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

**Prepared by
J. J. Brennan**

ANNUAL REPORT

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Only gram quantities of the Dow Corning crystalline SiC fibers were available during the first year of the program, thus, emphasis was placed on the mechanical, chemical, and microstructural characterization of the fibers themselves, as well as their fracture behavior, bonding characteristics, and interfacial compatibility with various glass-ceramic matrices. It was found that most of the SiC fiber lots from Dow Corning consisted of basically stoichiometric SiC (β -SiC) with a small amount of boron, with the fiber surface composition ranging from carbon rich to high boron plus nitrogen content. The grain size of these fibers averaged ~ 1500 - $2000\text{\AA}$ with some fibers exhibiting larger grains (3000 - $4000\text{\AA}$) near free surfaces with the fiber interior consisting of a mixture of smaller grains ($\sim 1000\text{\AA}$) surrounded by an extremely fine grained ($<100\text{\AA}$) structure which has as yet not been positively identified. Most of the SiC fiber/glass-ceramic matrix couples exhibited fiber/matrix interfacial debonding upon fracture and a very thin ($<200\text{\AA}$) carbon rich interfacial layer from scanning Auger analysis. However, examples within the same sample of very strong fiber/matrix bonding and no interfacial carbon layer formation could often be found. It appears that fiber surface compositional variability is playing a role in these observations. Questions dealing with fiber surface chemistry and structure, fiber strength and thermal stability, reproducibility and scale-up to larger fiber quantities for actual composite fabrication and testing, and the reactivity and bonding characteristics of the fibers with refractory glass-ceramic matrices are scheduled to be addressed during the second year of this program.



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

ANNUAL REPORT

Contract N00014-87-C-0699

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

SUMMARY

The main objective of this program is to characterize the chemistry and structure of new advanced small diameter SiC type 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 first year of this program included the new experimental polymer derived crystalline SiC fibers from Dow Corning Corp., as well as the new commercially available low oxygen "Lox M" Tyranno SiC type fibers from Ube Industries. Since the availability of the Dow Corning SiC fibers was limited, emphasis during the first year of this program 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.

The 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 $\sim 500\text{\AA}$ 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.

The Dow Corning crystalline SiC fibers appear to be in a very early stage of development. Of the seven small lots of fiber evaluated at UTRC, 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 $\sim 1500\text{\AA}$ for some fibers to a dual grain size morphology that consisted of rather large grains ($3000\text{-}4000\text{\AA}$) near the fiber surface to medium sized ($1000\text{-}1500\text{\AA}$) grains surrounded by an extremely fine grained ($<100\text{\AA}$) structure near the center of the fibers. Electron diffraction analysis of the medium to large grains indicated that they consist almost exclusively of $\beta\text{-SiC}$. The extremely fine grained structure is yet to be determined. 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 ($<200\text{\AA}$) 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 may be present at some of the fiber/matrix interfaces. High resolution TEM (HRTEM) will be necessary to characterize the exceedingly fine structure observed.

It appears that the Dow Corning crystalline SiC fibers may have potential as reinforcement for advanced refractory glass-ceramic matrices. However, a number of questions remain to be answered pertaining to the chemistry of the fibers, both overall and surface related, the strength of the fibers and their thermal stability at elevated temperatures, the reproducibility and scale-up of continuous fiber, and the reactivity and bonding characteristics of the fibers with refractory glass-ceramic matrices. The next year of effort under this program will attempt to address these questions.

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-ceramics¹⁻⁴ as well as whisker reinforced crystalline ceramics⁵⁻³⁴, and continuous fiber reinforced ceramics produced by methods that include hot-pressing of glasses and glass-ceramics³⁵⁻⁵⁰, sol-gel infiltration and pyrolysis of ceramics⁵¹, polymer precursor infiltration and pyrolysis⁵², reactive oxidation of metals⁵³, reactive sintering⁵⁴, and chemical vapor infiltration (CVI) of silicon based ceramics⁵⁵⁻⁶⁶.

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 decade, 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 fabrication⁶⁸. 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, and, if available, Textron's "Black" (Si-C-N-O) small diameter fiber, as well as sintered SiC fibers under development at Carborundum and DuPont. 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. 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 first year (Feb. 1, 1990 - Feb. 1, 1991) 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-0096⁶⁷, 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 composites⁵⁰.

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 zone⁶⁷, 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 new 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 Corning⁶⁹, the 10 μ m 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, since the availability of the Dow Corning SiC fibers was limited, 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.

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^{70,71} 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^{72,73} 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 during the first year of the program towards the evaluation of the interfacial chemistry and morphology, as well as composite properties, of the Lox M Tyranno fiber in both LAS and BMAS matrices.

III. TECHNICAL DISCUSSION

A. Materials

The fibers utilized during the first year of the program consisted of low oxygen "Lox M" Tyranno SiC fiber from Ube Industries, Ltd., Ube City, Japan, and distributed in the US by Textron Specialty Materials, Lowell, MA, as well as very small quantities of several different lots of crystalline SiC fiber from Dow Corning Corp., Midland, MI. As mentioned in the Background section of this report, sintered SiC fiber from both DuPont and Carborundum was attempted to be obtained for evaluation under this program, without success.

The Lox M Tyranno SiC fiber was obtained on continuous length (1000 m) spools of 400 filaments per tow. The average fiber diameter and RT tensile strength as measured at UTRC was 8.9 μm and 368 ksi (2530 MPa), respectively. The Dow Corning crystalline SiC fiber was obtained in short lengths (~8 cm) equivalent to either one tow or several tows formed into a mat. Additional characterization data on these fibers will be given in a later section of this report.

The glass-ceramic matrix materials used during the first year of this program consisted of two lithium aluminosilicate (LAS) matrices, with and without a small amount (3.4 wt%) of boron oxide additive (LAS-A and LAS-C in Ref. 67), and a barium-magnesium aluminosilicate (BMAS) matrix. Both of the LAS matrices, when heat-treated or "ceramed" at 900°C for 24 hrs, crystallized to the β -quartz/silica solid solution phase, while the BMAS matrix, when ceramed at 1200°C for 24 hrs, crystallized to the barium osumilite phase. All of the matrix materials were received as glassy powder of 5-15 μm average particle size.

B. Fiber Characterization

1. Lox M Tyranno Fiber

About the only characterization conducted on the Lox M Tyranno fiber itself, other than the RT UTS data previously discussed, was a scanning Auger (SAM) depth profile of a flame desized fiber surface to a depth of 4000Å. This analysis is shown in Fig. 1, and indicates that, other than the expected oxygen rich surface, the fiber composition is ~50 at% C, 38% Si, 10% O, and 2% Ti. Except for the Ti, this composition is very similar to previously reported⁵⁰ SAM depth profile data for NICALON fiber. It is, however, different from earlier data obtained on Tyranno fiber (Type TRN-M401)⁷⁰ in that the oxygen content is considerably less for the Lox M fiber (10% vs 17-20%).

2. Dow Corning Crystalline SiC Fibers

During the first year of the program, seven different lots of Dow Corning crystalline SiC fibers were received at UTRC. Three of these lots consisted essentially of single tows of fiber about 6 cm long. The other four lots, three of which came directly from Dow Corning and one of which was sent to UTRC by Ms. Janet Hurst of NASA-Lewis, consisted of mats of fiber of dimensions ~8-9 cm in length by 4-7 cm in width, with ~1 gm of fiber in each mat. Figure 2 shows these mats of fiber and their lot numbers. From this figure, it can be seen that lot 53C1 tended to be rather gold in color, as did lot 41C to a somewhat lesser extent, while lots 50C and 57C1 ranged in color from brown to black. One of the single tow lots (9217-27A) was a bright blue in color. All of these fiber lots were pyrolyzed at 1800°C utilizing a polycarbosilane polymer precursor⁶⁹.

The scanning Auger depth profiles into the fiber surfaces to a depth of 4000-6000Å are shown in Figs. 3-10 for these lots of fibers. Figure 3 indicates that the composition of the first tow of fibers received from Dow Corning (lot #8309-139C) was quite close to stoichiometric SiC except that the near surface region (0-500Å) was very carbon rich, with the actual fiber surface being essentially pure carbon. Starting at a depth into the fiber of ~300Å, a small amount of boron was detected that, by a depth of 4000Å into the fiber, leveled off at ~5 at%. The average RT tensile strength of this lot of fibers was measured at UTRC (20 fibers) and found to be 253 ± 82 ksi (1740 ± 565 MPa), with an average fiber diameter of 8.6 µm. All of the fiber lots received from Dow Corning exhibited average diameters of from 8.6 to 8.9 µm.

Figure 4 indicates that the second lot of fibers received (#9217-21DM) also was close to stoichiometric SiC with a carbon rich surface, although the surface was not as carbon rich as the previous lot of fiber. No boron was detected in this lot of fiber, except for a trace amount on the very surface of the fiber. The RT UTS of this fiber lot averaged 194 ± 93 ksi (1340 ± 640 MPa), with four of the fibers breaking at very low strengths at what appeared to be "kinks" in the fibers.

The blue colored tow of fibers (#9217-27A) was expected to have an oxygen rich surface, since oxidized NICALON fibers have often exhibited a blue appearance. However, as can be seen in Fig. 5, these fibers had a very distinct carbon rich surface layer of ~2000Å in thickness that also contained small amounts of boron and nitrogen. The bulk composition of the fiber was right on stoichiometric SiC with a trace of oxygen. This distinct surface layer can be seen in the SEM photo of a fractured fiber end in Fig. 5 that also shows a lenticular void in the center of the fiber. As will be shown later, this type of void or fiber splitting is quite prevalent in all of the crystalline SiC fiber lots from Dow Corning. Due to the very short lengths of this particular tow of fibers, no tensile tests were done.

Figures 6 and 7 show the scanning Auger depth profiles obtained on the gold colored lots of fiber mat (#9217-41C and 53C1), while Fig. 8 gives the SAM depth profile found for the brownish colored fibers from lot 9217-50C. The compositions of all of these fiber lots are quite similar, with the near-surface regions (0-500Å) exhibiting quite high amounts of both boron and nitrogen. At a depth of ~3000Å 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 from NASA-Lewis (#9217-57C1) ranged in color from brown to black. Scanning Auger depth profiles were obtained on a typical brown fiber (Fig. 9) and a typical black fiber (Fig. 10). 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 1000Å, with 4-5% boron beginning to appear at a depth of 4000Å. 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.

