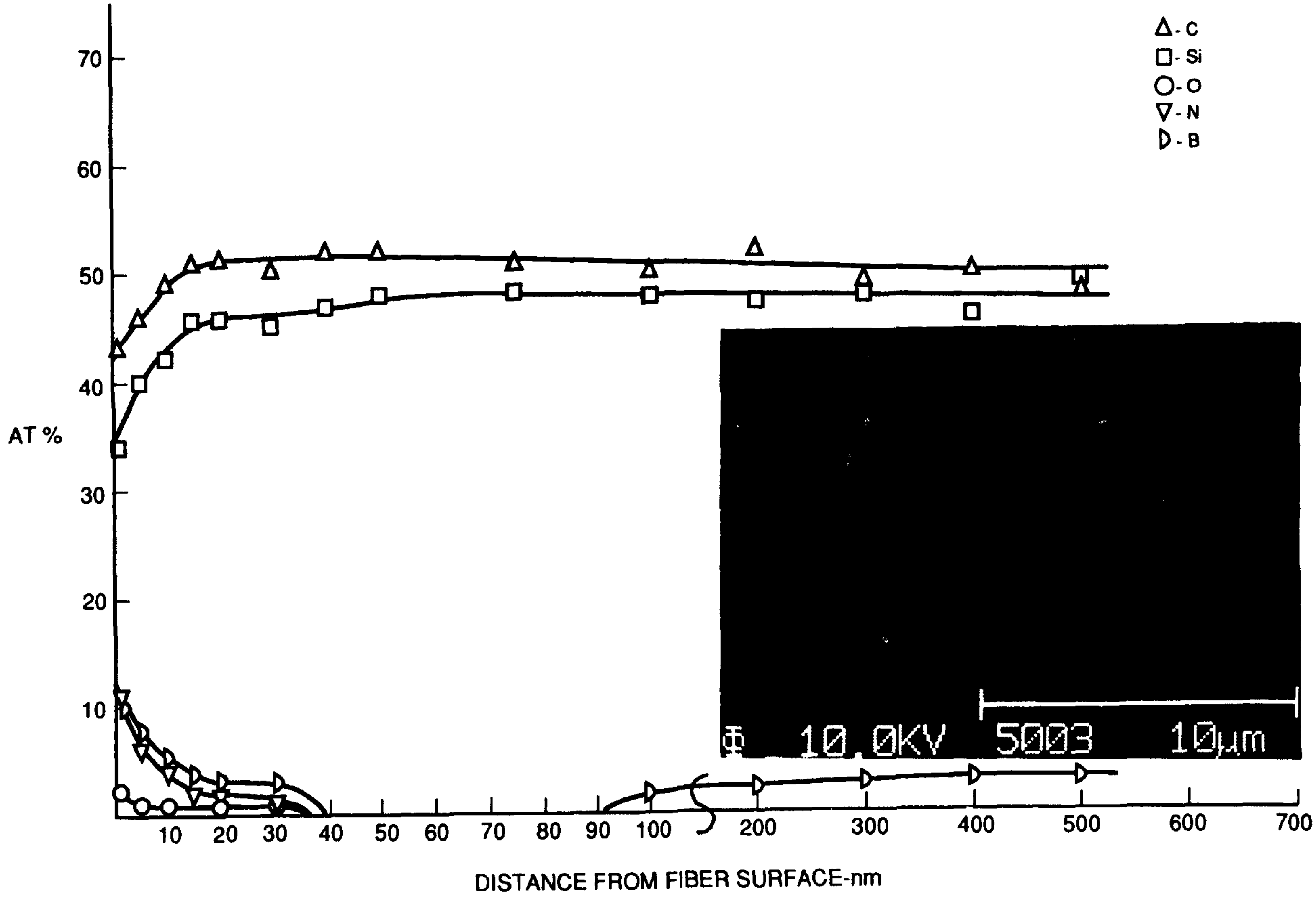


FIG. 4

DOW CORNING GOLD COLORED SiC FIBERS (LOT 9217-41C) AFTER ARGON ION SPUTTERING

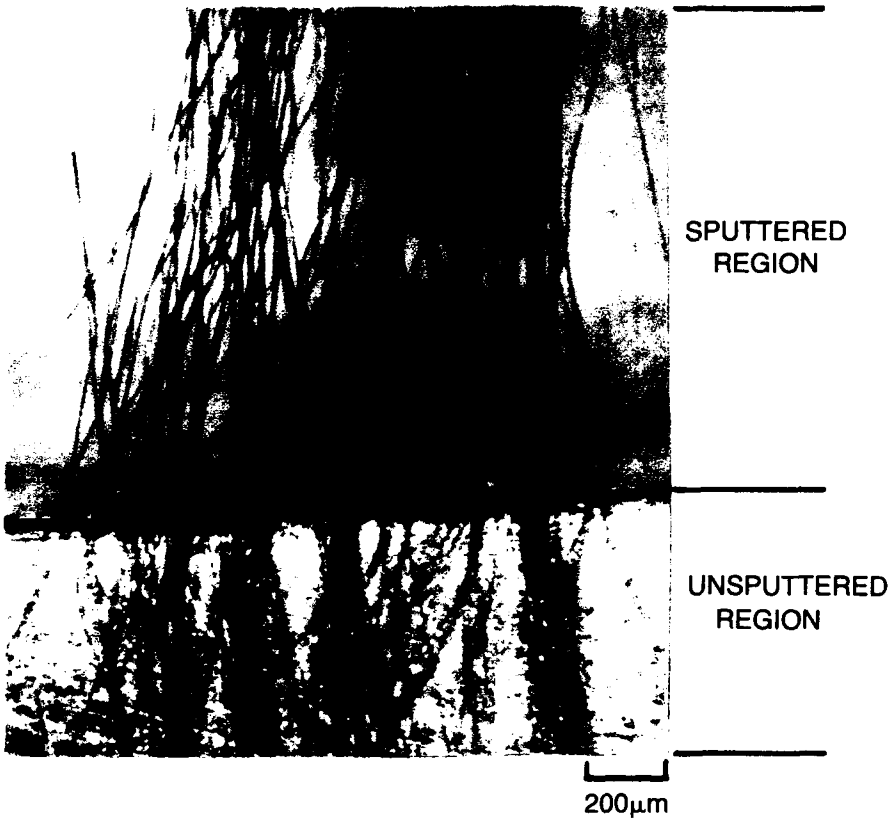


FIG. 5

DOW CORNING SiC FIBERS (LOT 9217-57C1)

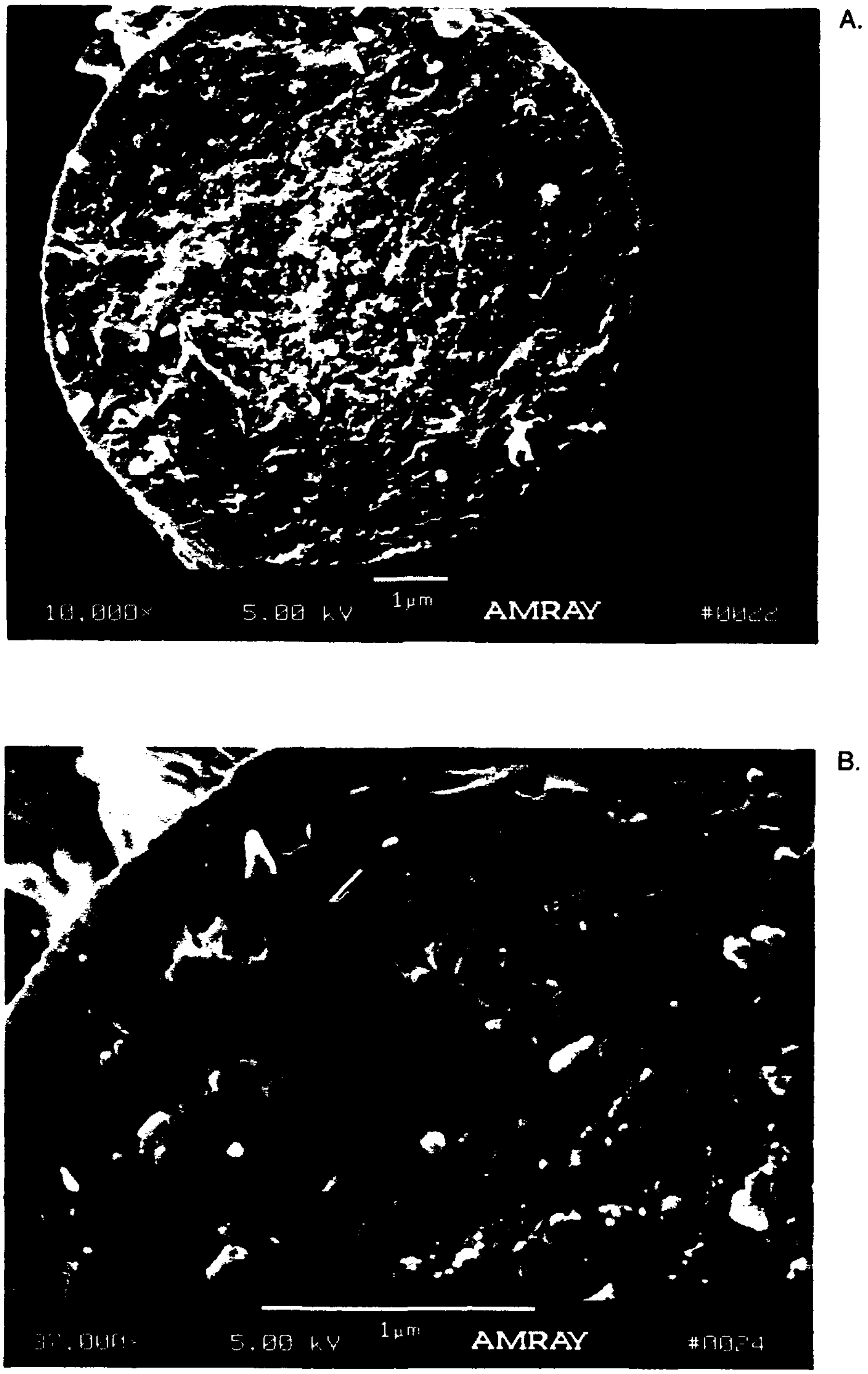
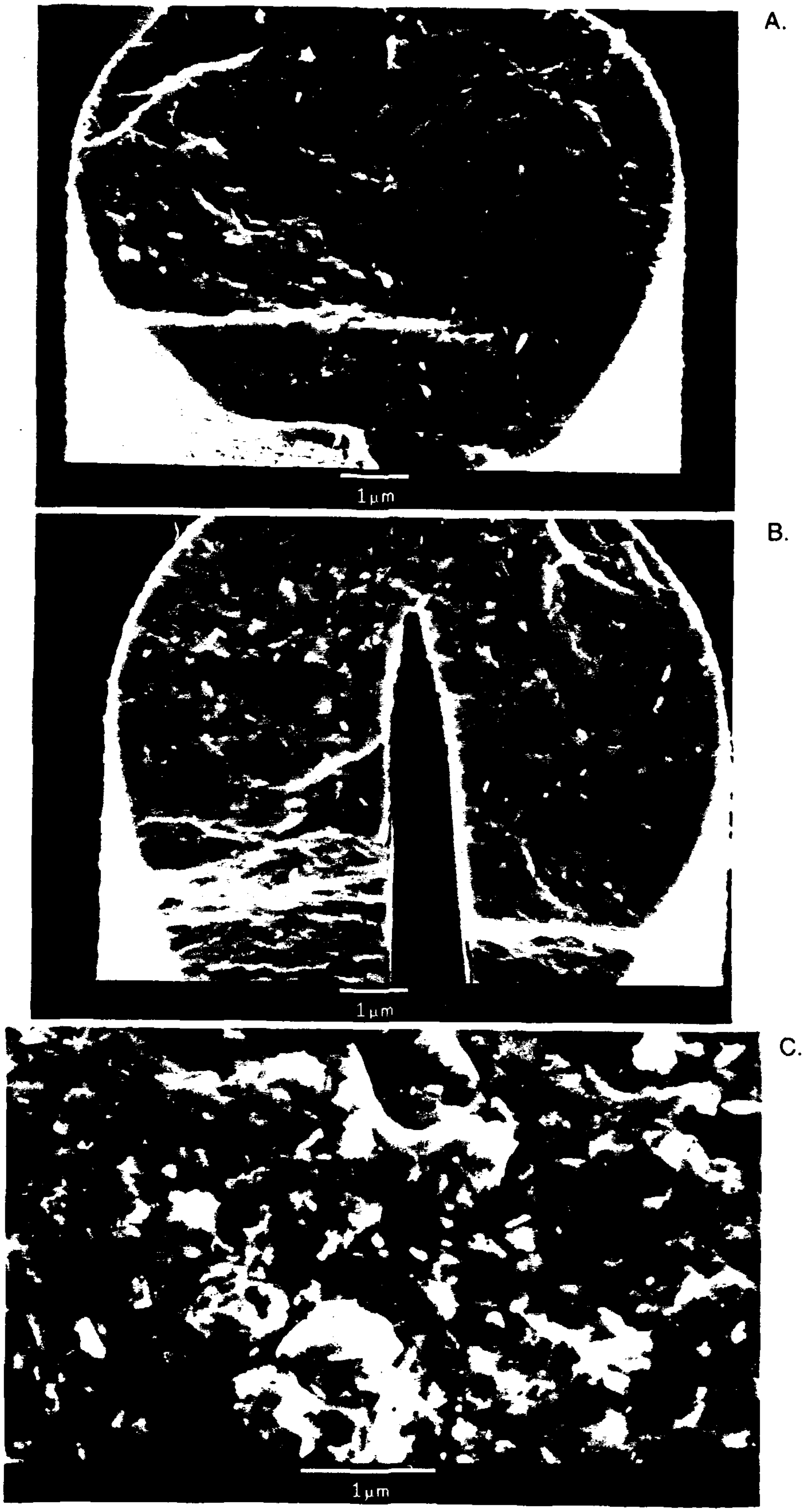


FIG. 6

DOW CORNING SiC FIBERS (LOT 9217-41C)



92-4-13-5

FIG. 7

DOW CORNING SiC FIBERS (LOT 9217-53C1)