A "kink" in one of the brown colored fibers can be seen in Fig. 9. If fibers with these types of kinks were tensile tested, very low values of UTS were obtained, undoubtedly due to the stress concentrations that occur when straightening a curved fiber that has a very high elastic modulus, as these fibers do. The data sheet obtained from NASA-Lewis with the lot #9217-57C1 fibers indicated that this fiber lot exhibited an average UTS of 348 ± 48 ksi (2400 ± 330 MPa). However, tensile tests done at UTRC indicated that the average UTS of 20 of these fibers was 131 ± 75 ksi (1250 ± 520 MPa), which is approximately half that measured by Dow Corning. Analysis of the UTS data obtained at UTRC indicated that the lower strength fibers were either kinked or they contained flaws, either internal as shown for the lower fiber in Fig. 11 for lot #9217-50C fibers, or external as shown in Fig. 12 for a fiber from lot #9217-53C1 that fractured at 58 ksi (404 MPa). In fact, tensile tests done at UTRC on the other fiber lots (9217-41C, 50C, and 53C1) all gave average UTS values of ~85 ksi (585 MPa) with a rather large spread. The low strength fibers [~45 ksi (310 MPa)] invariably fractured at either kinks or internal flaws, while the higher strength fibers [~200 ksi (1380 MPa)] appeared to fracture at surface flaws. A higher strength fiber from lot 9217-41C is shown in Fig. 13. It is difficult to discern the actual fracture origin for this fiber, however, the granular nature of the fracture surface attests to the crystalline morphology of the fiber.

Fracture surfaces for lot 9217-57C1 fibers are shown in Figs. 14 and 15. In Figs. 14A and B, the morphology of this particular fiber can be seen to consist of rather large grains (up to 5000Å) near the surface of the fiber with a much finer grained structure in the center region of the fiber. This dual nature of the microstructure of these fibers will be shown in more detail in a later section

of this report that will describe TEM thin foil characterization of lot 9217-57C1 fibers in an LAS matrix. Note that the fiber in Fig. 14C is split from edge to center and that along the split in the fiber the grain size appears to be uniformly large, even towards the center of the fiber. The origin of the dual grain size nature of this fiber lot is unknown at this time.

Figure 15 shows the SEM of a fractured lot 9217-57C1 fiber at the fiber surface/fracture surface intersection. A pattern of what appear to be either cracks or grain boundaries are quite visible on both the fiber and fracture surface in the higher magnification photo. At less than 1000Å in size, they would appear to be cracks rather than grain boundaries. Additional SEM characterization of these fibers close to and away from the fracture surface will be necessary to positively identify the origin of these features.

In an attempt to characterize the grain size of the Dow Corning SiC fibers, one of the early fiber lots (#8309-139C) was fractured and segments of the fractured fibers examined in the TEM. As shown in Fig. 16, the grain size of this particular fiber lot in the region that fractured thin enough to be analyzed in the TEM was on the order of 1000-2000Å. From selected area electron diffraction analysis, the great majority of grains were β -SiC, with a few possibly being α -SiC. While this technique allows the grain size and structure of the fibers to be determined, it is difficult to assess exactly what region of the fiber is being analyzed. Thus, if a fiber lot such as #9217-57C1, with its dual grain size nature, were characterized in the TEM by this method, a misleading result could be obtained concerning the grain size and distribution. As will be shown in a later section of this report, TEM thin foil characterization of the fibers in a glass or glass-ceramic matrix, assuming the fiber and matrix do not react significantly during matrix consolidation, is a much preferred method for characterization of fiber microstructures.

C. Glass-Ceramic Matrix Composite Characterization

1. Lox M Tyranno Fiber/Glass-Ceramic Matrix Composites

a. Composite Fabrication

Three glass-ceramic matrix composites were fabricated utilizing the Lox M Tyranno fibers. Two of the composites (a 0° and a 0/90° fiber layup) used the UTRC-200 boron doped LAS matrix, as described in detail as the LAS-C matrix in Ref. 67, while the third composite (0/90°) utilized a higher temperature barium magnesium aluminosilicate (BMAS) matrix. The composite panels (10 x 10 cm, 16 layers) were fabricated at maximum temperatures of 1300-1450°C, utilizing the usual tape layup procedures described previously⁴⁶. After fabrication, those composite samples to be

tested or characterized in the matrix crystallized or "ceramed" condition were subjected to a further heat treatment at temperatures from 900-1200°C in order to crystallize the matrix to either the β -quartz/silica solid solution LAS phase or the barium osumilite BMAS phase.

The microstructure of the 0/90° UTRC-200 LAS matrix/Lox M Tyranno SiC fiber composite #49-90 is shown in Fig. 17. This micrograph indicates that complete consolidation of the LAS matrix around the fibers occurred during composite fabrication, with some evidence of pullout of the 90° fibers during composite polishing, indicative of weak bonding between fibers and matrix. The volume fraction fibers in this composite was ~40%. A NICALON SiC fiber composite microstructure would appear essentially identical to this.

b. Composite Testing

Composite #49-90 was machined into flexural test specimens of dimensions 5 mm wide x 3 mm thick x 10 cm in length and subjected to 3-pt flexural testing in the ceramed condition from RT to 1100°C. A typical RT fracture surface of this composite is shown in Fig. 18. From this figure, it can be seen that the mode of fracture of this composite was very tough and fibrous, indicative of high retained fiber strength and a weak fiber/matrix interfacial bond. The flexural strength of this composite vs temperature in air is shown in Fig. 19, along with previously generated composite data on older Tyranno SiC fiber. From this figure, it can be seen that the Lox M Tyranno fiber results in composites with much improved properties over the older Tyranno fiber. The reduction in composite strength above 900°C is due to the residual glassy phase in the UTRC-200 LAS matrix becoming somewhat soft. This type of behavior and comparable composite strengths are observed for NICALON fiber/UTRC-200 LAS matrix composites, as well.

The 0° fiber orientation Lox M Tyranno/UTRC-200 LAS matrix composite (#200-90) was utilized primarily for TEM studies as well as composite tensile test measurements. The RT flexural strength of the unidirectional Tyranno fiber composite in the ceramed condition was measured as 110 ksi (760 MPa), with the RT tensile strength being 70 ksi (483 MPa). These values are comparable to similar tests done on NICALON fiber/UTRC-200 LAS matrix composites.

The BMAS matrix/Lox M Tyranno fiber composite (0/90°) fabricated under this program (#371-90) was also machined into flexural specimens and tested as a function of temperature to 1300°C and after exposure to flowing oxygen from 550° to 900°C, and compared to both UTRC-200 LAS matrix/Lox M Tyranno fiber composite data and previously obtained data for NICALON fiber/BMAS matrix composites. Table I compares the flexural strength of the Lox M Tyranno fiber/BMAS and UTRC-200 LAS matrix composites, while Table II compares BMAS matrix composite data for both

Lox M Tyranno and NICALON fibers. From Table I, it can be seen that the RT strengths of the UTRC-200 and BMAS matrix composites are quite similar, except after the flowing oxygen exposure at 550°, 700°, and 800°C. The degradation in strength for the BMAS matrix composite is comparable to that seen for non-boron containing LAS matrix/NICALON fiber composites⁶⁷, and is due to the oxidation of the carbon rich fiber/matrix interfacial phase which, as shall be shown from scanning Auger and TEM studies in the next section of this report, exists in the Tyranno fiber composites, as well. Although the absolute strength values for the BMAS matrix composite tested in air at elevated temperatures from 900° and 1000°C are not as high as the UTRC-200 matrix composite values, due to the same oxidative instability problems of the carbon rich fiber/matrix interface, the strength and elastic modulus remain quite high to 1200°C. This indicates that the BMAS matrix/Lox M Tyranno fiber composite system has potential application to 1200°C, if the oxidative instability problems associated with the carbon rich interface can be alleviated.

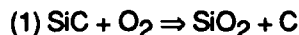
From Table II, it can be seen that the BMAS matrix composite strength values utilizing either Lox M Tyranno fiber or NICALON fiber are very similar, both as a function of temperature and after oxidative exposure. It thus appears that, while the Lox M Tyranno fiber does not exhibit any distinct advantages over the NICALON SiC type 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 if the situation warrants.

c. Composite Microchemical and Microstructural Analysis

A sample of the UTRC-200 LAS matrix/Lox M Tyranno fiber composite #49-90 was fractured along the fiber direction in one of the 90° layers of the 0/90° composite, and an exposed fiber surface and a matrix trough from which a fiber had been extracted during fracture were depth profiled in the scanning Auger multiprobe (SAM). This technique has been utilized extensively in the past to analyze the interface in NICALON⁶⁷ and high oxygen Tyranno⁷⁰ fiber/glass-ceramic matrix composites. The results of this analysis are shown in Fig. 20, and are very similar to that found for NICALON fibers in UTRC-200 LAS matrices except for the small amount of Ti in the fiber and the larger amount (~5 at %) of Ti in the matrix near the fiber/matrix interface. This analysis is also very similar to that found on another ONR contract⁷⁰ for the high oxygen Tyranno fibers in an LAS-I matrix, except for the higher oxygen content of the earlier fibers, the greater amount of Al diffusion from the matrix into the fibers, and the absence of boron in the LAS-I matrix.

The carbon layer formation at the fiber/matrix interface is also very similar in thickness and composition to that found previously for NICALON fiber/UTRC-200 LAS matrix composites⁶⁷. This weak layer accounts for the toughness of these composites due to its ability to deflect matrix

cracks, with subsequent fiber pullout from the matrix accounting for a large part of the toughening due to the presence of these fibers. The formation of this carbon interfacial layer is due to the carbon-condensed oxidation displacement reaction of the Tyranno or NICALON fiber with free oxygen during composite processing:



as described in detail by Cooper, et al^{49,74}. As stated previously, while this carbon interfacial layer accounts for the high toughness of these composites, it also is responsible for the oxidative instability and strength degradation of non-boron doped composites, as was shown in Tables I and II.

TEM thin foil analysis was also conducted on the 0° UTRC-200 LAS matrix/Lox M Tyranno fiber composite #200-90. Figure 21 shows a thinned section of a Lox M Tyranno fiber from a region away from the fiber/matrix interface. Electron diffraction of this fiber shows a somewhat diffuse ring pattern corresponding to β -SiC (similar to NICALON) with a superimposed pattern for TiC. The fiber microstructure shown appears to consist of extremely fine grained β -SiC (<40Å) with dispersed TiC crystallites of up to 200Å in size. Since TEM studies were not done on as-received Lox M Tyranno fibers, this microstructure could have evolved during composite processing. However, since the fibers only experienced a maximum temperature of 1350°C for less than 30 min, it is more likely that this microstructure is fairly representative of as-received fibers.

In Fig. 22, the fiber/matrix interfacial region is shown from the TEM thin foil analysis of composite #200-90. The EDX analyses shown in this figure are from the carbon rich interface (A), and two crystalline precipitates; one (B) in the carbon rich layer and the other (C) at the LAS matrix/carbon rich layer interface. Both of the precipitates contain a large amount of titanium, with one (C) also containing a large amount of zirconium, which is added to the LAS composition as a ZrO₂ nucleating aide. An electron diffraction pattern was obtained from precipitate C, but could not be identified. Figure 23 shows a higher magnification TEM micrograph of the interfacial region of composite #200-90. A row of very fine precipitates can be seen at the carbon layer/LAS matrix interface. These precipitates were too fine to be analyzed by themselves, but from EDX analysis of point A, there was an indication of slightly enhanced aluminum content over that of the matrix itself.

2. Dow Corning Crystalline SiC Fiber/Glass-Ceramic Matrix Compatibility Studies

Since a sufficient quantity of the Dow Corning SiC fibers were not available to make actual glass-ceramic matrix composites for thermal and mechanical property studies, examples of the black colored fibers (#9217-57C1) that exhibited a somewhat carbon rich surface from Auger studies (Fig. 10) and the gold colored fibers (#9217-41C) that exhibited a surface containing a significant amount of boron and nitrogen (Fig. 6) were hot-pressed into both LAS (non-boron doped) and BMAS glass-ceramic matrices for fiber/matrix compatibility studies. The hot-pressing parameters were those utilized previously for Lox M Tyranno fiber/LAS and BMAS matrix composites, except the panel size was much smaller (3.7 x 7.6 cm).

a. Fracture Characteristics of Dow Corning SiC Fiber Composites

Figures 24-27 show typical examples of the fracture characteristics of these pseudo-composites. From these figures, it can be seen that in all cases there exists a considerable amount of fiber/matrix debonding, but very little in the way of fiber pullout similar to that shown in Fig. 18 for the Lox M Tyranno fibers in an LAS matrix. However, as can be seen in Figs. 25B and 26B, and, to a lesser extent in Fig. 27A, there also exist regions in these composites that did not exhibit fiber/matrix debonding to any great extent, which is indicative of a rather strongly bonded fiber/matrix interface. No apparent correlation exists between fiber/matrix debonding and the particular fiber or matrix utilized.

b. Microchemical and Microstructural Analysis

Samples of each of the Dow Corning SiC fiber/LAS and BMAS matrix pseudo-composites were fractured parallel to the fiber direction so that an exposed fiber surface and matrix trough could be subjected to scanning Auger depth profiling, similar to that previously discussed for the Lox M Tyranno fiber composite. Figures 28-31 show the results of these SAM depth profiling studies for the four fiber/matrix combinations. From these analyses, it can be seen that in three of the four samples, a carbon rich interfacial layer has formed between fiber and matrix, similar to but considerably thinner than that found previously for the Lox M Tyranno fiber/LAS matrix composite (Fig. 20). In all of the samples, matrix elemental (Al, Ba, O) diffusion into the SiC fibers was observed, which is also similar to that observed for either NICALON or Tyranno SiC fibers in these matrices. The increase in oxygen content observed on the fiber side of the carbon rich layer (and in some cases on the matrix side as well) may be a result of the SiO_2 formed during the carbon-condensed oxidation reaction of the SiC fiber according to equation (1), and is observed for LAS⁶⁷ and CAS⁷⁴ matrix composites with NICALON fibers.

No trace of the nitrogen or boron that was in the surface region of SiC fiber lot #9217-41C could be found in either the LAS (Fig. 29) or BMAS (Fig. 30) matrix composites, although boron was found in all of the fibers analyzed at sputter depths of 3000-4000Å or greater, even though it was not always found in the SAM depth profiles of as-received fibers. The surface B and N in these fibers probably diffused out into the matrix during composite fabrication. The only sample that did not exhibit a true carbon rich interfacial layer was the BMAS matrix/SiC lot #9217-57C1 fiber composite #462-90 shown in Fig. 31. The exact fiber and matrix trough analyzed are shown in this figure prior to sputtering as A and B, respectively, and while the matrix trough appears to have been debonded quite easily from the fiber that formed it, the fiber (A) appears to still have quite a bit of well-bonded matrix phase adhered to it. From the SAM depth profiles of the fiber and matrix trough shown in this figure, it appears that while the fiber surface was oxygen rich with no carbon enhancement, the matrix trough surface was relatively high in carbon. It is speculated that while fiber (A) did not form the carbon rich layer during the short (3 min) time at the maximum hot-pressing temperature of 1430°C, the fiber that was adjacent to the matrix trough (B) did form the carbon interfacial reaction product. These differences in interfacial chemistry within the same composite, indeed between two adjacent fibers, may account for the different fracture characteristics observed within the same composite, as was shown in Figs. 25, 26, and 27.

The reason that the carbon interfacial layer forms around some fibers but may not form around others may relate to the particular stoichiometry of the SiC fiber surface. As discussed in Ref. 74, the carbon making up the interface may come from two sources, the oxidation of the SiC fiber plus the condensed carbon originally in the fiber. Off stoichiometric (C-rich) SiC fibers such as NICALON and Tyranno and some SiC whiskers from Tokai Carbon Co., American Matrix, and Advanced Composite Materials Co. (formerly ARCO Chemical Co.), form a distinct carbon rich interface when incorporated into glass-ceramic matrices^{67,68}. However, stoichiometric SiC whiskers from Los Alamos National Laboratory have been found from studies at UTRC⁶⁸ not to form a distinct carbon rich interface during glass-ceramic matrix composite processing and, being well-bonded to the matrix, do not contribute to significant crack deflection and toughening. It is proposed that, while some of the crystalline SiC fibers from Dow Corning do exhibit a carbon rich surface and thus do form a distinct carbon interfacial layer during composite hot-pressing, other fibers may indeed retain their stoichiometric SiC composition on the very surface of the fiber, and thus may not form a carbon interfacial layer in the glass-ceramic matrices. Those that do not form the carbon interface are well bonded to the matrix and do not significantly improve the toughness of the composite or act as matrix crack deflectors.

TEM replica analysis of polished cross-sections and TEM thin foil analysis is being done on the four LAS and BMAS matrix composite samples previously discussed. While this study has not

been completed, examples of the type of microstructures in these composites can be given. Figures 32 and 33 show optical and TEM replica micrographs of composites #1-91 and #462-90, which contain SiC fibers from lot #9217-41C in an LAS matrix, and lot #9217-57C1 fibers in a BMAS matrix, respectively. It can be seen from the lower magnification optical photos that not enough fibers were incorporated into these samples to form true composites, but the fiber, matrix, and fiber/matrix interfacial structure and/or reactivity can be assessed. It can be seen that a significant number of the fibers are split, as was first observed in the as-received fiber SEM analysis, with more split fibers but with smaller sized splits being observed for the lot #9217-57C1 fibers compared to the #9217-41C fibers. The as-pressed matrix in both composites is primarily glassy, with some mullite crystals being formed as well as fine precipitates of the barium osumilite phase in the BMAS composite.

Figure 34 shows a TEM replica of two different lot #9217-57C1 SiC fibers in an LAS matrix (composite #414-90), one that is split and one that is not. The split fiber shows a more uniform microstructure than the unsplit fiber, which gives the indication that the interior of the fiber is different than the exterior region. This was previously shown from SEM analysis of fractured fiber ends to relate to the dual grain size nature of this particular lot of fibers. Unfortunately, polishing of these composites was very difficult, due to a combination of the large spacing between fibers and the marked difference in hardness between the fibers and the matrix. Thus, the true microstructure of the fibers and, in particular, the fiber/matrix interface cannot be clearly discerned.

TEM thin foil analysis of these composite samples was quite successful, however, in distinctly showing the fiber and fiber/matrix interfacial structure. While this work is still in progress, Figs 35-37 show examples of the fiber/matrix interface and the fiber microstructure itself in two of the LAS matrix composites with lots #9217-41C and 57C1 SiC fibers. In Fig. 35, the fiber/matrix interfacial region is shown for composite #1-91 with lot #9217-41C SiC fibers. Auger analysis of this composite (Fig. 29) showed that a very thin carbon rich layer existed at the fiber/matrix interface, but, as was shown in Fig 25, not all of the fibers debonded from the matrix, indicating that carbon interfacial layer formation may not have been universal in this system. In the TEM thin foil analysis shown in Fig. 35, there may be an extremely thin interfacial layer of some sort, as can be rather indistinctly seen on the right hand side of Fig. 35, but it is too thin to characterize, other than by high resolution TEM (HRTEM). It is certainly exceedingly thin, unlike that formed in LAS matrix/NICALON or Tyranno fiber composites, as was shown in Fig. 22. One interesting aspect of the SiC fiber microstructure shown in Fig. 35, is that a layer of rather large (3000-4000Å) SiC crystals appears to exist on the surface of the fiber, with the underlying fiber structure consisting of a mixture of medium to very small SiC grains. It also appears that some porosity may exist in the fiber region just under the large grained surface layer.

Figure 36 shows the microstructure of the lot #9217-57C1 fibers, incorporated in an LAS matrix. These fibers showed a distinct dual grain size (Fig. 14), with larger grains in the outer third of the fibers and small grains in the central region of the fibers. In Fig. 36, the grains near the fiber edge can be seen to be quite large ($\sim 3000\text{-}4000\text{\AA}$), with the grain size becoming much smaller towards the center of the fiber. In the central region of this fiber, the microstructure appears to consist of medium sized grains ($\sim 1000\text{-}1500\text{\AA}$) surrounded by an extremely fine grained structure. This fine grained structure appears to consist of very small SiC grains, that may have a small amount of chlorine present in or around them, as shown in Fig. 37. The Mo in the EDX pattern comes from the Mo holder for the thin foil. The determination of the exact nature of this fine grained structure, in which the features appear to be on the order of $100\text{\AA}$ or less, will require additional analysis. Electron energy loss spectroscopy (EELS) is scheduled to be done as part of the additional analysis.

IV. CONCLUSIONS AND RECOMMENDATIONS

From the results of the first year's work on this program, certain conclusions and recommendations can be made. Pertaining to the new polymer derived low oxygen "Lox M" Tyranno SiC type fibers from Ube Industries, Ltd., it was found that the mechanical properties of 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 $\sim 500\text{\AA}$ 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 are 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.

The Dow Corning crystalline SiC fibers appear to be in a very early stage of development. Of the seven small lots of fiber evaluated at UTRC, 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 $\sim 1500\text{\AA}$ for some fibers to a dual grain size morphology that consisted of rather large grains ($3000\text{-}4000\text{\AA}$) near the fiber surface to medium sized ($1000\text{-}1500\text{\AA}$) grains surrounded by an extremely fine grained ($<100\text{\AA}$) structure near the center of the fibers. Electron diffraction analysis of the medium to large grains indicated that they consist almost exclusively of β -SiC. The extremely fine grained structure is yet to be determined. 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 ($<200\text{\AA}$) 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 may be present at some of the fiber/matrix interfaces. High resolution TEM (HRTEM) will be necessary to characterize the exceedingly fine structure observed.

It appears that the Dow Corning crystalline SiC fibers may have potential as reinforcement for advanced refractory glass-ceramic matrices. However, a number of questions remain to be answered pertaining to the chemistry of the fibers, both overall and surface related, the strength of the fibers and their thermal stability at elevated temperatures, the reproducibility and scale-up of continuous fiber, and the reactivity and bonding characteristics of the fibers with refractory glass-ceramic matrices. In either of the situations where the bonding of the fibers to the matrices is too strong, or where a carbon rich layer is formed at the fiber/matrix interface that subsequently degrades due to oxidative instability at elevated temperatures, a fiber coating may be necessary in order to obtain a weakly bonded yet oxidatively stable interface. The next year of effort under this program will attempt to address these questions.