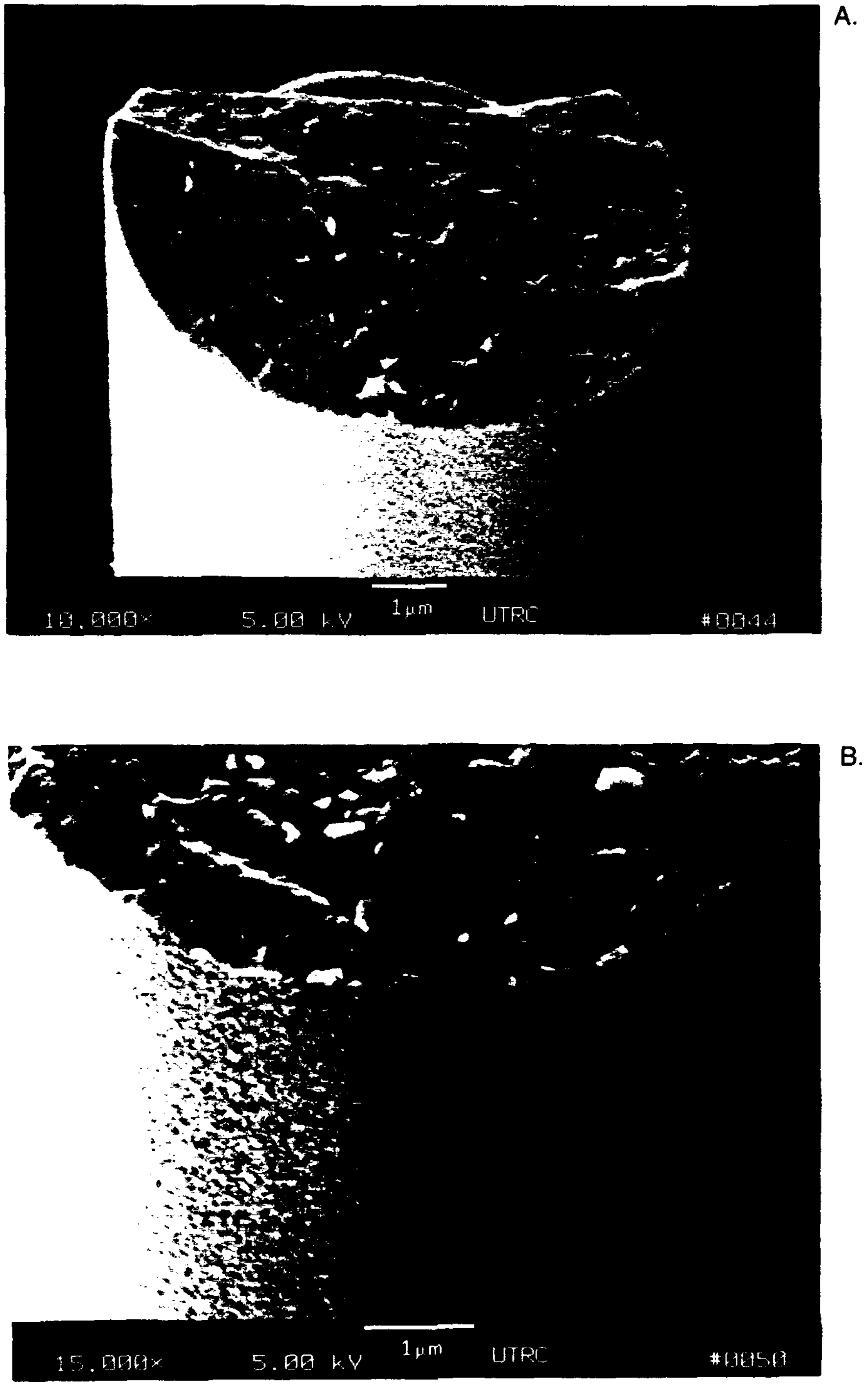
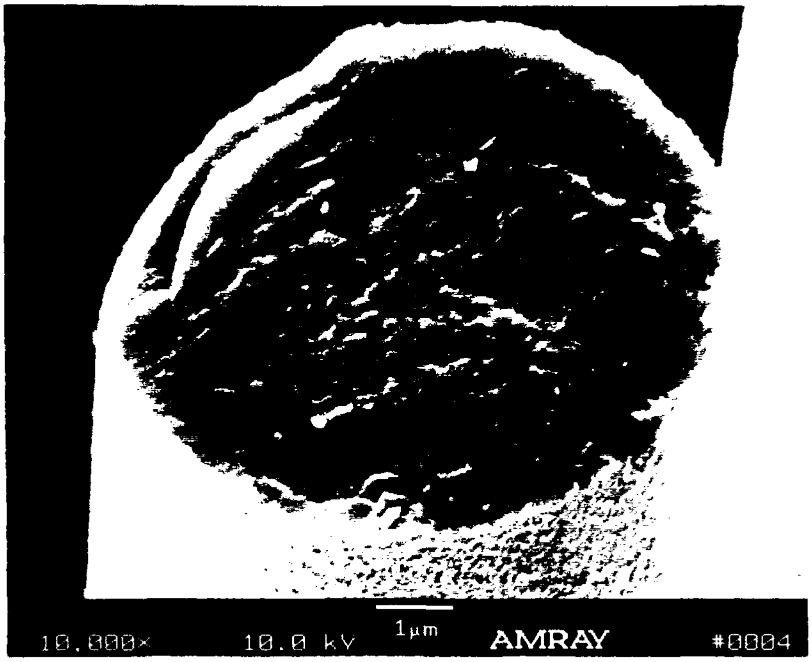
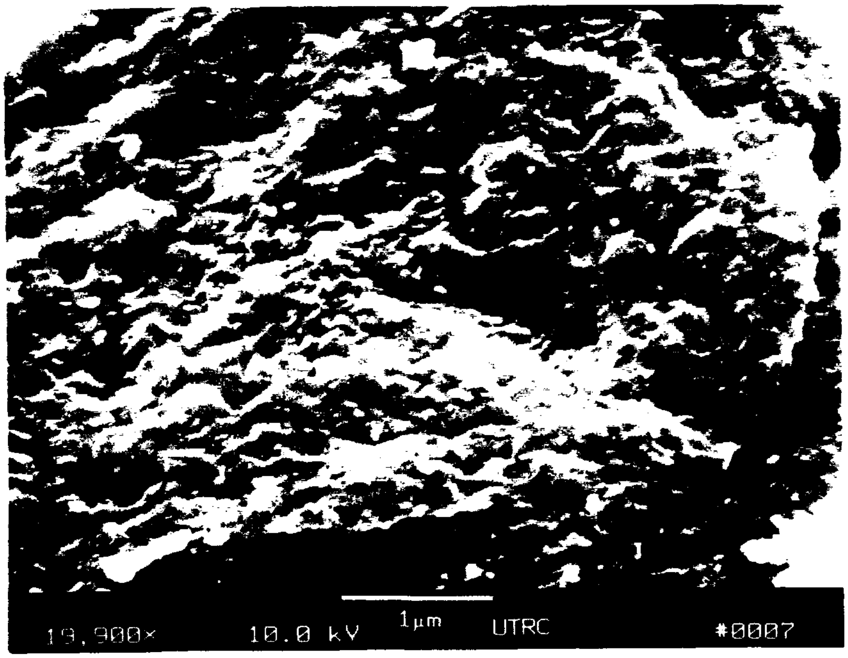


FIG. 8

DOW CORNING SiC FIBERS (LOT 9217-50C)

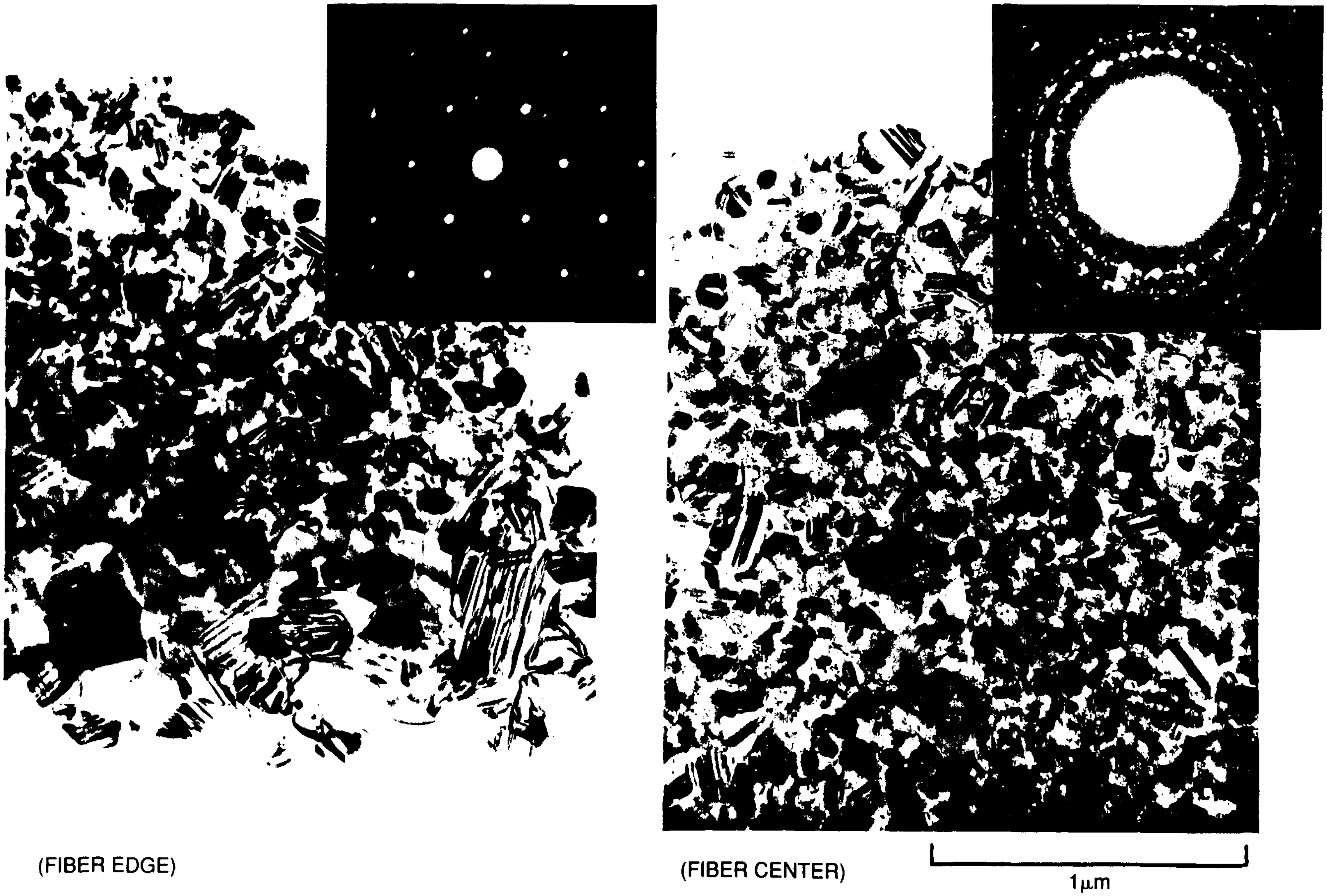


A.



B.

TEM/SAED THIN FOIL CHARACTERIZATION OF LAS/DOW CORNING SiC FIBER
#9217-57C1 (BLACK); (COMPOSITE #414-90)



(FIBER EDGE)

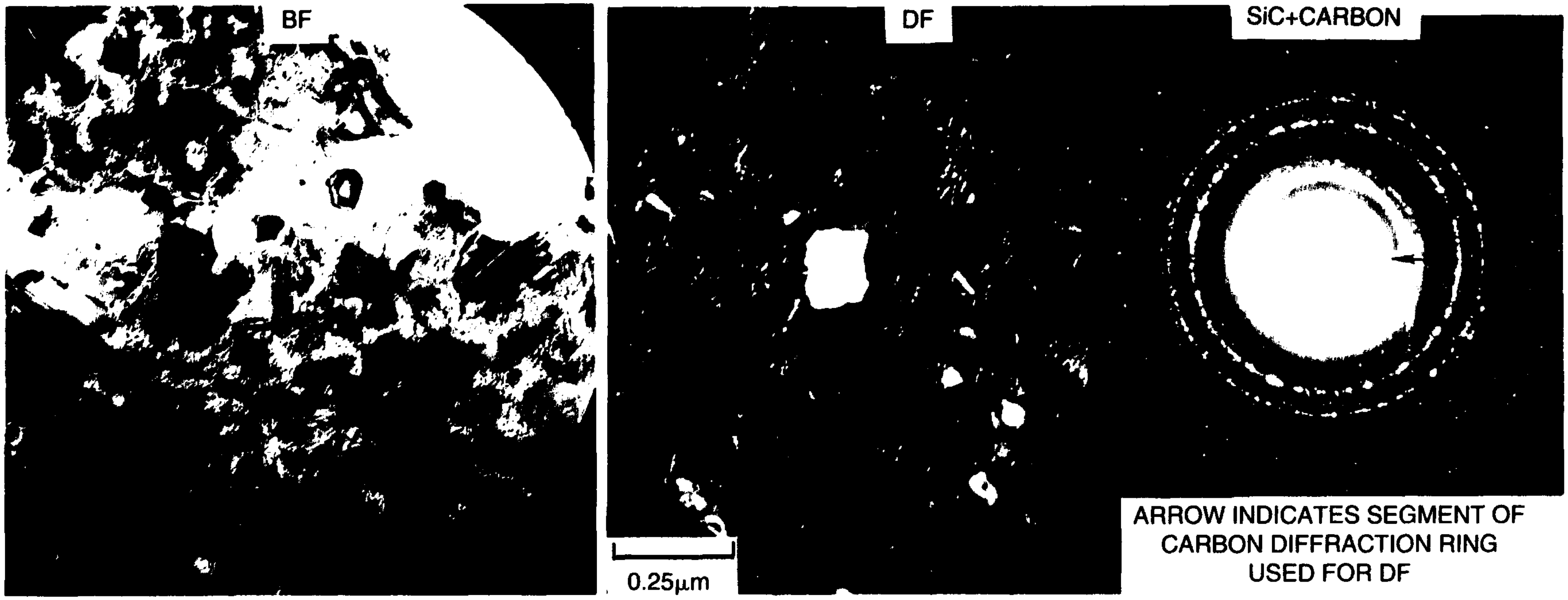
(FIBER CENTER)

FIG. 9

FIG. 10

TEM THIN FOIL ANALYSIS OF DOW CORNING SiC FIBER #9217-57C1 (BLACK)

TEM THIN FOIL ANALYSIS OF DOW CORNING SiC FIBER #9217-57C1 (BLACK)



ARROW INDICATES SEGMENT OF CARBON DIFFRACTION RING USED FOR DF

C

Carbon

Graphite, syn

Rad: CuKa Lambda: 1.54178 Filter: d-sp: Calculated
Cutoff: Int: Calculated I/Icor:
Ref: Holcombe, USAEC Oak Ridge Y-12 Plant, Report Y1887 (1973), Private Communication, (1974)

Sys: Hexagonal S.G.: P63/mmc (194)
a: 2.456 b: c: 6.696 A: C: 2.7264
α: β: γ: Z: 4 mp:
Ref: Ibid.

Dx: 2.26 Dm: SS/FOM: F19=200(.003, 24)

εα: nωβ: εγ: Sign: 2V:
Ref:

Peak height intensities. CAS no.: 7440-44-0. C type. PSC: hP4. Mwt: 12.01.
Volume[CD]: 34.98.

d Å	Int.	h	k	l
3.348	100	0	0	2
2.127	3	1	0	0
2.027	15	1	0	1
1.795	3	1	0	2
1.674	6	0	0	4
1.5378	4	1	0	3
1.3154	1	1	0	4
1.2280	4	1	1	0
1.1529	6	1	1	2
1.1333	1	1	0	5
1.1160	1	0	0	6
1.0503	1	2	0	1
0.9902	4	1	1	4
0.9601	1	2	0	3
0.8724	1	1	0	7
0.8370	1	0	0	8
0.8320	1	2	0	5
0.8259	4	1	1	6
0.7982	2	2	1	1

beta-SiC

Silicon Carbide

Rad: Mo Lambda: 0.70930 Filter: d-sp:
Cutoff: Int: I/Icor:
Ref: For original reference see PDF card set prior to 1980.

Sys: Cubic S.G.:
a: 4.358 b: c: A: C:
α: β: γ: Z: (4) mp:
Ref: Ibid.

Dx: 3.210 Dm: SS/FOM: F15=4(.113, 37)

εα: nωβ: εγ: Sign: 2V:
Ref:

CAS no.: 409-21-2. Deleted by 29-1129. Mwt: 40.10. Volume[CD]: 82.77.

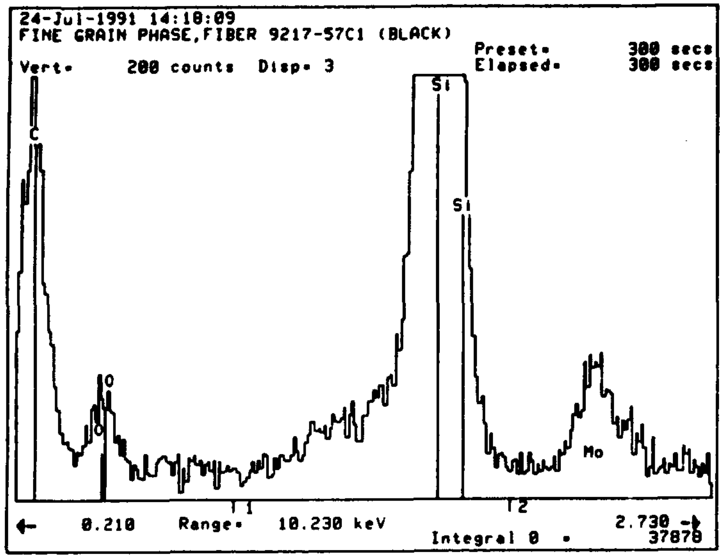
d Å	Int.	h	k	l
2.51	100	1	1	1
2.17	20	2	0	0
1.54	63	2	2	0
1.31	50	3	1	1
1.25	3	2	2	2
1.09	6	4	0	0
1.00	16	3	3	1
0.97	6	4	2	0
0.89	13	4	2	2
0.84	10	5	1	1
0.77	2	4	4	0
0.74	6	5	3	1
0.72	2	6	0	0
0.69	3	6	2	0
0.66	1	5	3	3

FIG. 11

FIG. 12

TEM THIN FOIL ANALYSIS OF DOW CORNING SiC FIBER #9217-57C1 (BLACK)

A.



B.

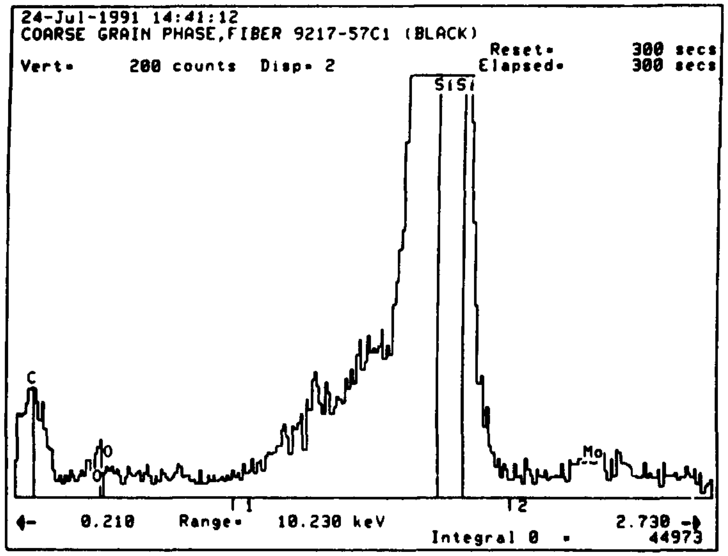


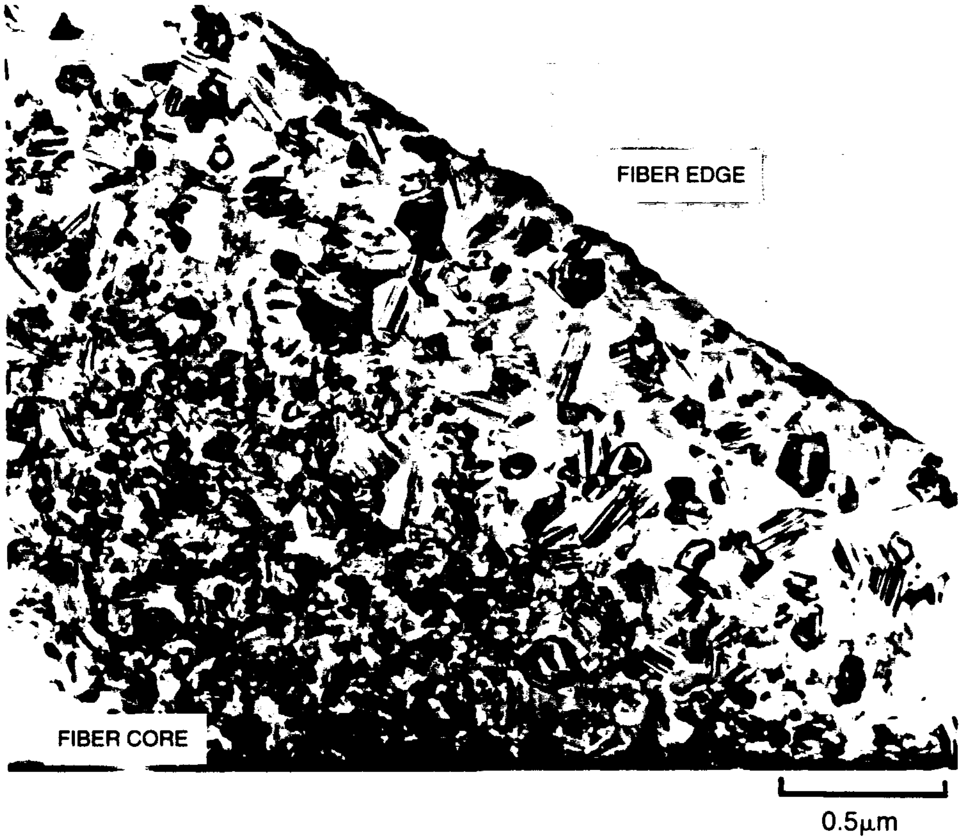
FIG. 13

HRTEM THIN FOIL ANALYSIS OF DOW CORNING SiC FIBER #9217-57C1 (BLACK)

92-4-13-11

FIG. 14

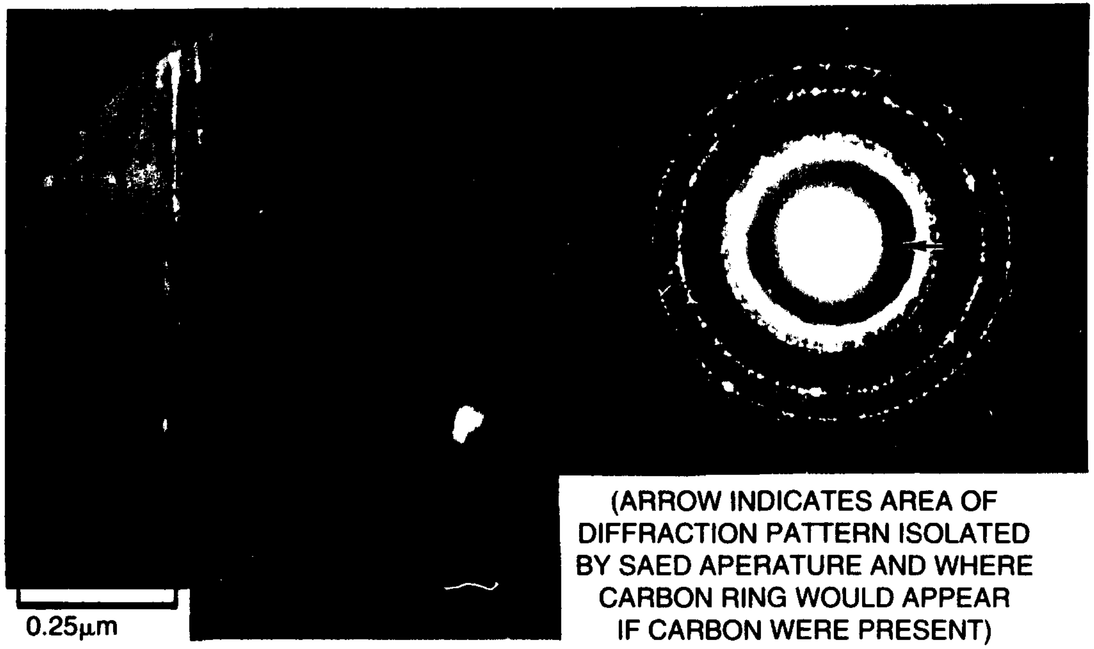
TEM THIN FOIL ANALYSIS OF DOW CORNING SiC FIBER #9217-53C1 (GOLD)



TEM THIN FOIL ANALYSIS OF DOW CORNING SiC FIBER #9217-53C1 (GOLD)

BF

DF



(ARROW INDICATES AREA OF DIFFRACTION PATTERN ISOLATED BY SAED APERATURE AND WHERE CARBON RING WOULD APPEAR IF CARBON WERE PRESENT)

C

Carbon

Graphite, syn

Rad: CuKa1 Lambda: 1.54178 Filter: d-sp: Calculated
Cutoff: Int: Calculated I/Icor:
Ref: Holcombe, USAEC Oak Ridge Y-12 Plant, Report Y1887 (1973), Private Communication, (1974)

Sys: Hexagonal S.G.: P63/mmc (194)
a: 2.456 b: c: 6.696 A: C: 2.7264
A: B: C: Z: 4 mp:
Ref: Ibid.

Dx: 2.26 Dm: SS/FOM: F19=280(.003,24)

ea: nwB: ey: Sign: 2V:
Ref:

Peak height intensities. CAS no.: 7440-44-0. C type. PSC: hP4. Mwt: 12.01.
Volume[CD]: 34.98.

d Å	Int.	h	k	l
3.348	100	0	0	2
2.127	3	1	0	0
2.027	15	1	0	1
1.795	3	1	0	2
1.674	6	0	0	4
1.5398	4	1	0	3
1.3154	1	1	0	4
1.2280	4	1	1	0
1.1529	6	1	1	2
1.1333	1	1	0	5
1.1160	1	0	0	6
1.0503	1	2	0	1
0.9902	4	1	1	4
0.9601	1	2	0	3
0.8724	1	1	0	7
0.8370	1	0	0	8
0.8328	1	2	0	5
0.8259	4	1	1	6
0.7982	2	2	1	1

beta-SiC

Silicon Carbide

Rad: Mo Lambda: 0.70930 Filter: d-sp:
Cutoff: Int: I/Icor:
Ref: For original reference see PDF card set prior to 1980.

Sys: Cubic S.G.:
a: 4.358 b: c: A: C:
A: B: C: Z: (4) mp:
Ref: Ibid.

Dx: 3.210 Dm: SS/FOM: F15=4(.113,37)

ea: nwB: ey: Sign: 2V:
Ref:

CAS no.: 409-21-2. Deleted by 29-1129. Mwt: 40.10. Volume[CD]: 82.77.

d Å	Int.	h	k	l
2.51	100	1	1	1
2.17	20	2	0	0
1.54	63	2	2	0
1.31	50	3	1	1
1.26	5	2	2	2
1.09	6	4	0	0
1.00	10	3	3	1
0.97	6	4	2	0
0.89	13	4	2	2
0.84	10	5	1	1
0.77	2	4	4	0
0.74	6	5	3	1
0.72	2	6	1	0
0.69	3	6	2	0
0.66	1	6	2	2

FIG. 15

FIG. 16

TEM THIN FOIL ANALYSIS OF DOW CORNING SIC FIBER #9217-53C1 (GOLD)

92-4-13-14

FIG. 17

HRTEM THIN FOIL CHARACTERIZATION OF DOW CORNING SiC FIBER #9217-53C1 ("GOLD") SHOWING LATTICE IMAGES OF SiC GRAINS AND GRAPHITE "RIBBONS" AT INTERGRANULAR AREAS