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Table I

**Properties of UTRC-200 LAS and BMAS Matrix/Lox M Tyranno Fiber Composites
(0/90°)**

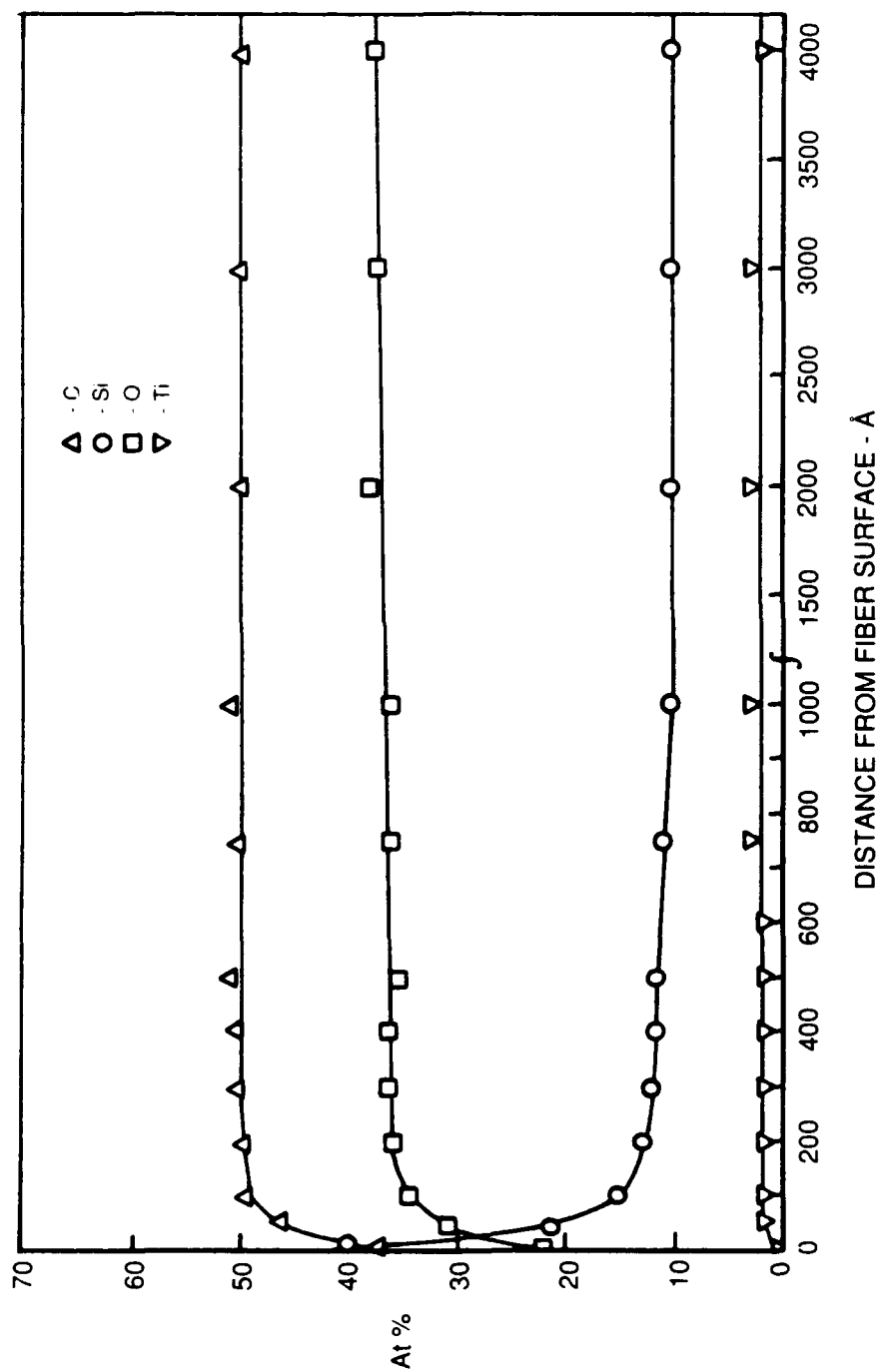
Matrix	<u>RT Flexural Strength - MPa/(ksi)</u>					<u>Elevated Temperature Flex Strength - MPa/(ksi)</u>				
	<u>AP</u>	<u>Cer</u>	<u>After 70 hrs. O₂, T =</u>			<u>900°C</u>	<u>1000°C</u>	<u>1100°C</u>	<u>1200°C</u>	<u>1300°C</u>
			<u>550°</u>	<u>700°</u>	<u>800°</u>					
UTRC-200	496 (72)	462 (67)	496 (72)	434 (63)	462 (67)	662 (96)	504 (73)	338 (49)	~0	-
BMAS	448 (65)	476 (69)	248 (36)	242 (35)	165 (24)	317 (46)	414 (60)	400 (58)	572 (83)	127 (17)

Table II

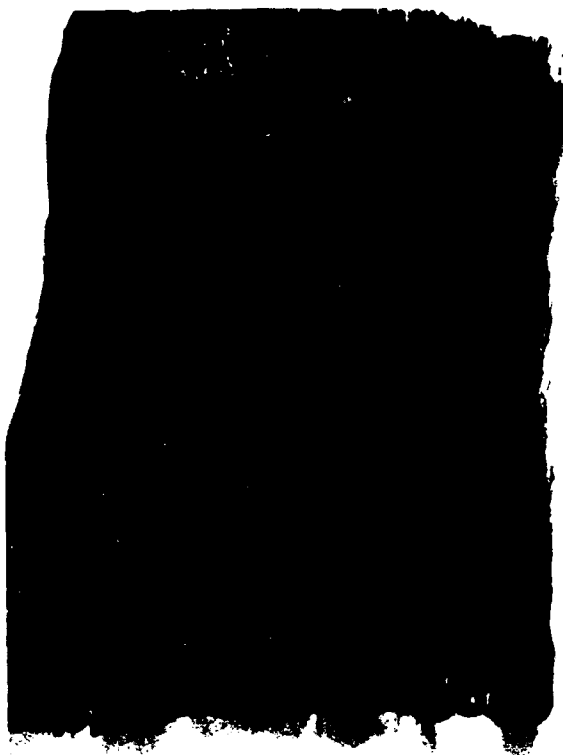
**Properties of BMAS Matrix/NICALON CG and Lox M Tyranno Fiber Composites
(0/90°)**

Fiber	<u>RT Flexural Strength - MPa/(ksi)</u>					<u>Elevated Temperature Flex Strength - MPa/(ksi)</u>				
	<u>AP</u>	<u>Cer</u>	<u>After 70 hrs. O₂ T =</u>			<u>900°C</u>	<u>1000°C</u>	<u>1100°C</u>	<u>1200°C</u>	<u>1300°C</u>
			<u>550°</u>	<u>700°</u>	<u>900°</u>					
NICALON	441 (64)	428 (62)	152 (22)	242 (35)	310 (45)	358 (52)	345 (50)	462 (67)	552 (80)	165 (24)
Tyranno	448 (65)	476 (69)	248 (36)	242 (35)	234 (34)	317 (46)	414 (60)	400 (58)	572 (83)	127 (17)

SAM DEPTH PROFILE
UBE IMPROVED TYRANNO SiC FIBER (LOX M) - (DESIZED) UTS=368 ksi (2530 MPa)



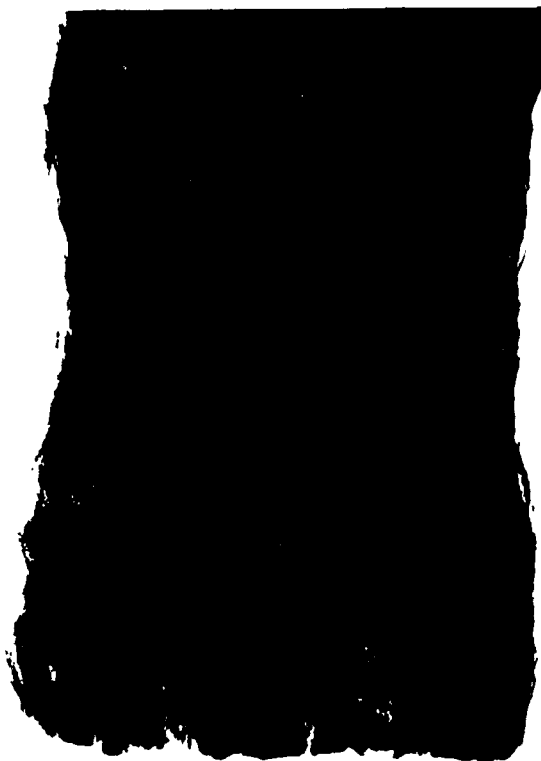
DOW CORNING CRYSTALLINE SiC FIBERS



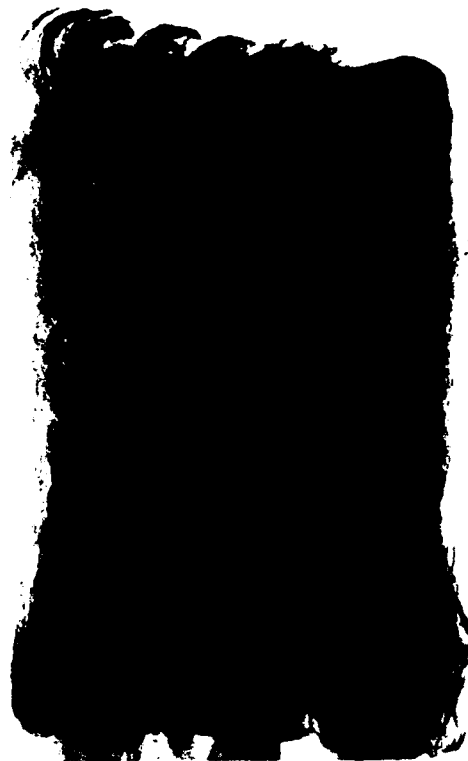
LOT 9217-57C1



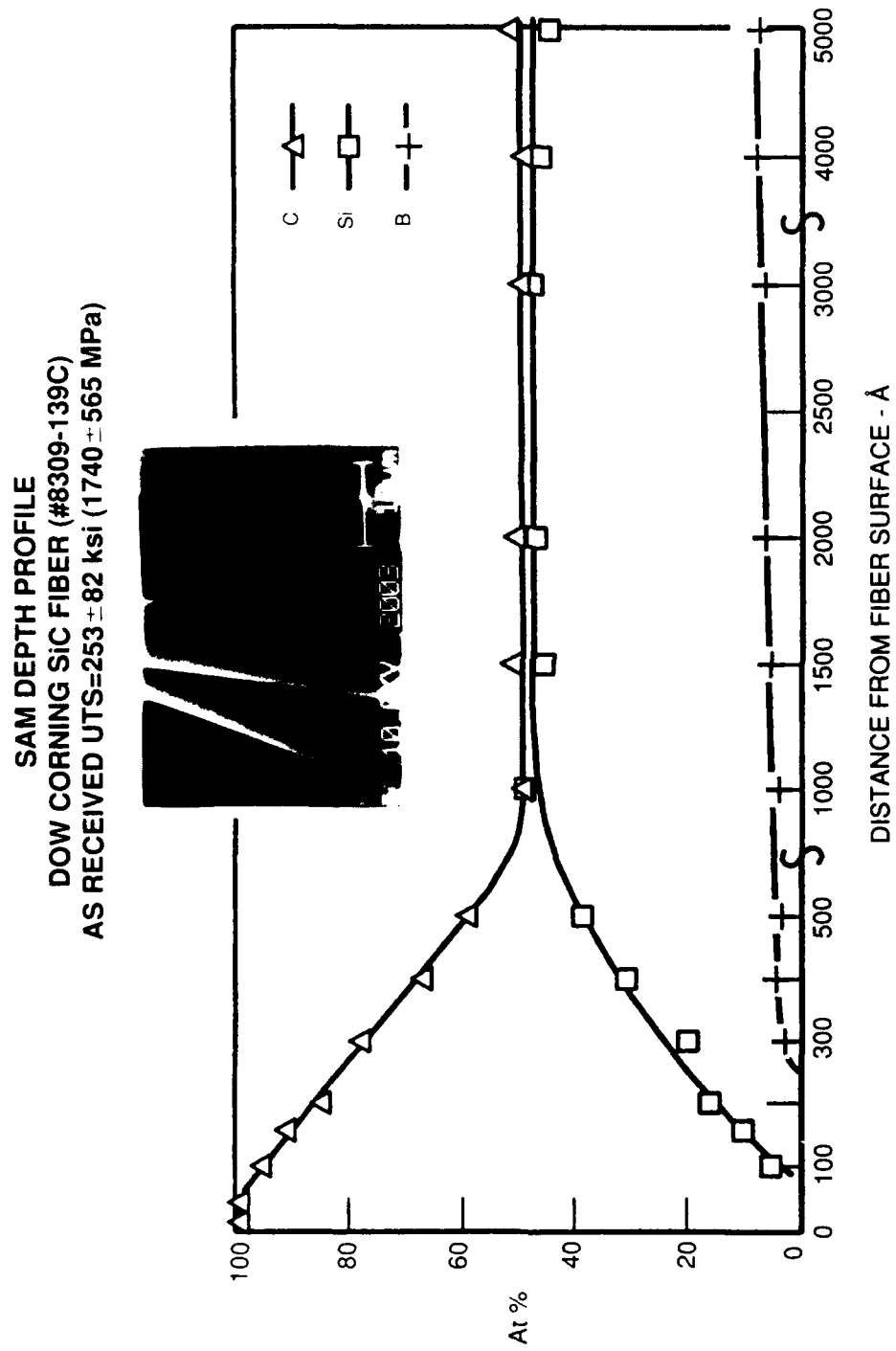
LOT 9217-41C



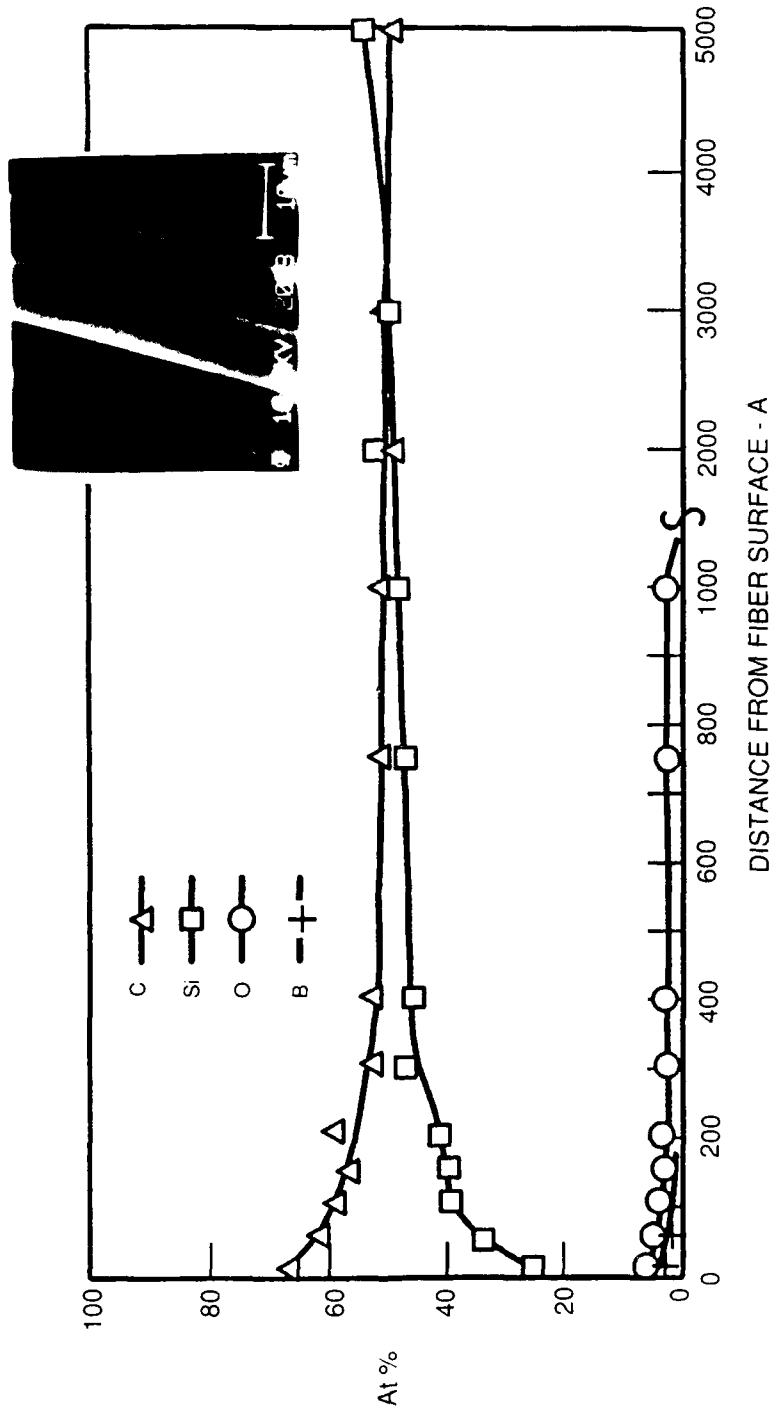
LOT 9217-50C

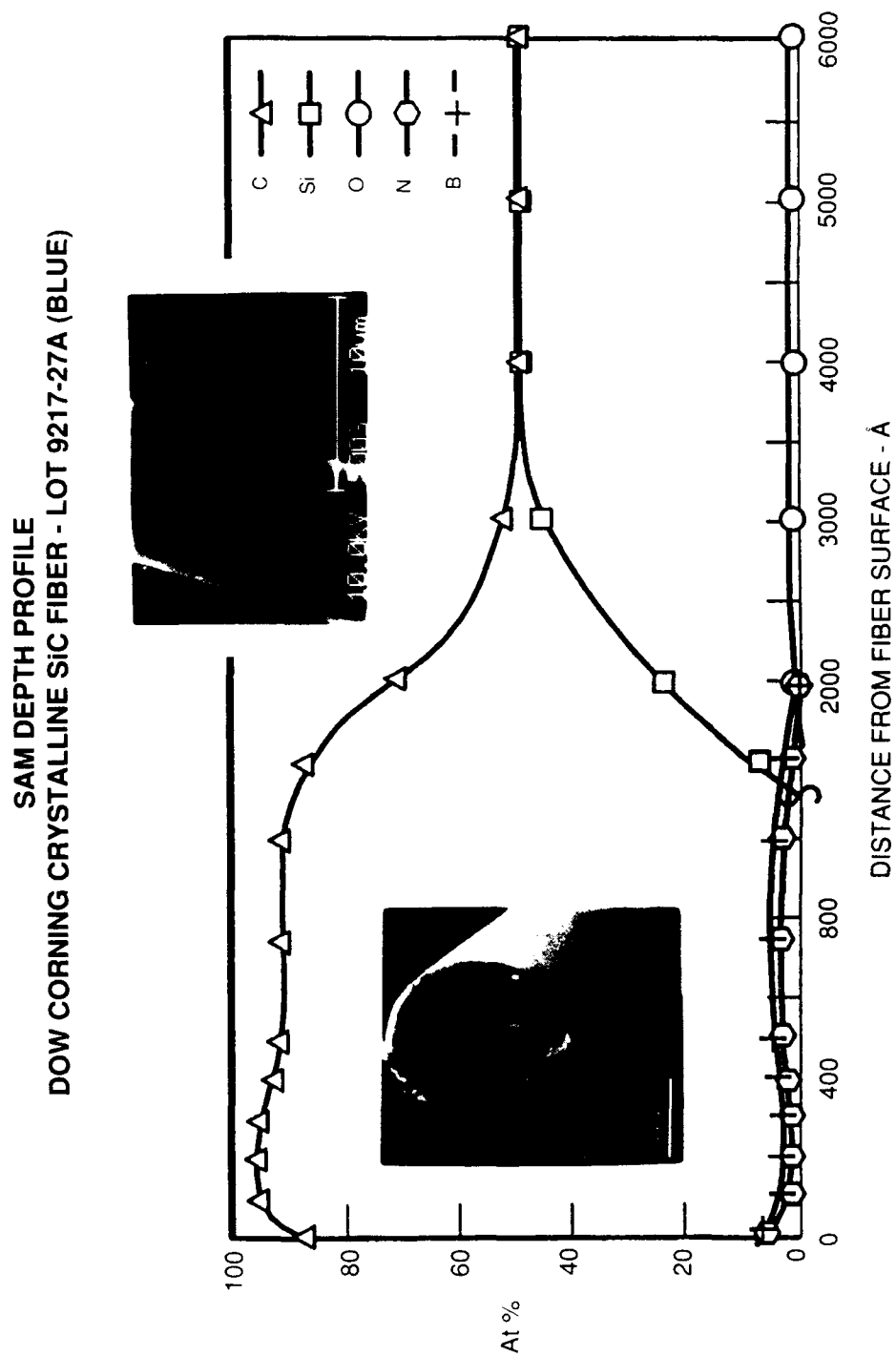


LOT 9217-53C1