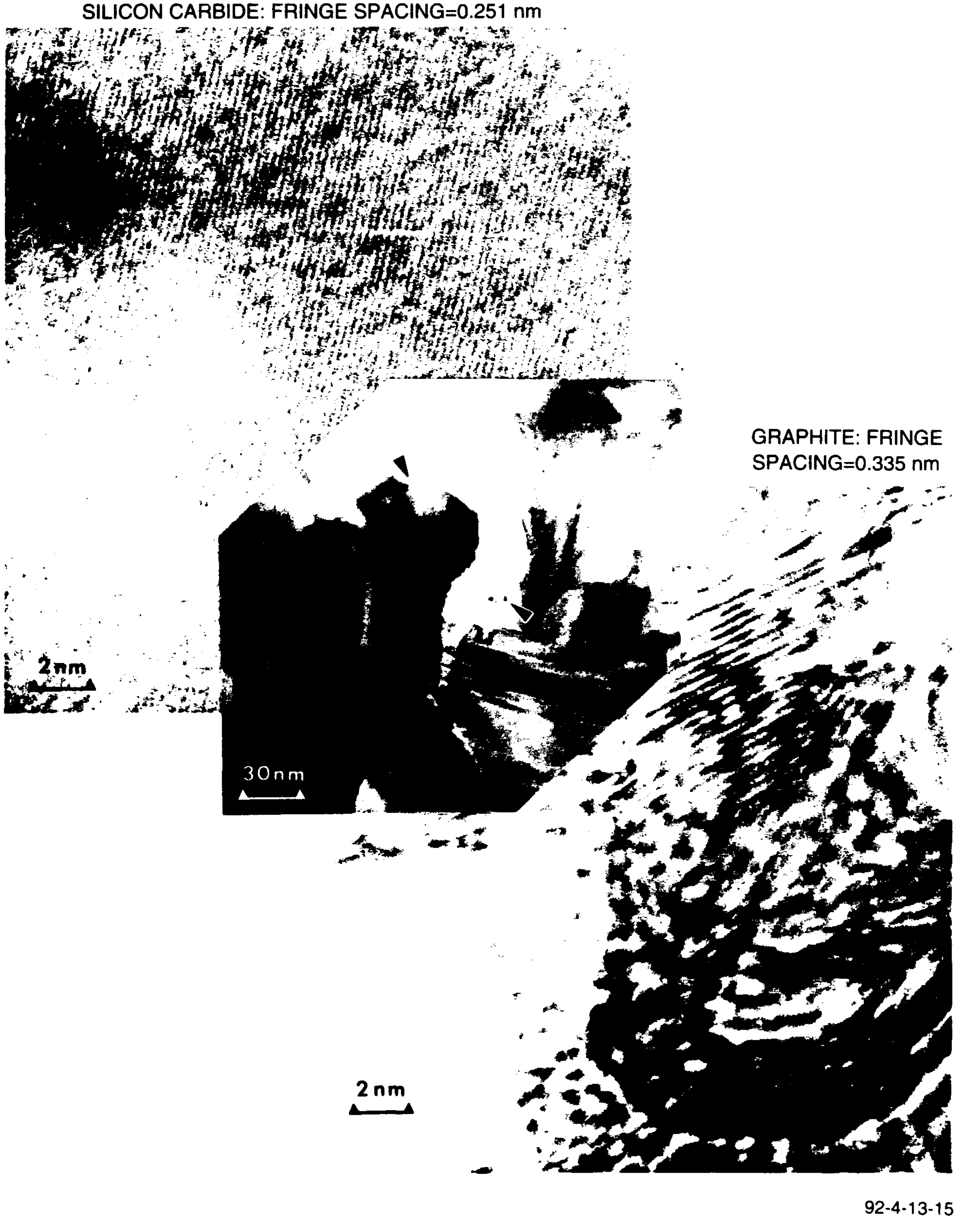


FIG. 18

TEM REPLICA AND THIN FOIL ANALYSIS OF LAS MATRIX/DOW CORNING SiC FIBER (9217-41C) COMPOSITE #1-91

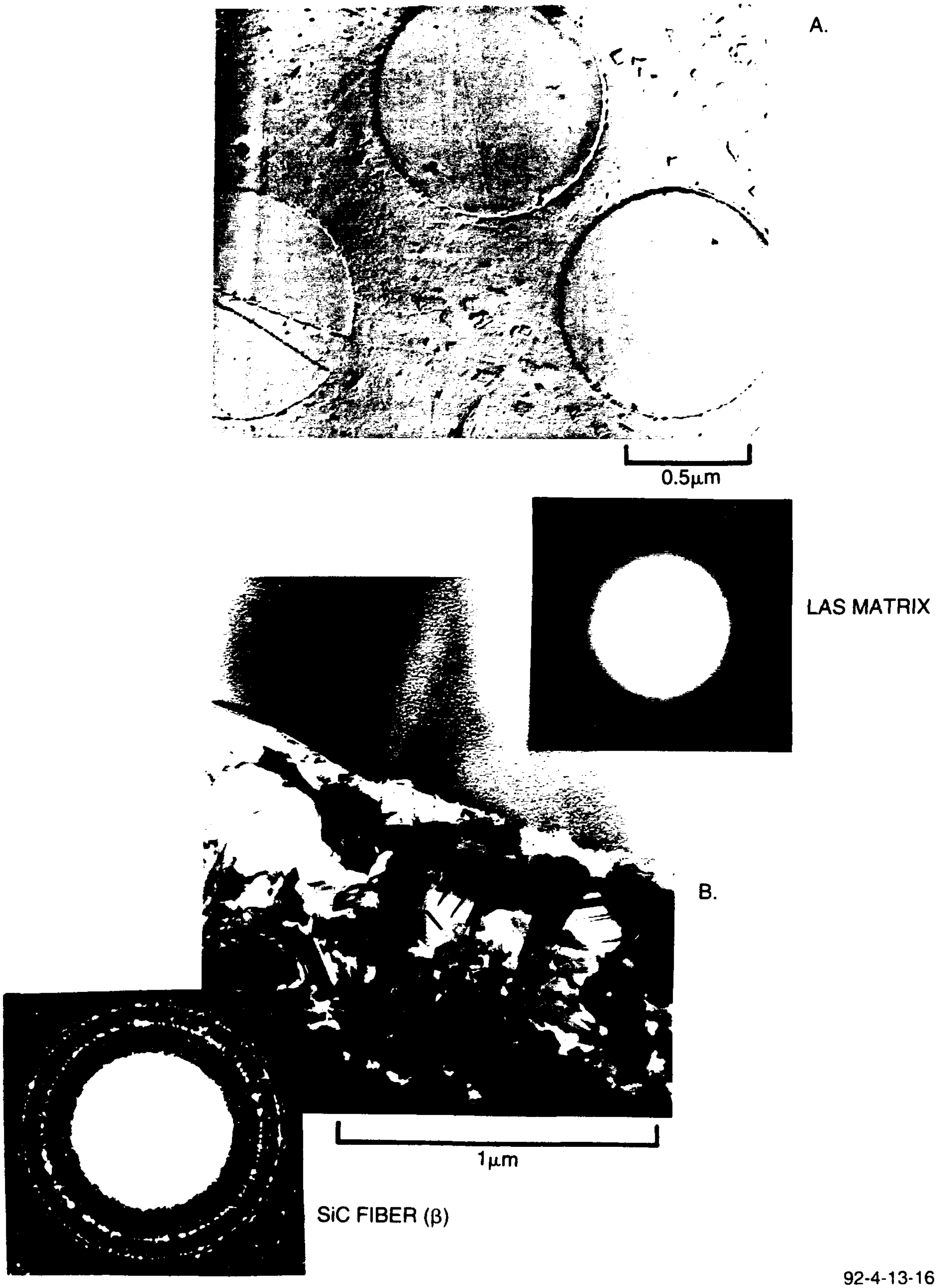


FIG. 19

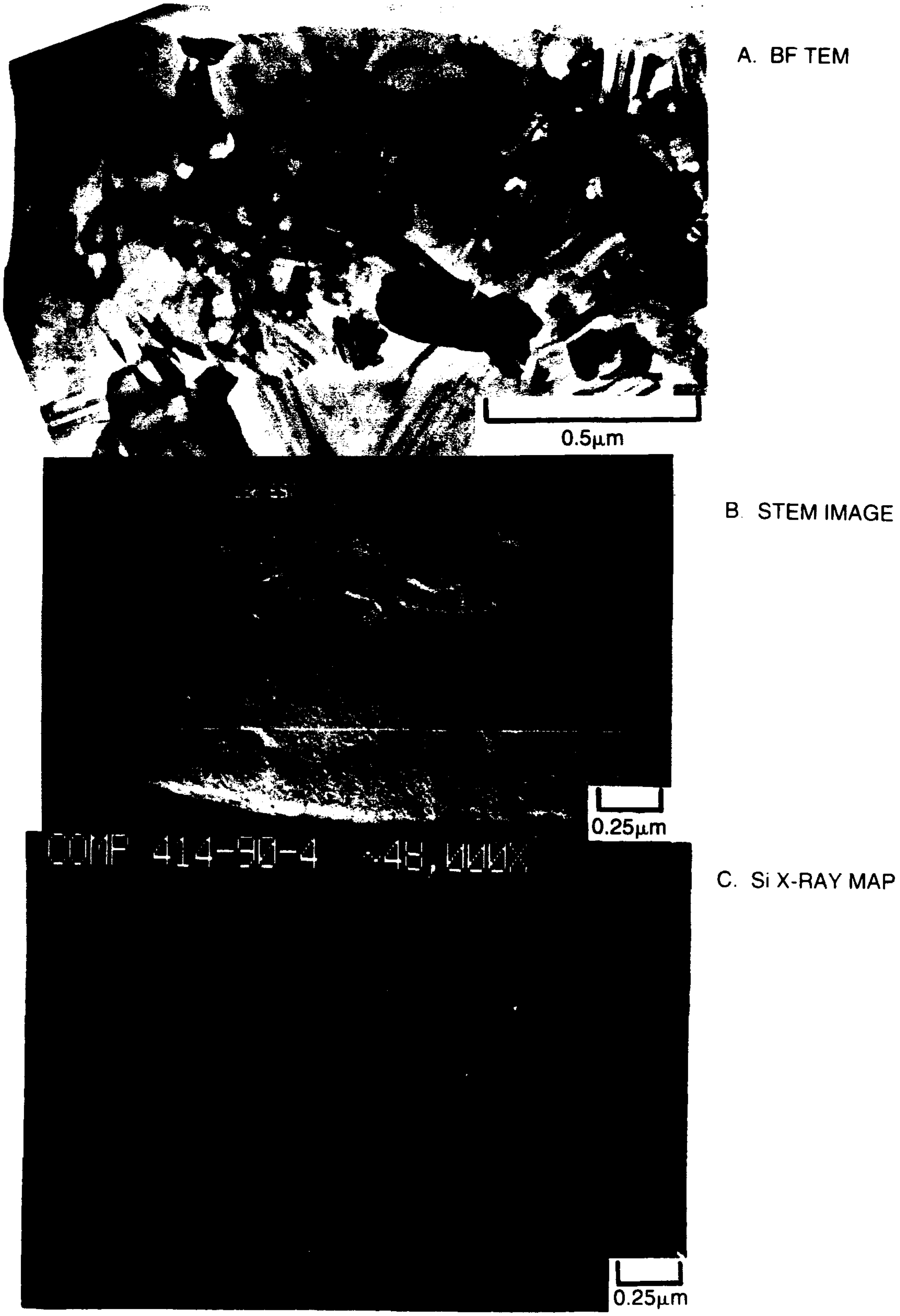
HRTEM THIN FOIL CHARACTERIZATION OF LAS MATRIX/DOW CORNING SiC FIBER (9217-41C) COMPOSITE #1-91 FIBER/MATRIX INTERFACE

(MATRIX/FIBER INTERFACE, FRINGE SPACING: 0.33 nm)

92-4-13-17

FIG. 20

TEM ANALYSIS OF DOW CORNING LOT 57C1 SiC FIBER IN LAS MATRIX COMPOSITE #414-90 (FOR PEELS ANALYSIS)



A. BF TEM

B. STEM IMAGE

C. Si X-RAY MAP

92-4-13-18

PEELS ANALYSIS OF DOW CORNING LOT 57C1 SIC FIBER IN LAS MATRIX COMPOSITE #414-90

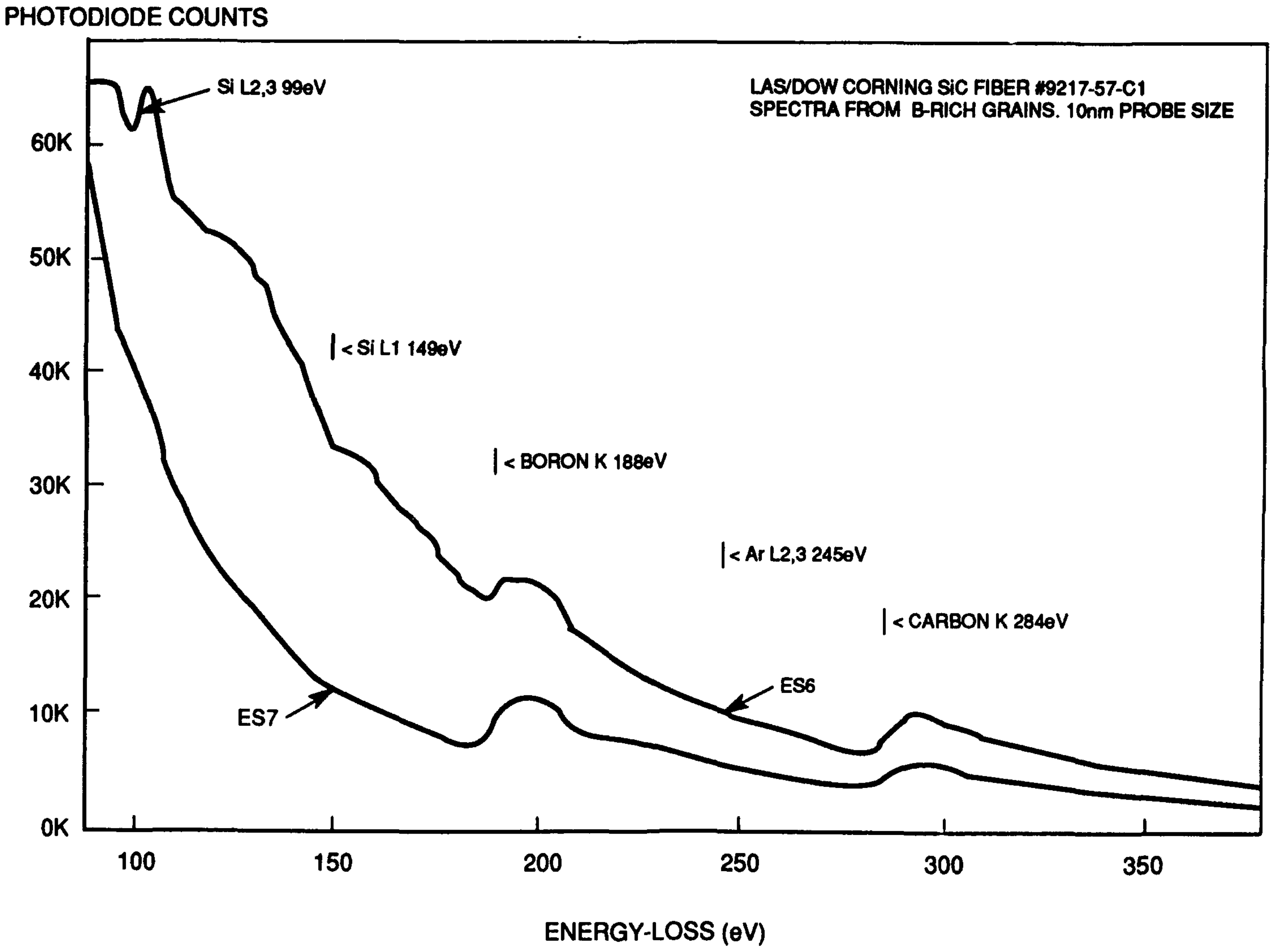
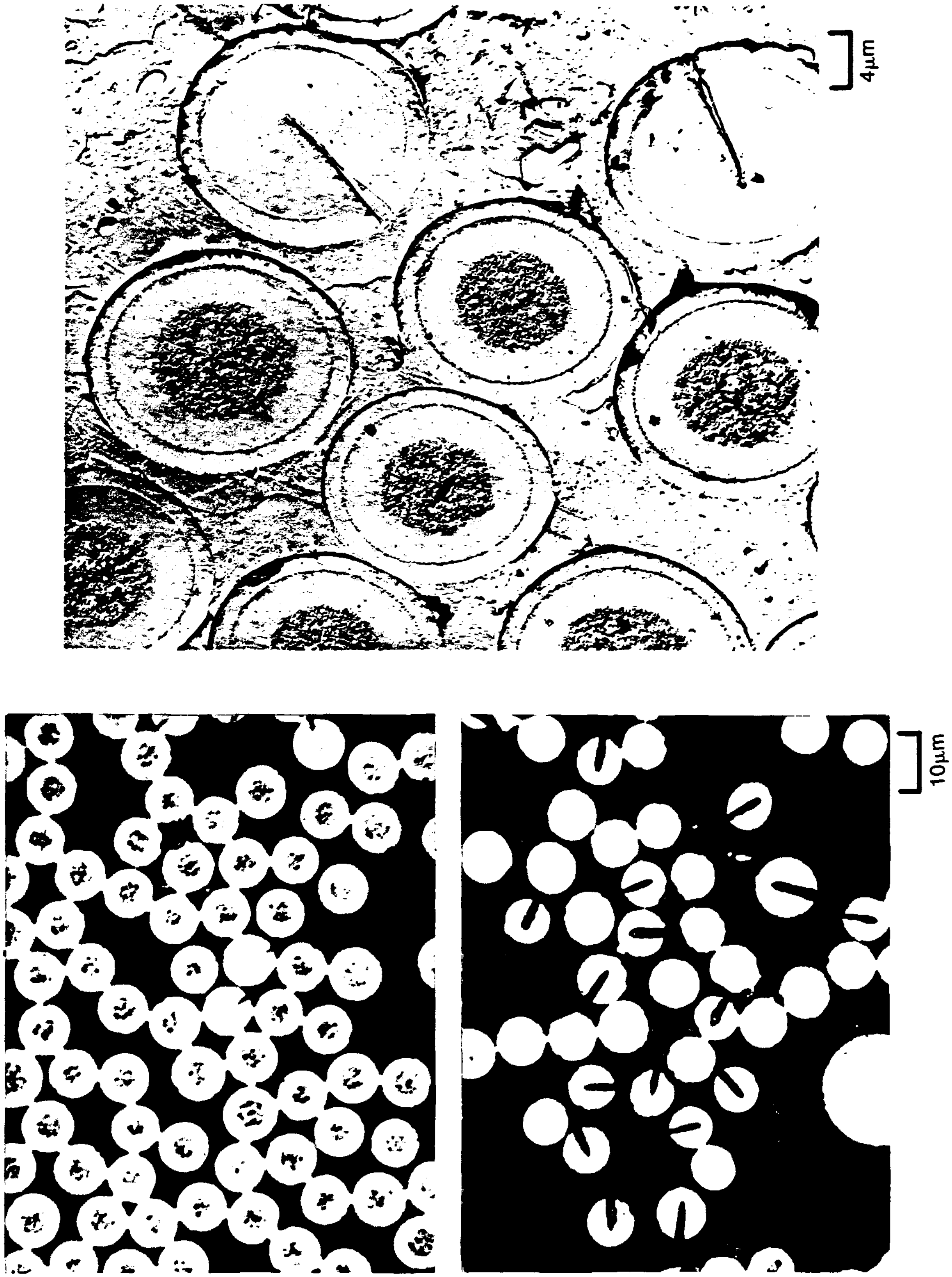