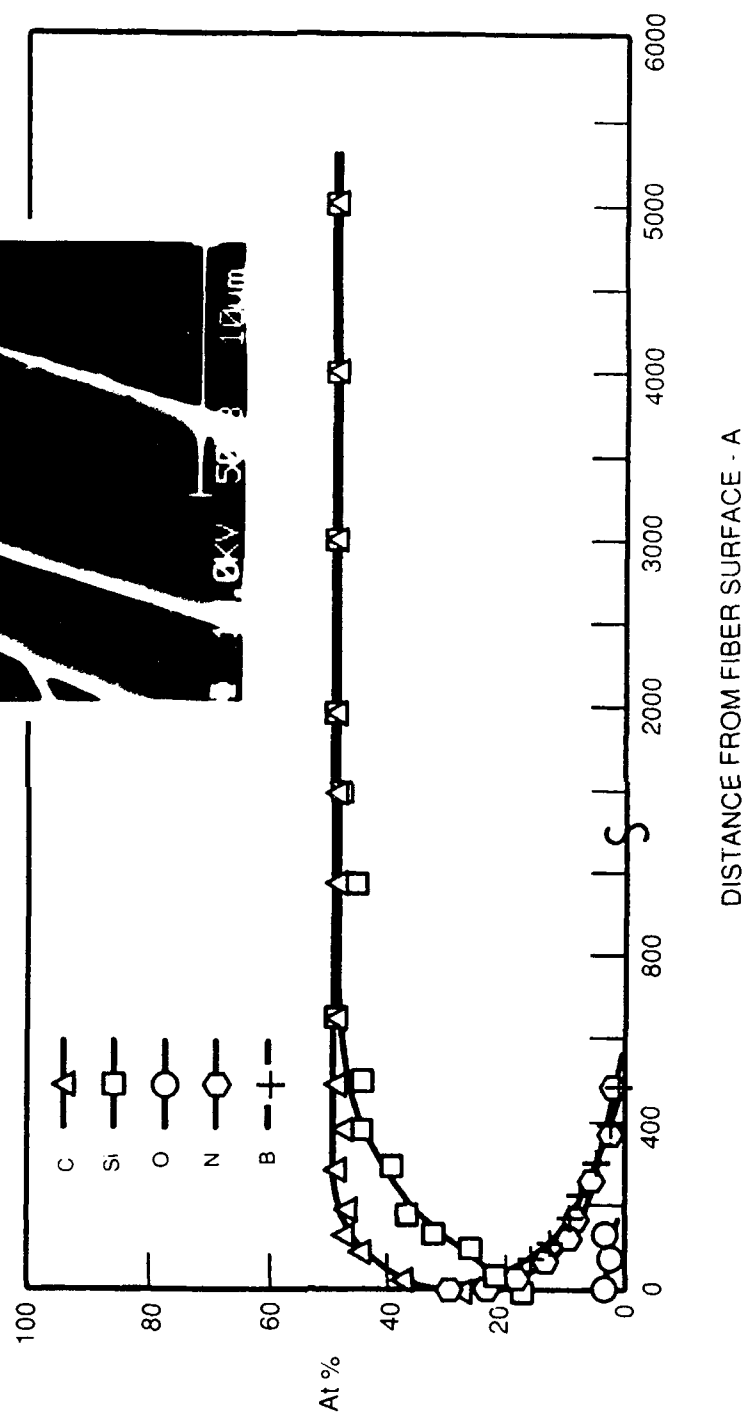


SAM DEPTH PROFILE
DOW CORNING SiC FIBER - LOT 9217-21DM
AS-RECEIVED UTS=194±93 ksi (1240±640 MPa)

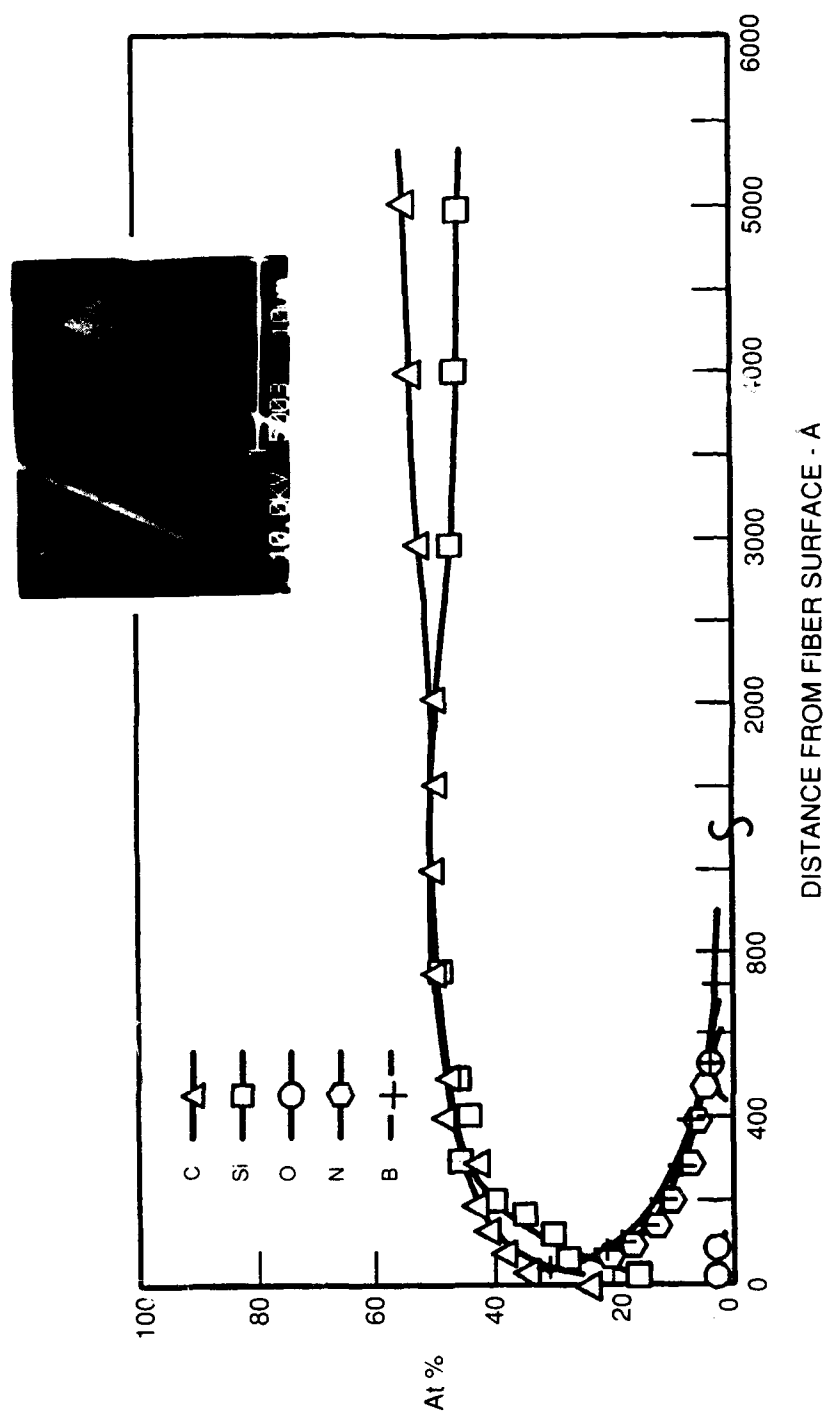


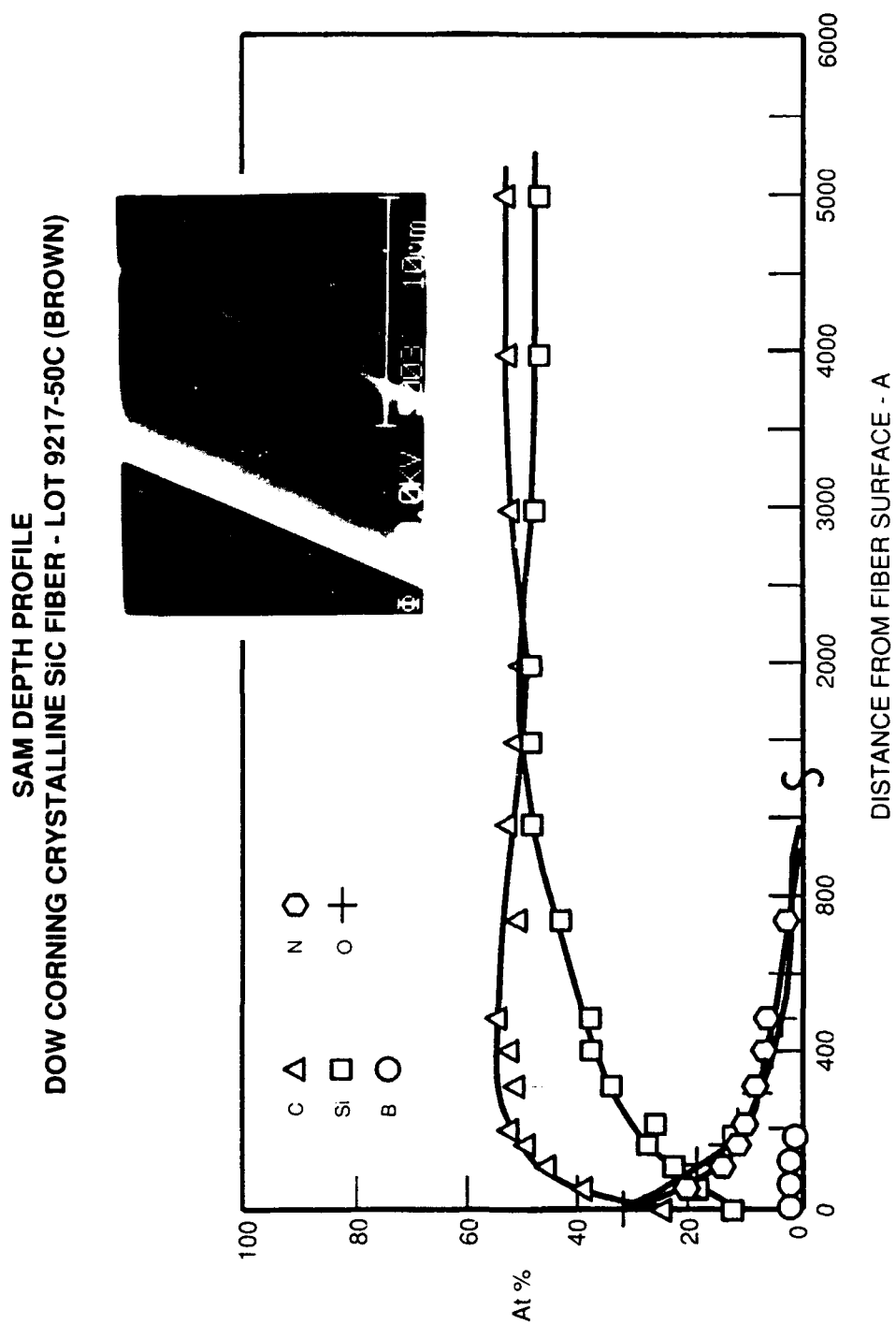


SAM DEPTH PROFILE
DOW CORNING CRYSTALLINE SiC FIBER - LOT 9217-41C1 (GOLD-BROWN)