FIG. 21

FIG. 22

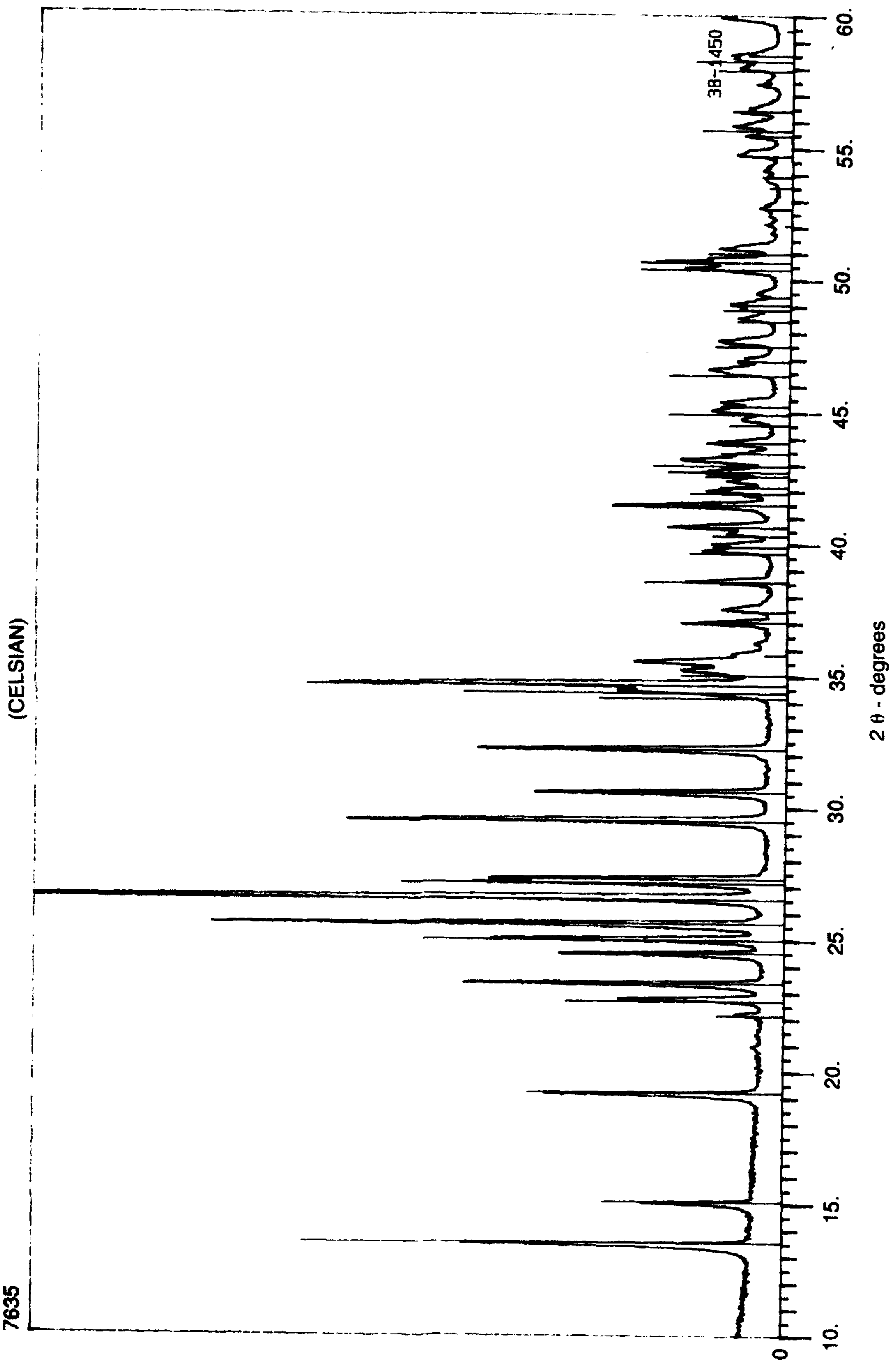


OPTICAL/TEM REPLICA CHARACTERIZATION OF BARIUM ALUMINOSILICATE (BAS) MATRIX/DOW CORNING CRYSTALLINE SIC FIBERS (LOT #9217-50C) (COMPOSITE #212-91) AS-PRESSED

FIG.23

X-RAY DIFFRACTION ANALYSIS OF BAS MATRIX / DOW CORNING SiC FIBER COMPOSITE #212-91

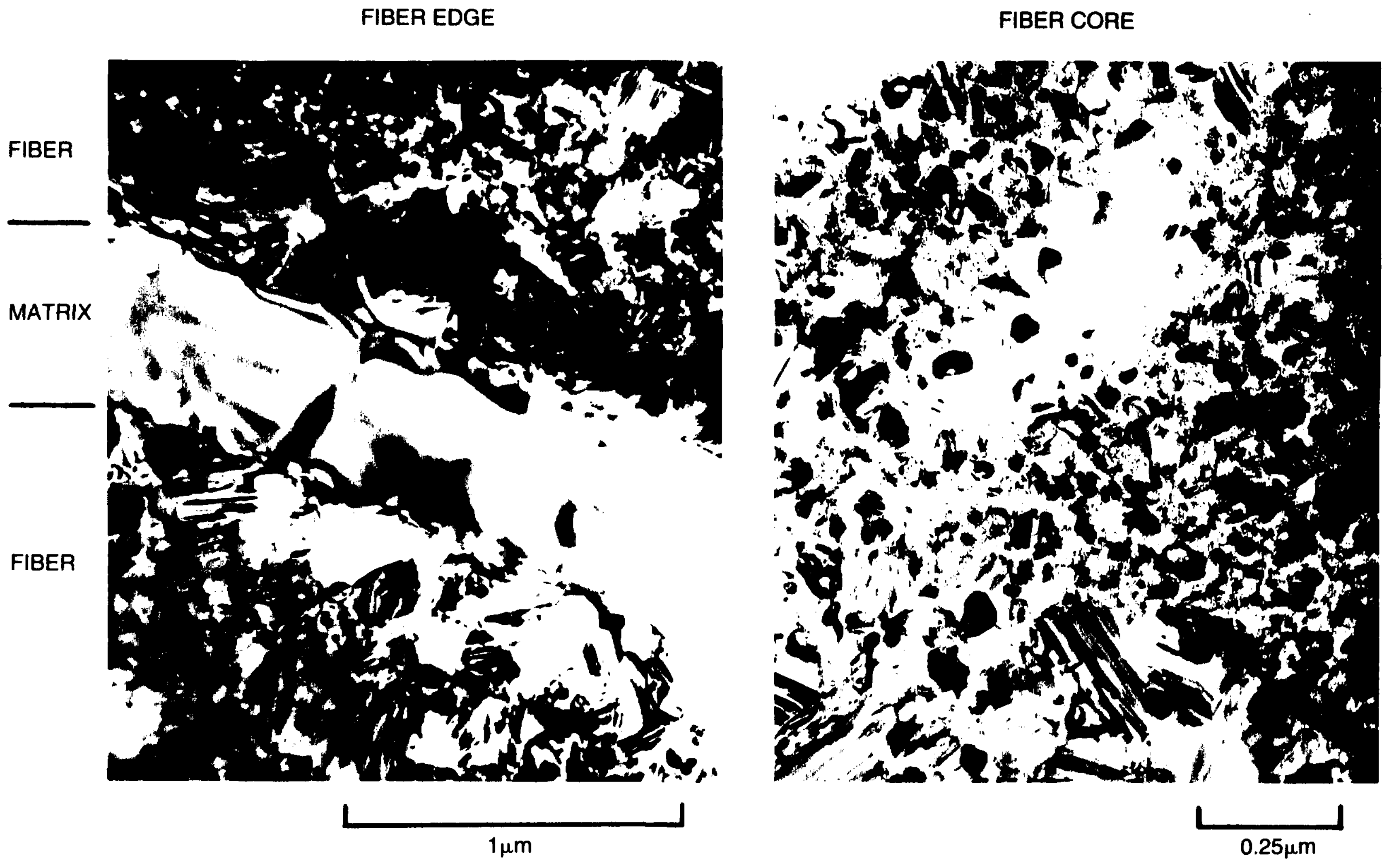
(CELSIAN)



92-4-13-21

FIG. 24

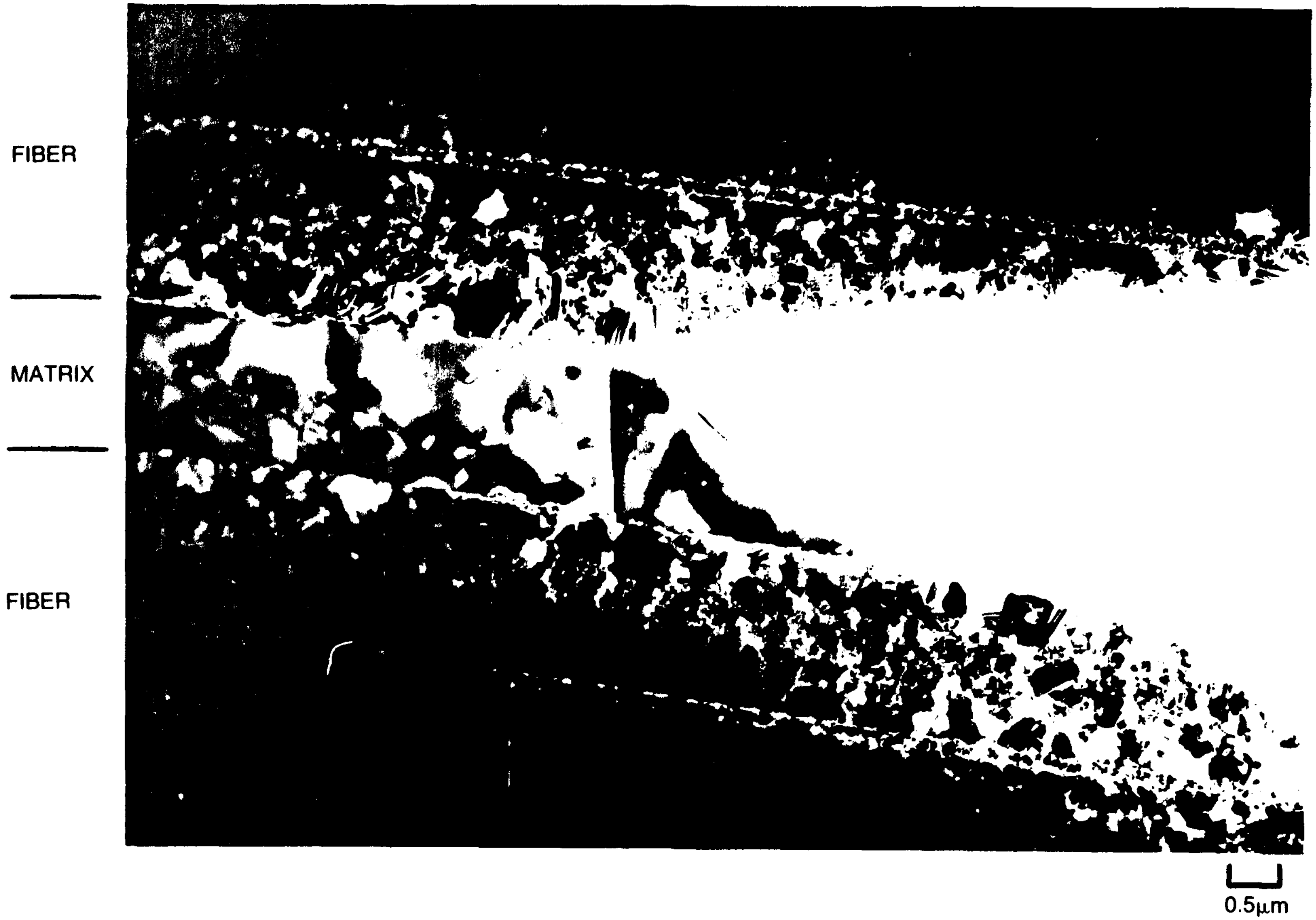
TEM THIN FOIL CHARACTERIZATION OF BARIUM ALUMINOSILICATE (BAS) MATRIX/DOW CORNING CRYSTALLINE SIC FIBERS (LOT #9217-50C) COMPOSITE - #212-91 (AS-PRESSED)



92-4-13-22

FIG. 25

TEM THIN FOIL CHARACTERIZATION OF BARIUM ALUMINOSILICATE (BAS)
MATRIX/DOW CORNING CRYSTALLINE SiC FIBERS (LOT #9217-50C)
COMPOSITE - #212-91



92-4-13-23

FIG. 26

TEM THIN FOIL CHARACTERIZATION OF BARIUM ALUMINOSILICATE (BAS) MATRIX/DOW CORNING CRYSTALLINE SiC FIBERS (LOT #9217-50C) COMPOSITE - #212-91

INTERNAL INTERFACIAL REGION

LATTICE SPACING=0.33 nm
GRAPHITE=0.336 nm
BN (HEX)=0.332 nm

92-4-13-24

FIG. 27

SAM DEPTH PROFILE
BAS MATRIX/DOW CORNING SiC FIBER (9217-50C) COMPOSITE #212-91 INTERFACIAL CHEMISTRY

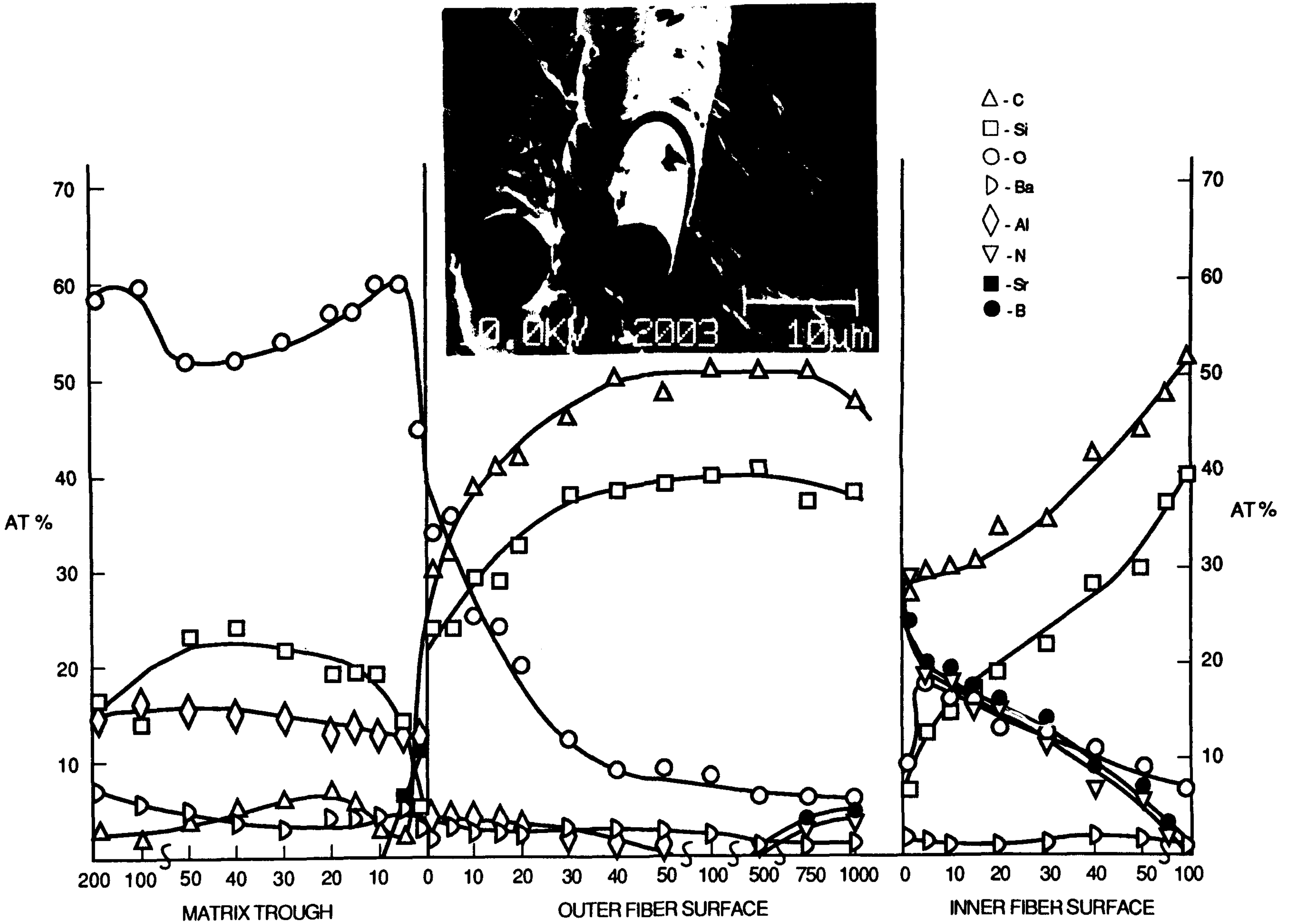


FIG. 28

SAM DEPTH PROFILE
TEXTRON "BLACK" FIBER (LOT 053-1A)

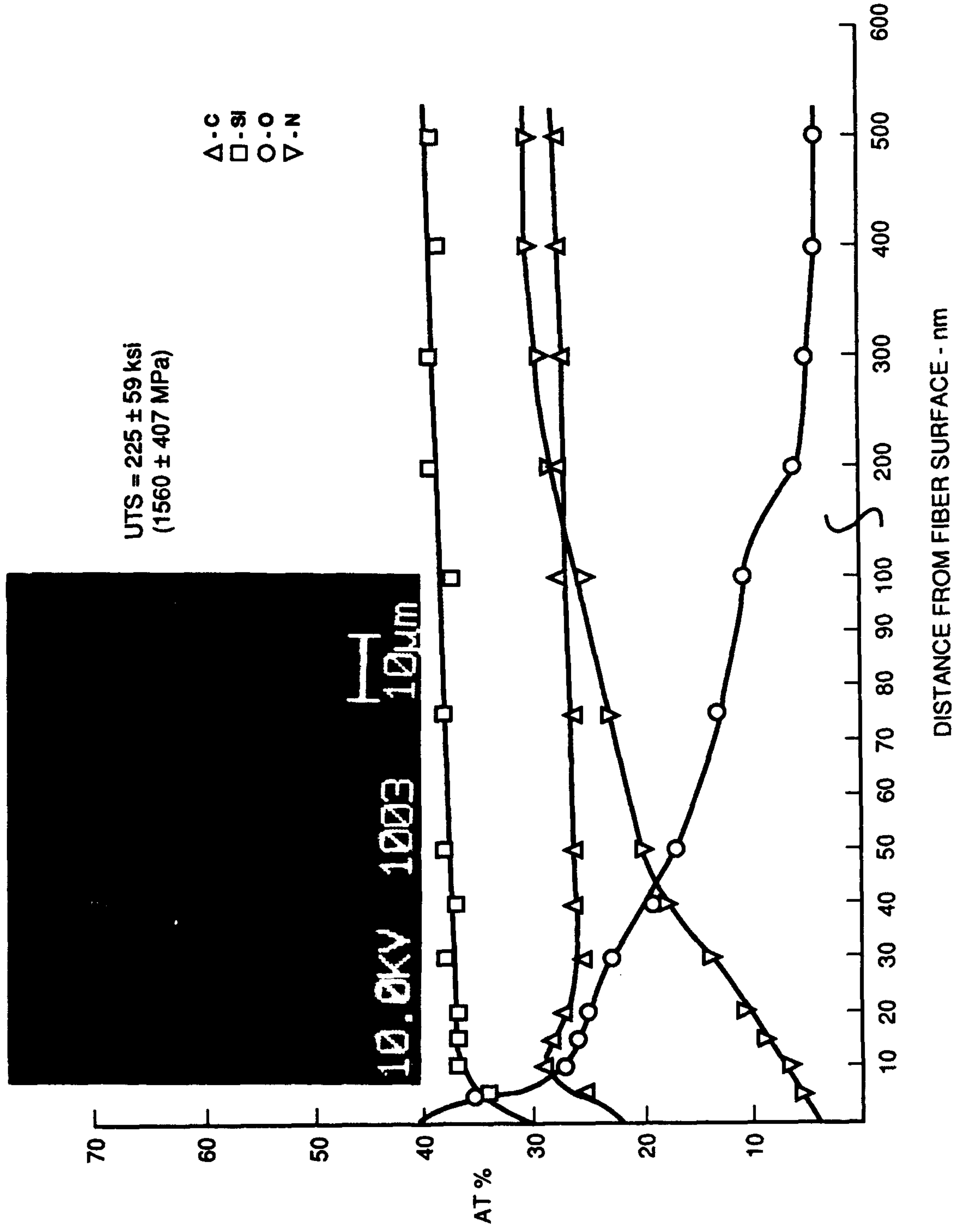
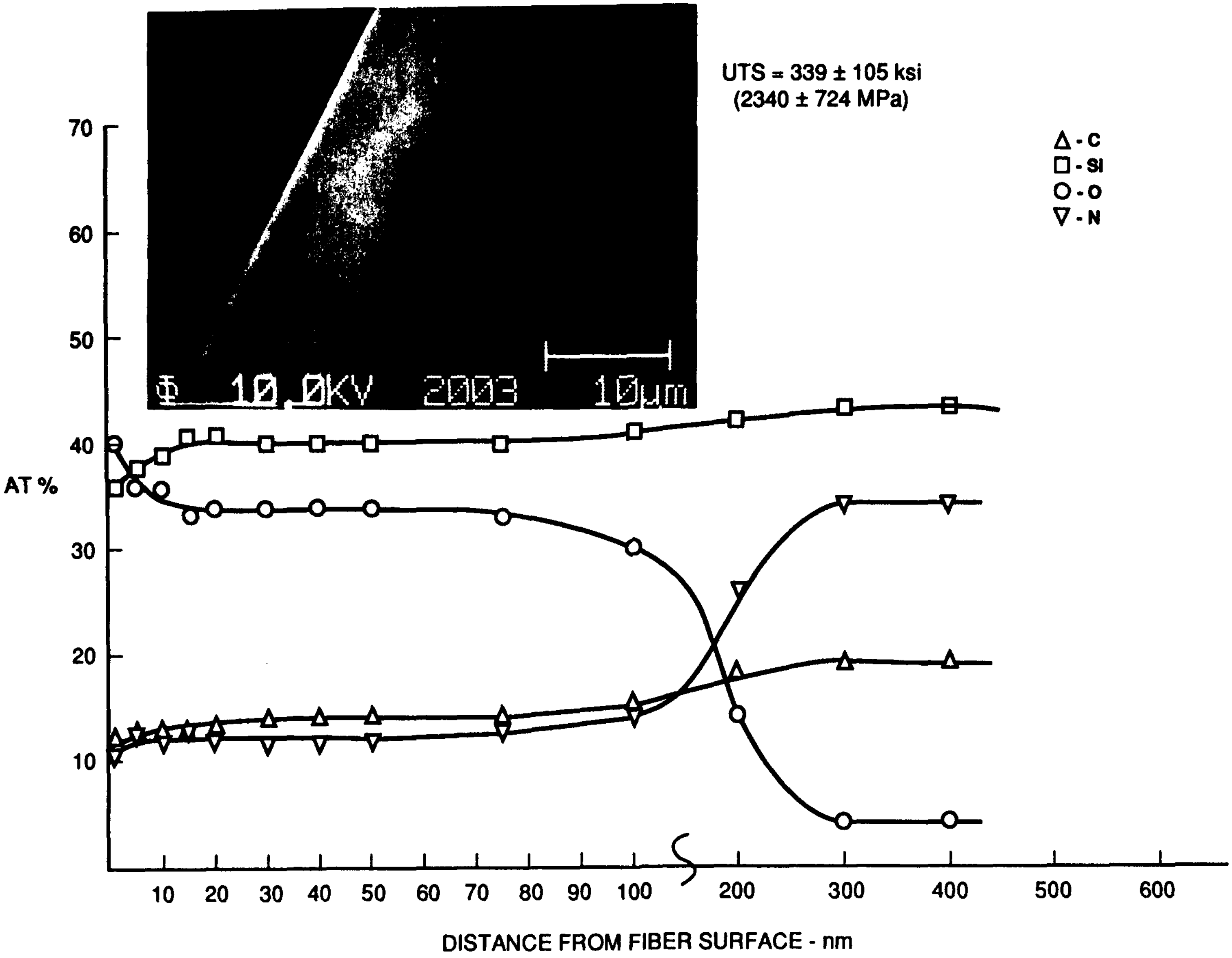


FIG. 29

SAM DEPTH PROFILE
DOW CORNING HPZ FIBER - LOT #100173 - 1 AS-RECEIVED



UTS = 339 ± 105 ksi
(2340 ± 724 MPa)