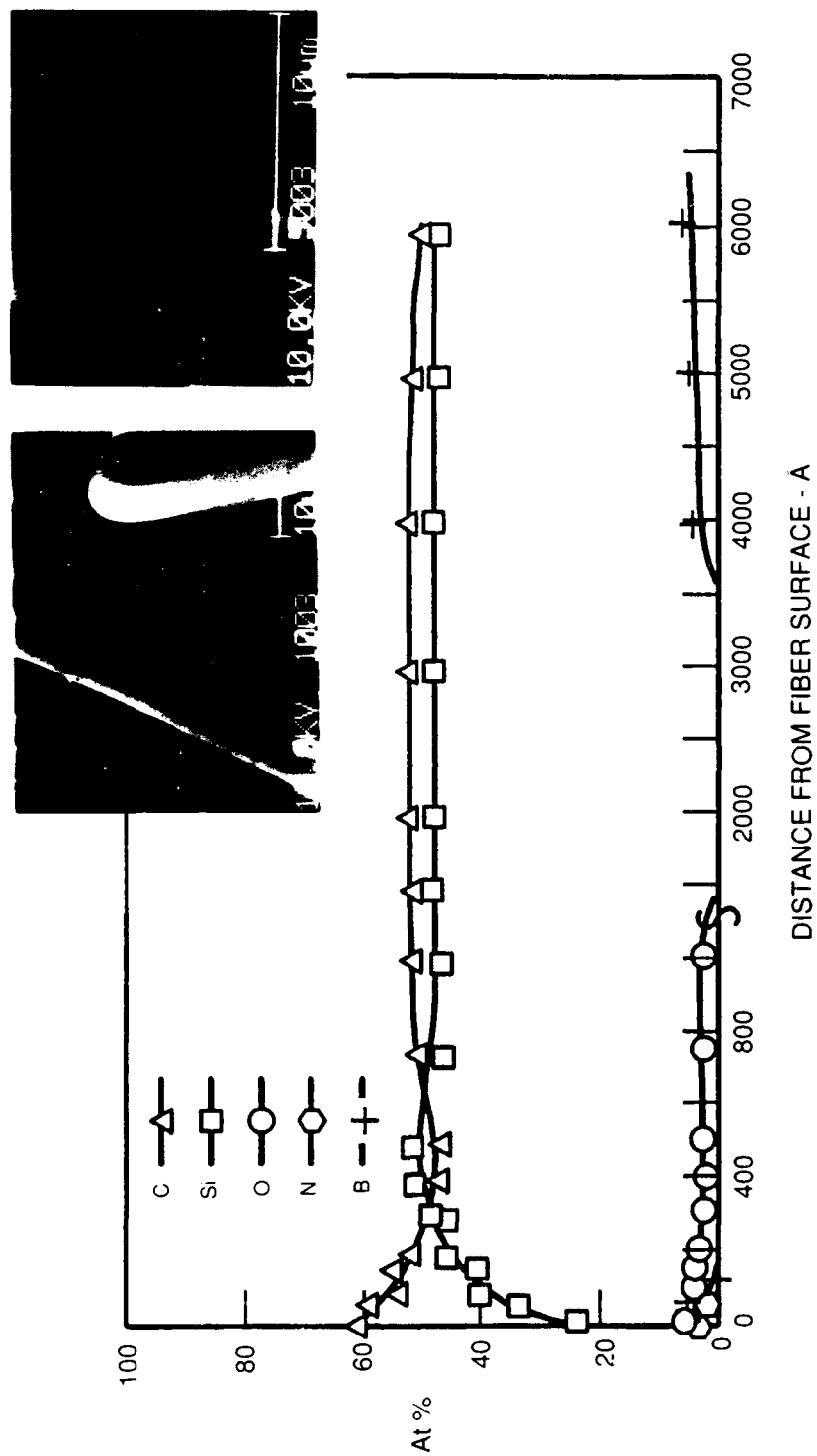


SAM DEPTH PROFILE
DOW CORNING CRYSTALLINE SiC FIBER - LOT 9217-53C1 (GOLD COLORED)

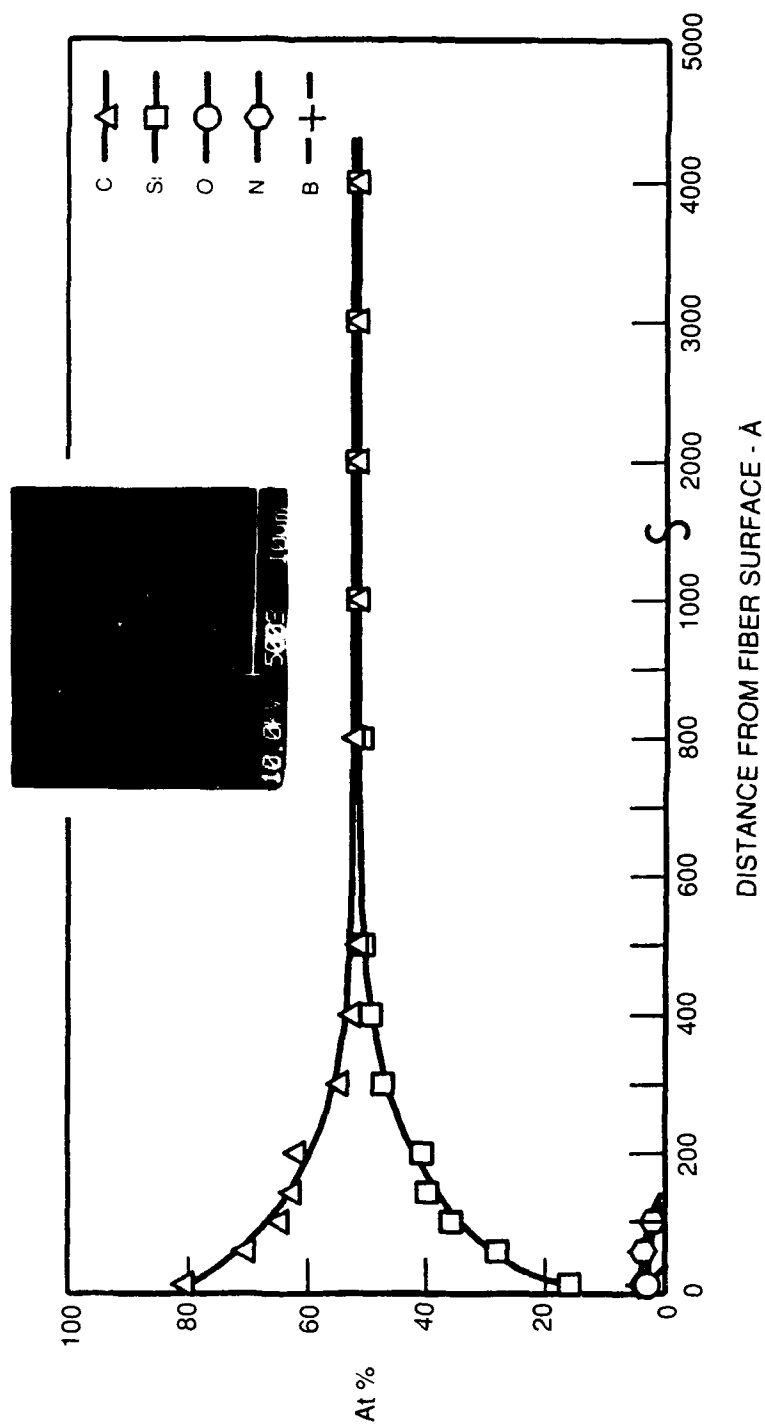




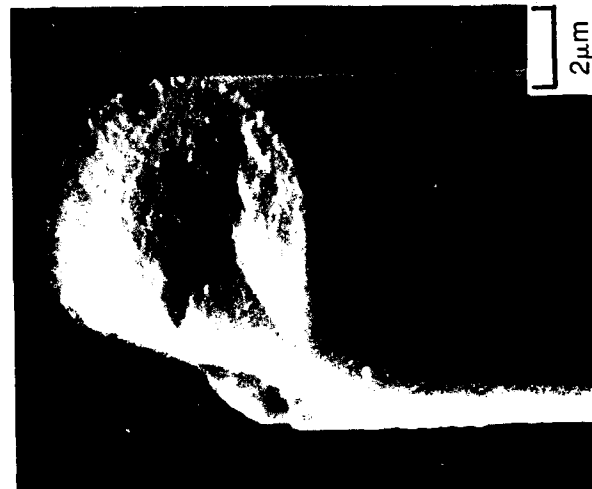
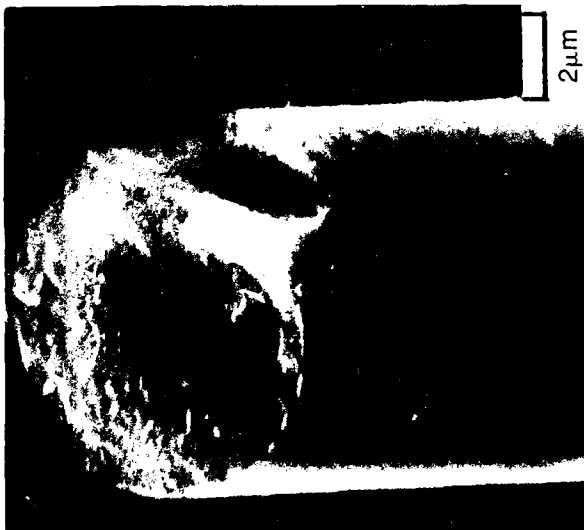
SAM DEPTH PROFILE
DOW CORNING CRYSTALLINE SIC FIBER - LOT 9217-57C1 (BROWN-GOLD COLOR)



SAM DEPTH PROFILE
DOW CORNING CRYSTALLINE SiC FIBER - LOT 9217-57C1 (BLACK)
UTS=181 $\pm$ 75 ksi (1250 $\pm$ 520 MPa)