OPTICAL/TEM REPLICA CHARACTERIZATION OF TRANSVERSELY SECTIONED BMAS MATRIX/TEXTRON "BLACK" FIBER COMPOSITE - #239-91

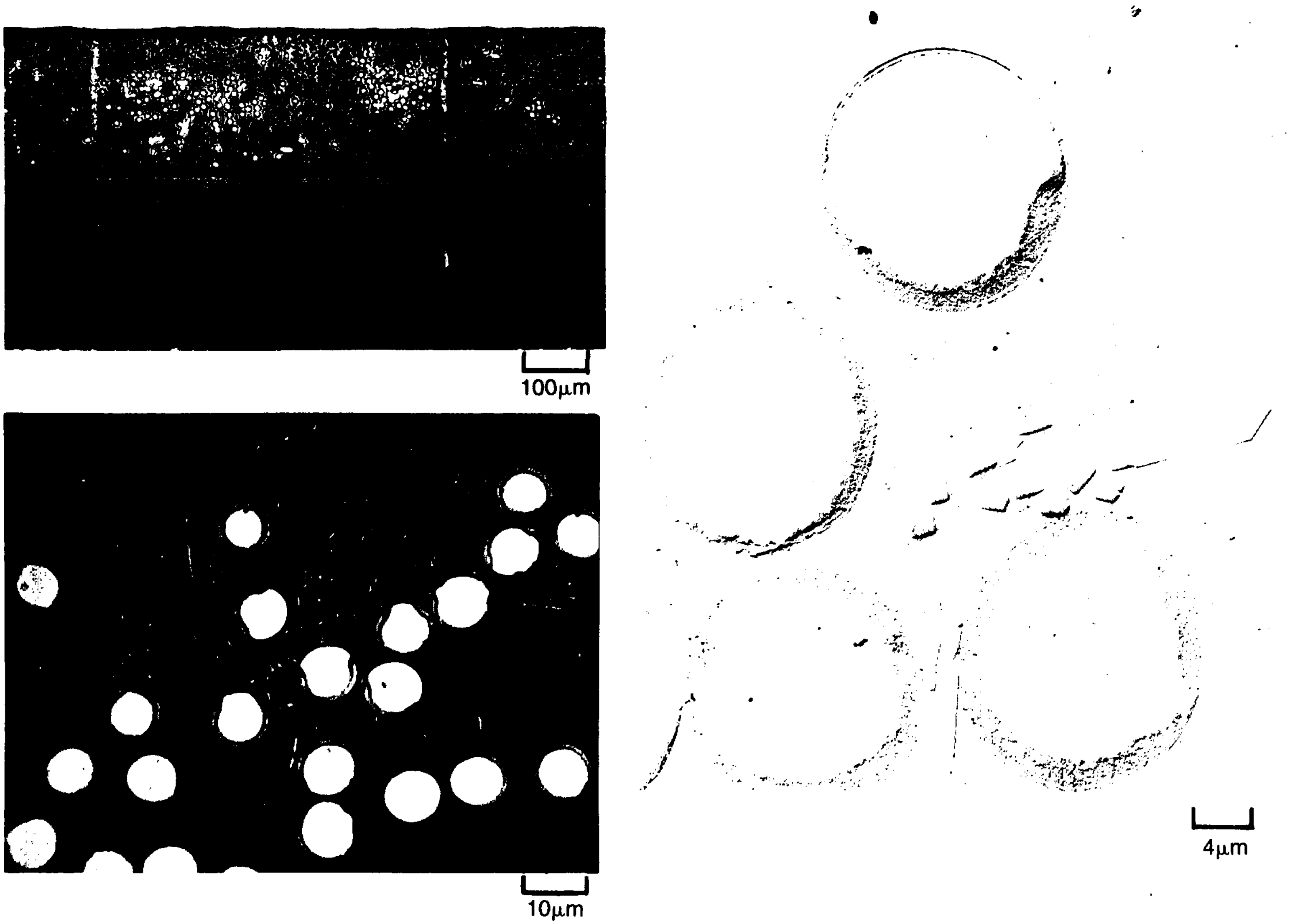


FIG. 30

TEM/EDX THIN FOIL CHARACTERIZATION OF LONGITUDINALLY SECTIONED BMAS MATRIX/TEXTRON "BLACK" FIBER COMPOSITE #239-91

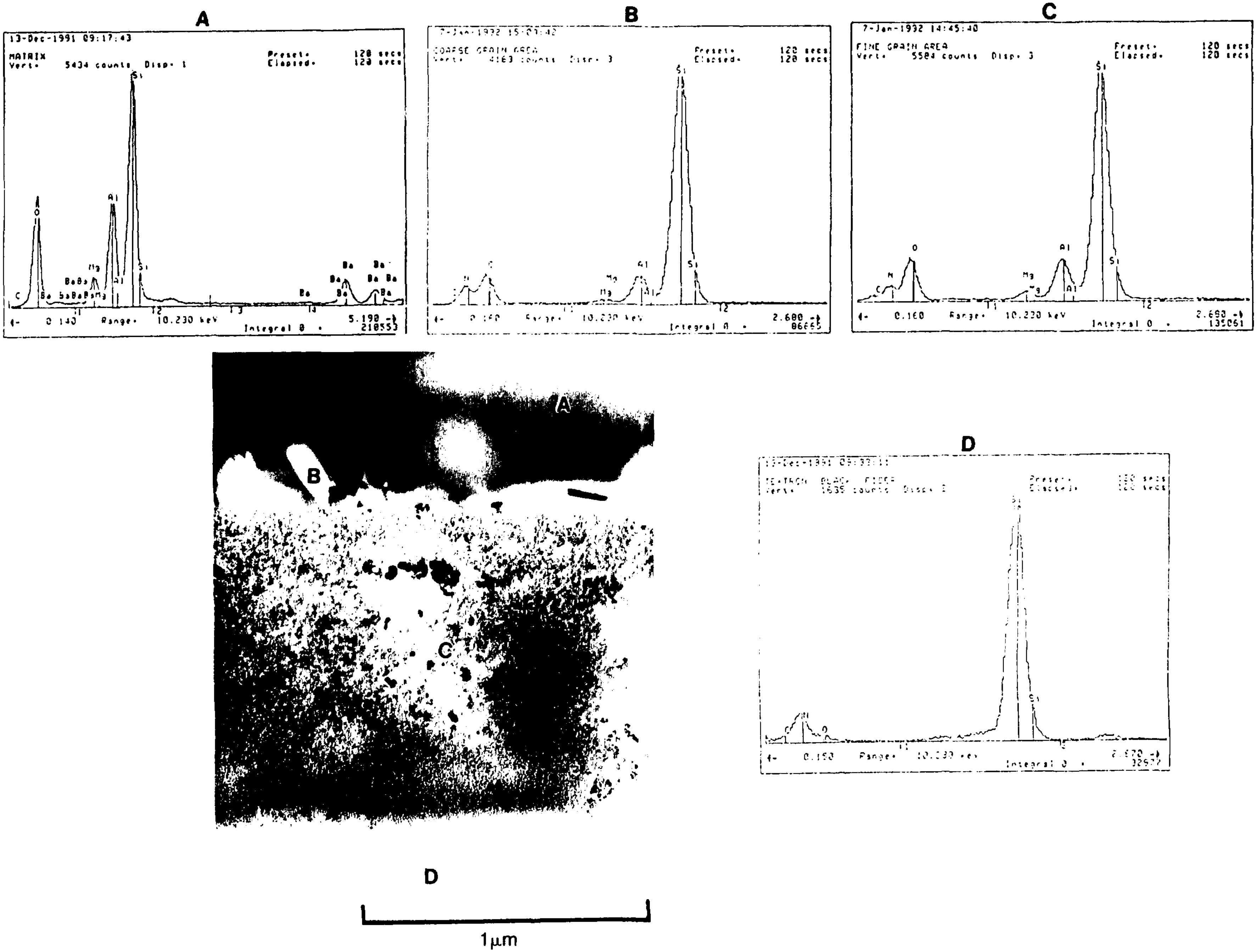
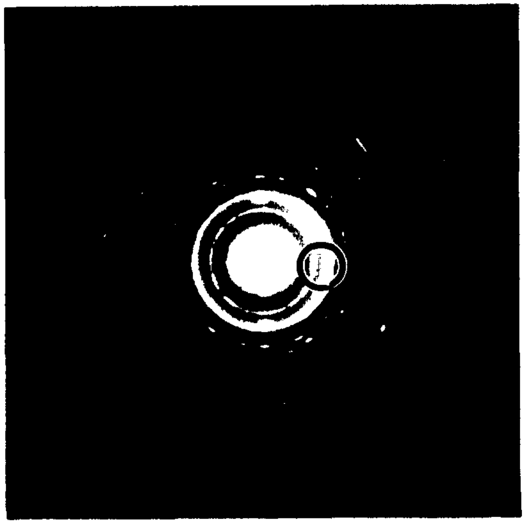
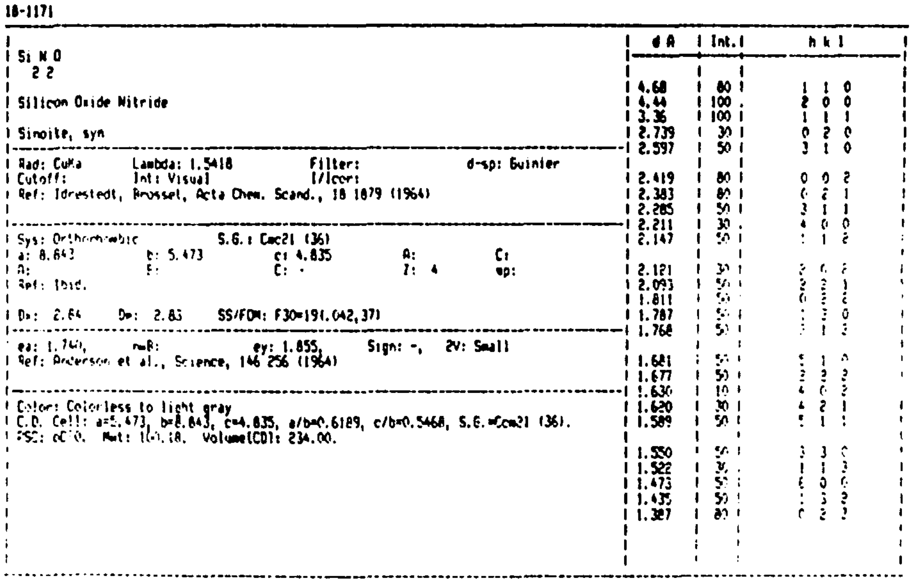


FIG. 31

TEM/SAED THIN FOIL CHARACTERIZATION OF LONGITUDINALLY SECTIONED BMAS MATRIX/TEXTRON "BLACK" FIBER COMPOSITE #239-91

DF





18-1171

Si_2N_2O

Silicon Oxide Nitride

Sinoite, syn

Rad: CuKa Lambda: 1.5418 Filter: d-sp: Guinier
Cutoff: Int: Visual I/Icor:
Ref: Idrestedt, Brosset, Acta Chem. Scand., 18 1879 (1964)

Sys: Orthorhombic S.G.: Cmc21 (36)
a: 8.843 b: 5.473 c: 4.835 A: C:
α: β: γ: - Z: 4 mp:
Ref: Ibid.

Dx: 2.84 Dm: 2.83 SS/FOM: F30=191(.042, 37)

εα: 1.740, nωβ: εγ: 1.855, Sign: -, 2V: Small
Ref: Andersen et al., Science, 146 256 (1964)

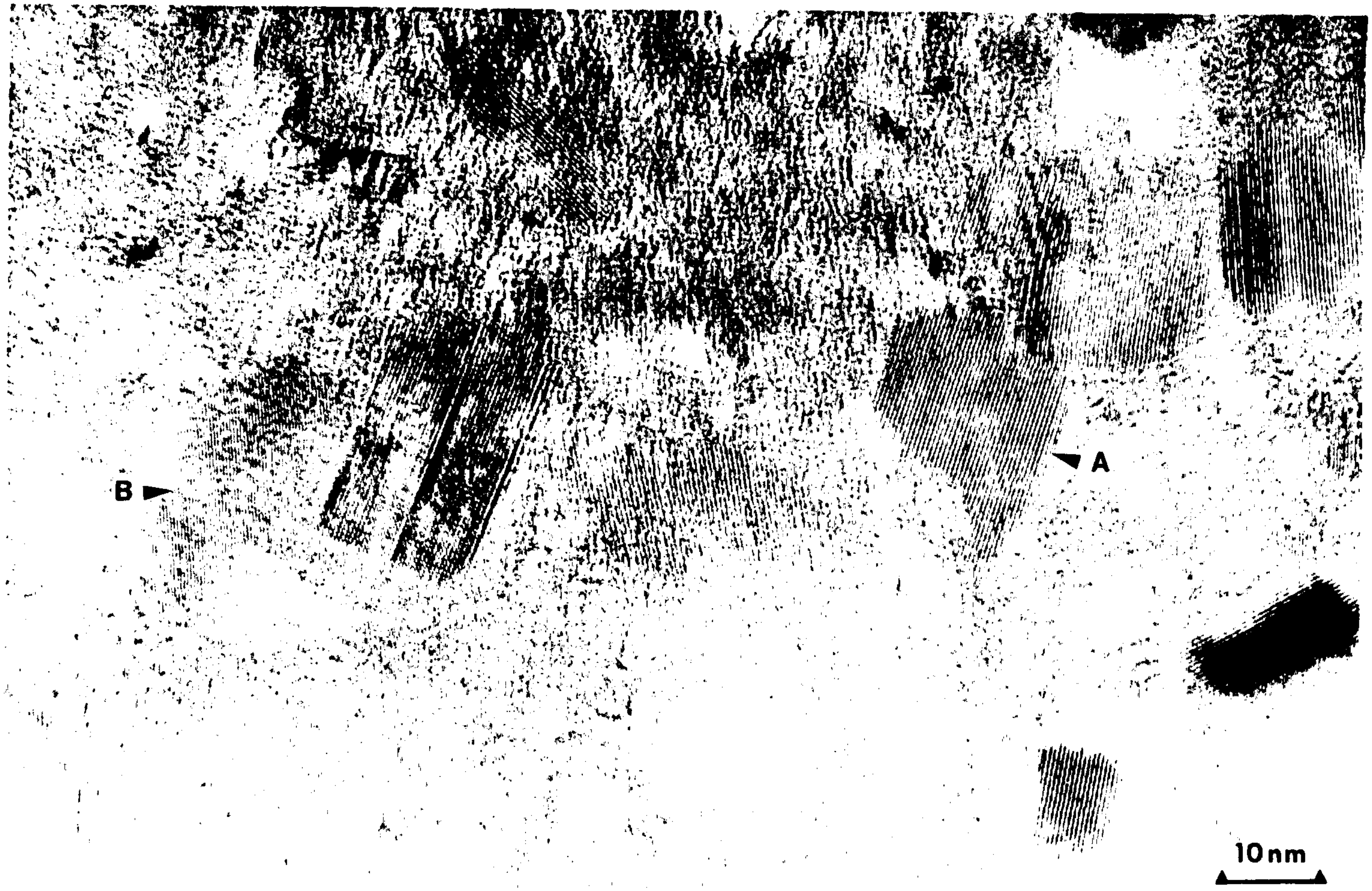
Color: Colorless to light gray
C.D. Cell: a=5.473, b=8.843, c=4.835, a/b=0.6189, c/b=0.5468, S.G.=Ccm21 (36).
PSC: oC20. Mwt: 100.18. Volume[CD]: 234.00.

d A	Int.	h k l
4.68	80	1 1 0
4.44	100	2 0 0
3.36	100	1 1 1
2.739	30	0 2 0
2.597	50	3 1 0
2.419	80	0 0 2
2.383	80	0 2 1
2.285	50	3 1 1
2.211	30	4 0 0
2.147	50	1 1 2
2.121	30	2 0 2
2.093	50	2 2 1
1.811	50	0 2 2
1.787	50	1 3 0
1.768	50	3 1 2
1.681	50	5 1 0
1.677	50	2 2 2
1.630	10	4 0 2
1.620	30	4 2 1
1.589	50	5 1 1
1.550	50	3 3 0
1.522	30	1 1 3
1.473	50	6 0 0
1.435	50	1 3 2
1.387	80	0 2 3

FIG. 32

TEM THIN FOIL CHARACTERIZATION OF LONGITUDINALLY SECTIONED BMAS MATRIX/TEXTRON "BLACK" FIBER COMPOSITE #239-91

SMALL GRAIN SIZE REACTION PRODUCT



FRINGE SPACING:
A=0.468 nm
(110) Si_2N_2O

B=0.336 nm
(111) Si_2N_2O

FIG. 33

TEM THIN FOIL CHARACTERIZATION OF LONGITUDINALLY SECTIONED
BMAS MATRIX/TEXTRON "BLACK" FIBER COMPOSITE #239-91

FIG. 34

FIG. 35

FRACTURE SURFACE OF A LOW OXYGEN NICALON FIBER (LOT 45)

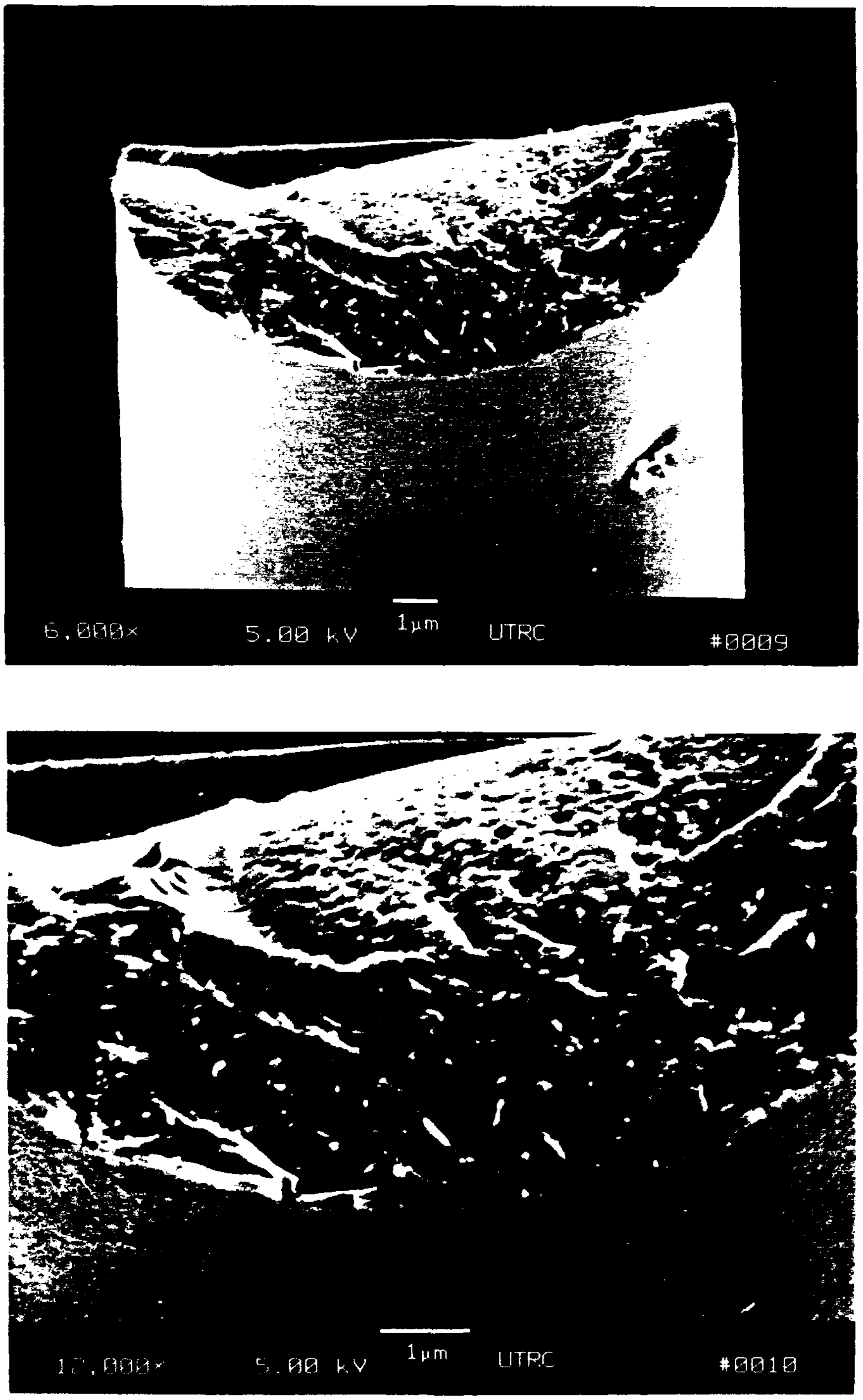


FIG.36

SAM DEPTH PROFILE
LOW OXYGEN NICALON FIBER - LOT 46

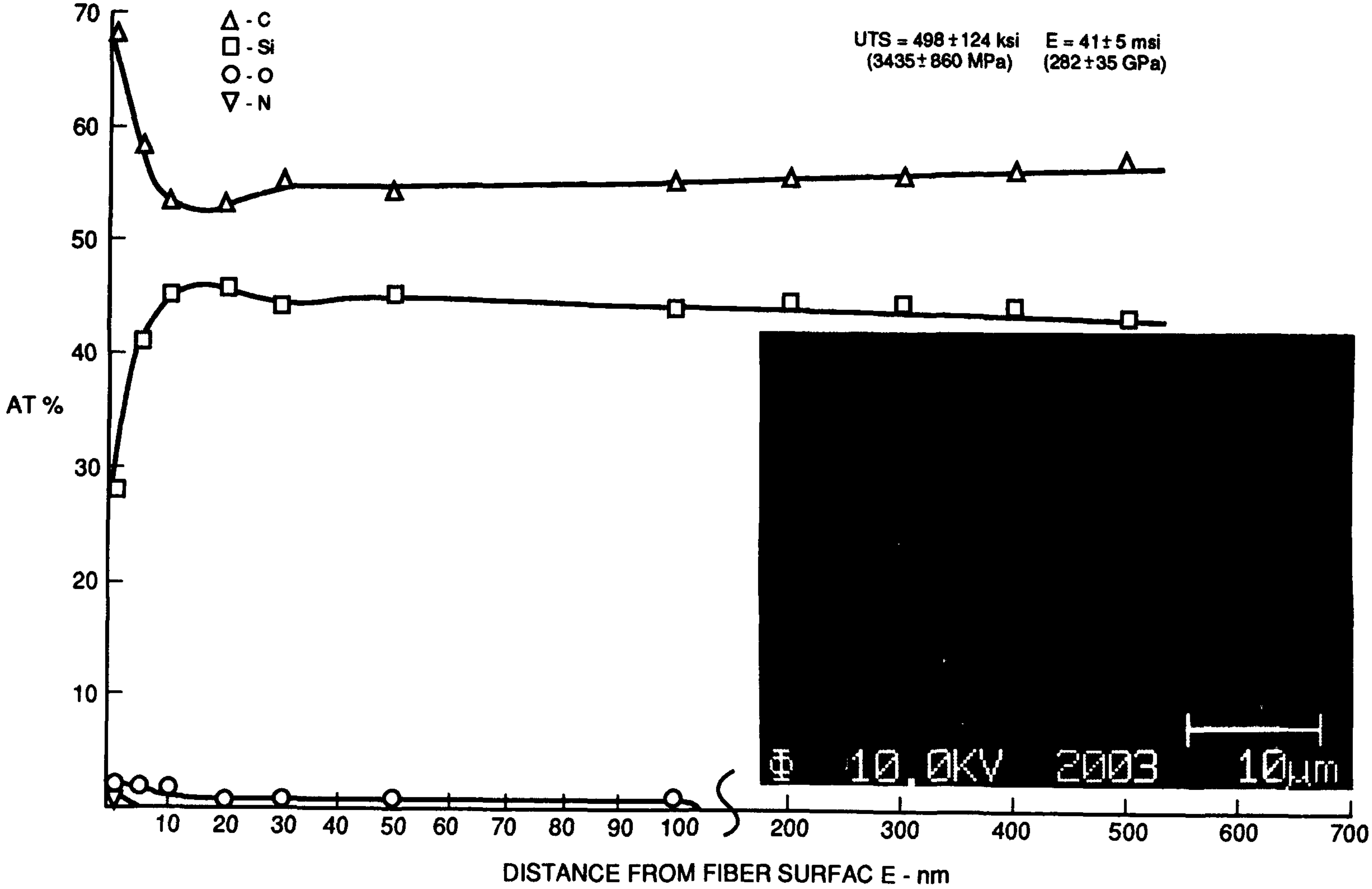
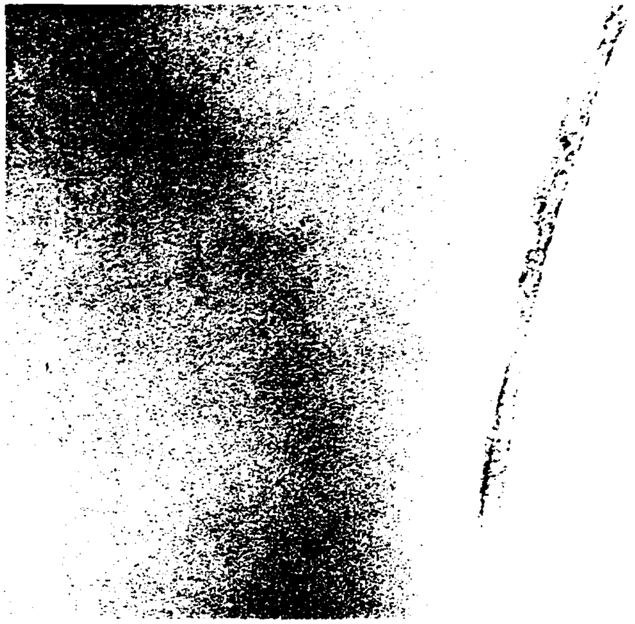
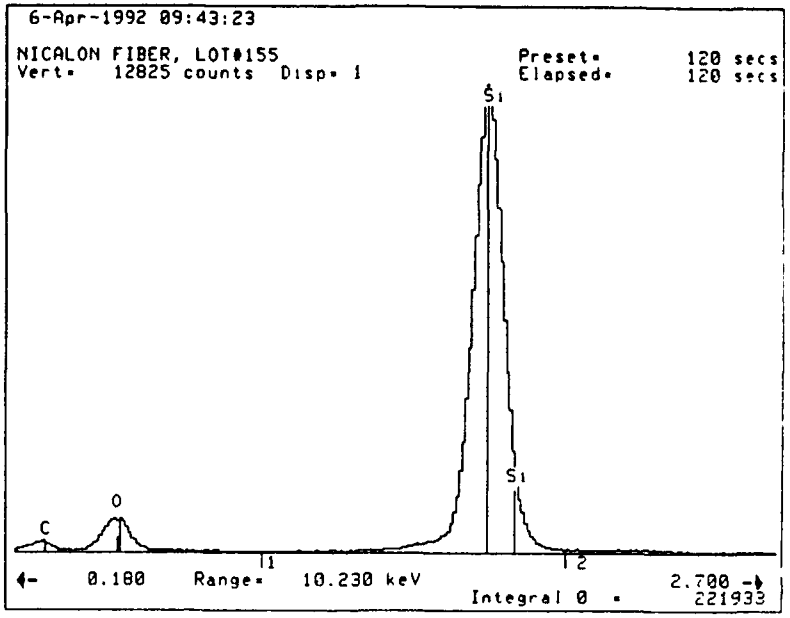


FIG. 37

TEM/EDX/SAED ANALYSES OF CERAMIC GRADE NICALON FIBER - LOT #155

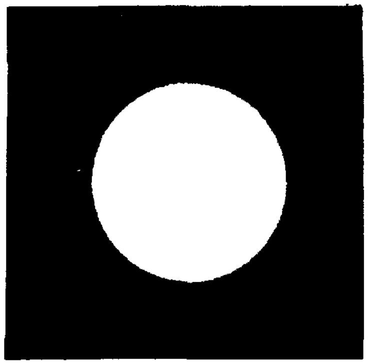
BF

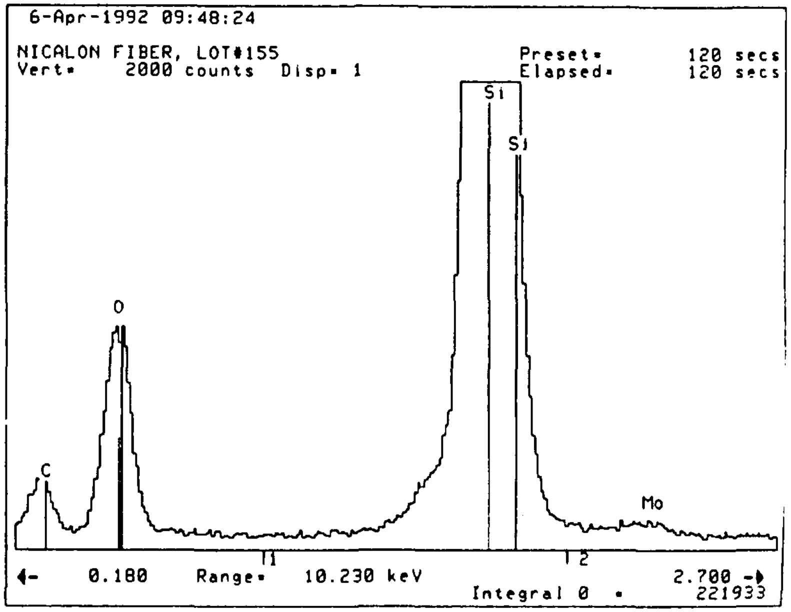




GRAIN SIZE (AVG)=2 nm

DF





TEM/EDX/SAED ANALYSES OF LOW OXYGEN NICALON FIBER - LOT #45

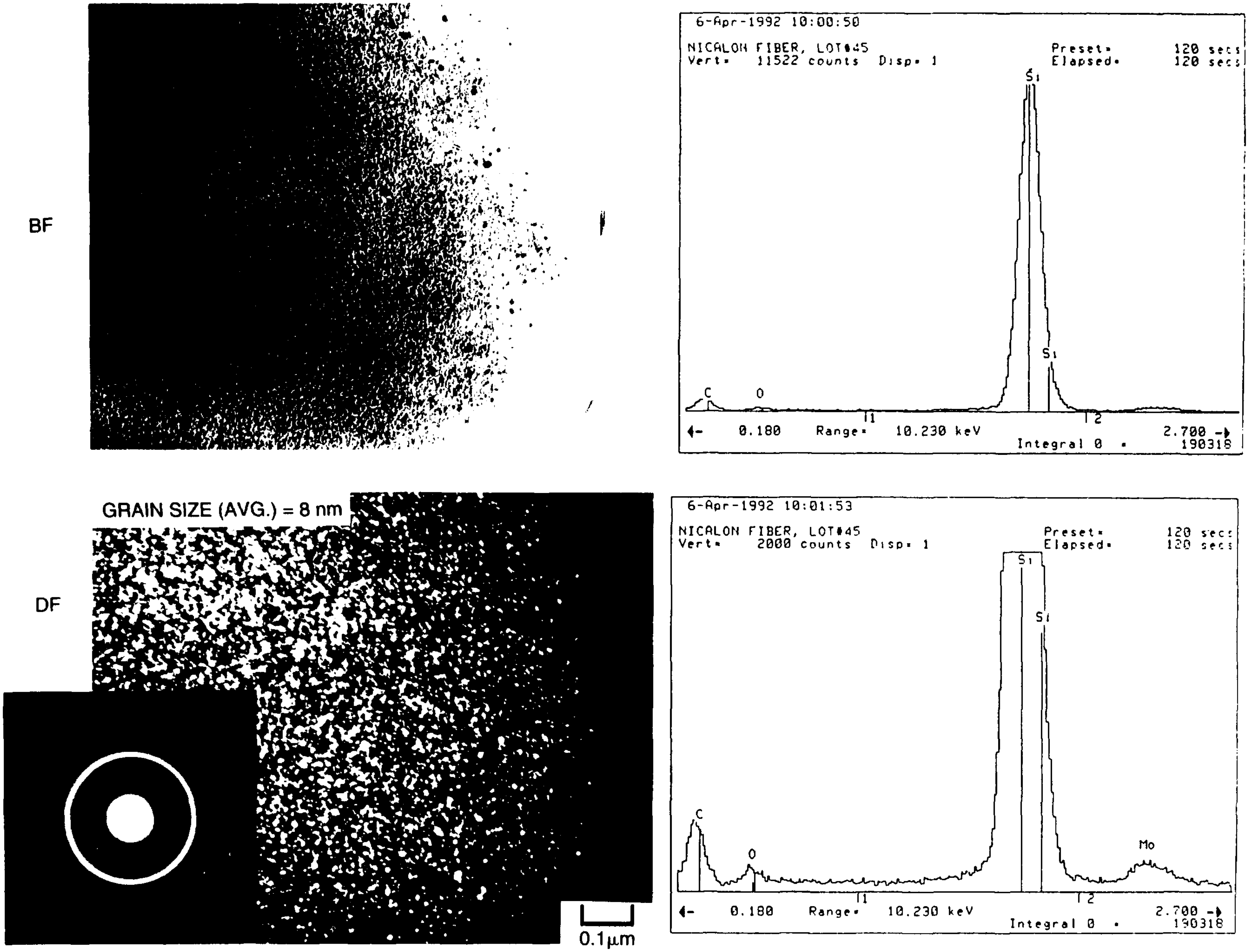


FIG. 38

92-4-13-36

FIG. 39

SAM DEPTH PROFILE
INTERFACIAL CHEMISTRY OF BMAS MATRIX/LOW OXYGEN NICALON (LOT 45) COMPOSITE #66-92