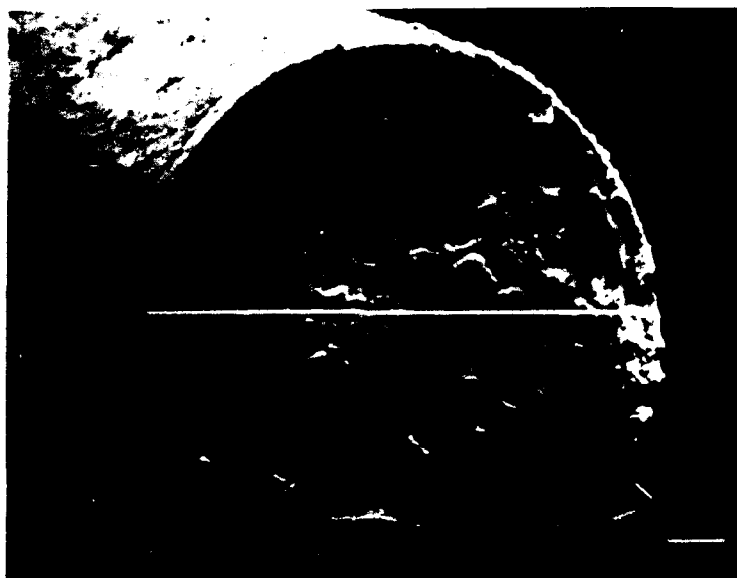
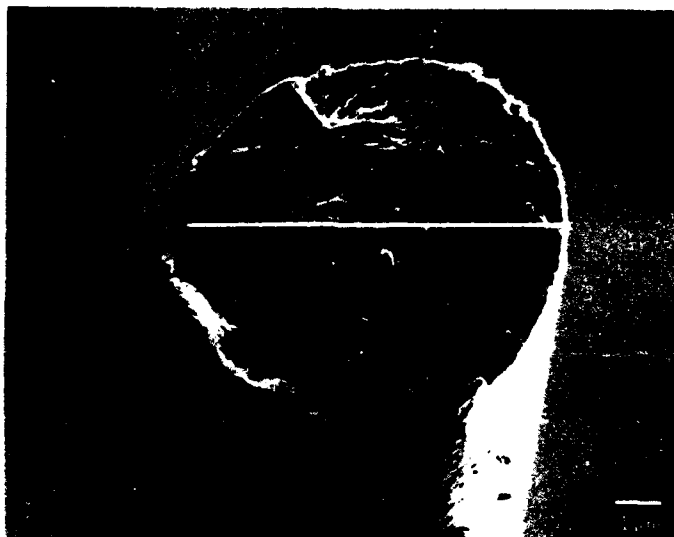
DOW CORNING SiC FIBERS (LOT 9217-50C)



FRACTURED END OF A LOT 9217-53C1 DOW CORNING SiC FIBER
UTS=58 ksi (400 MPa)



DOW CORNING SiC FIBERS (LOT 5217-41C)

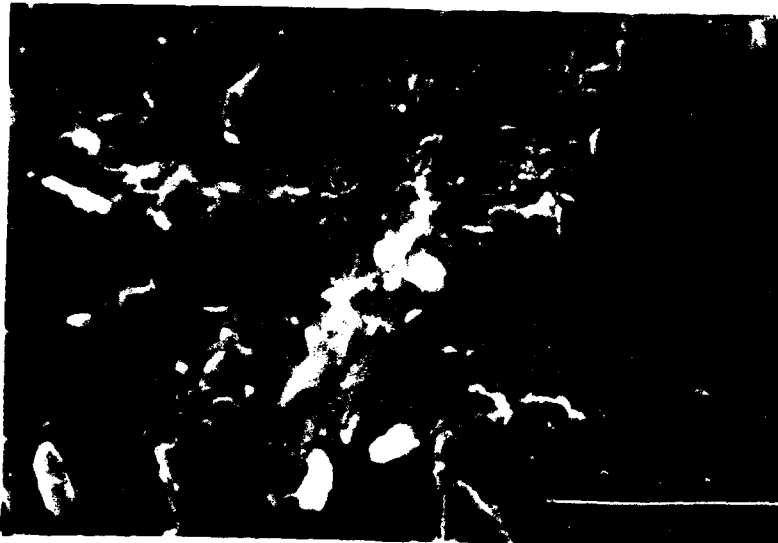


DOW CORNING SiC FIBERS (LOT 9217-57C1)

a)



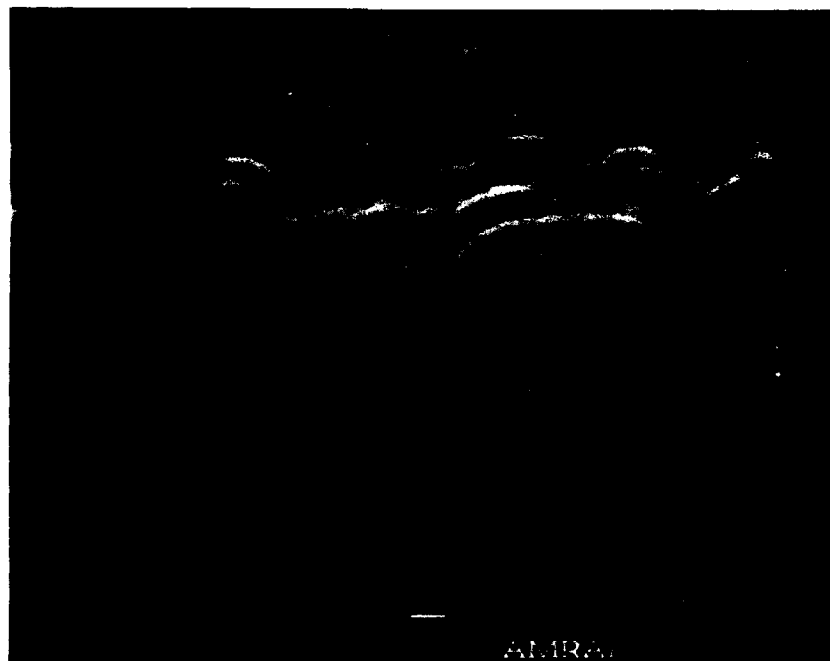
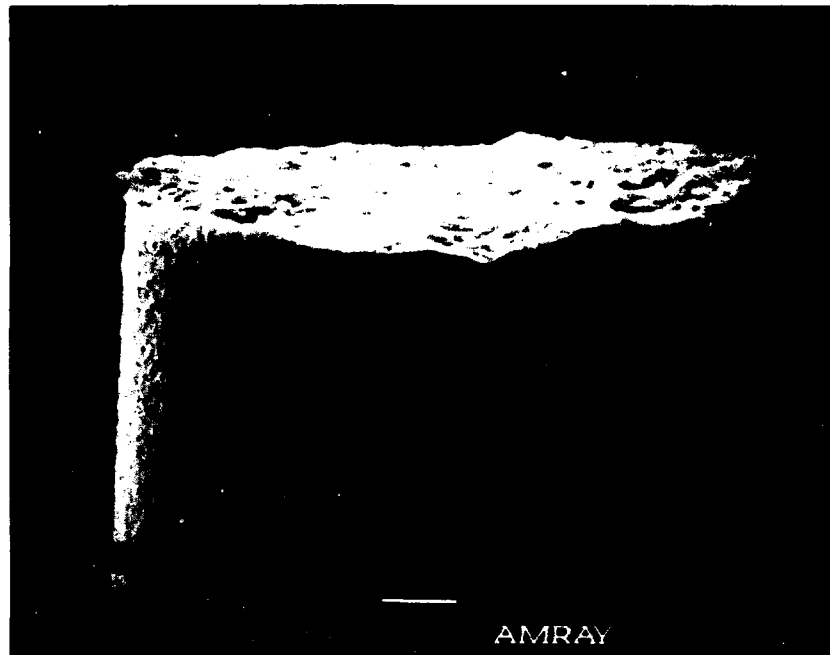
b)



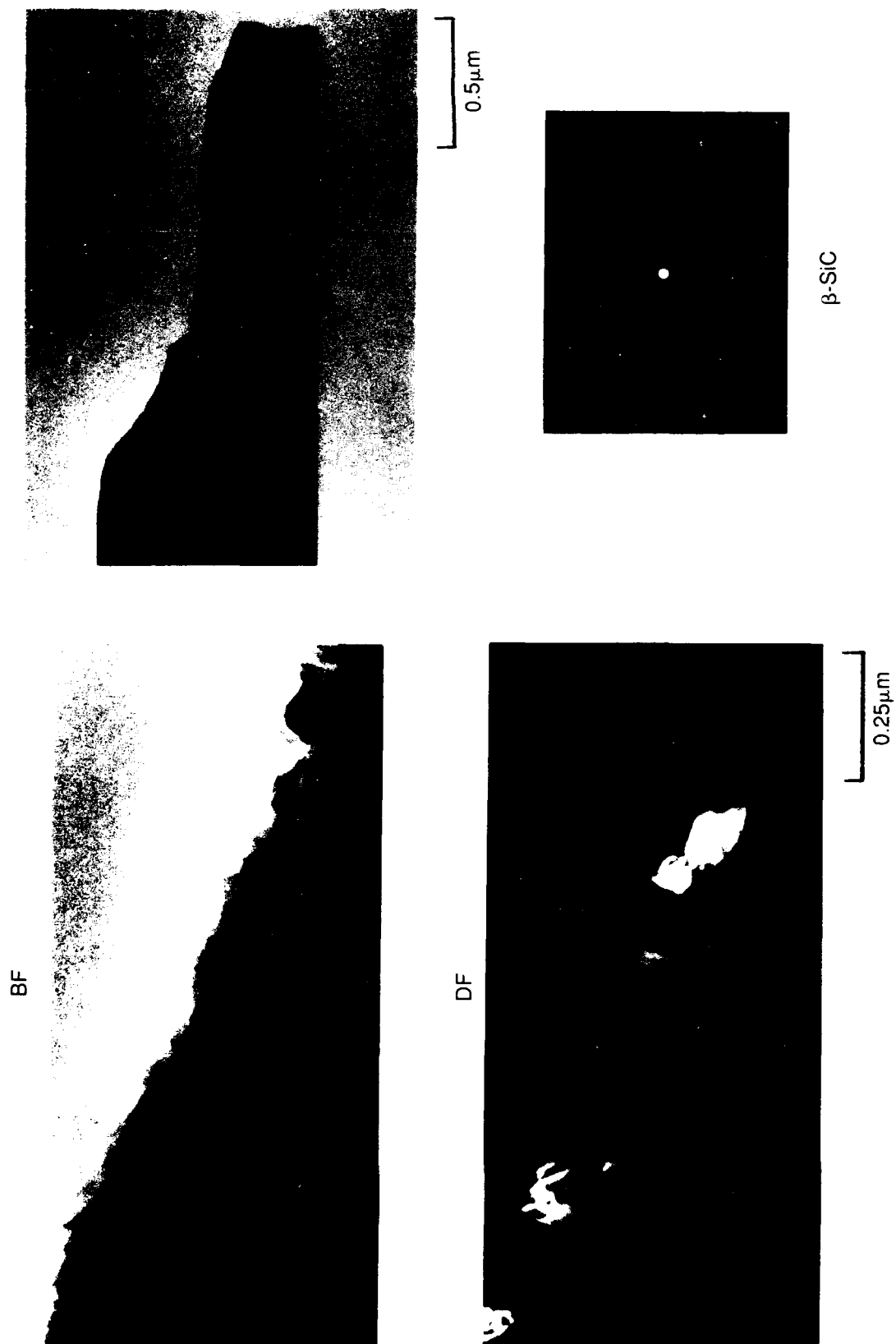
c)



DOW CORNING SiC FIBERS (LOT 9217-57C1)



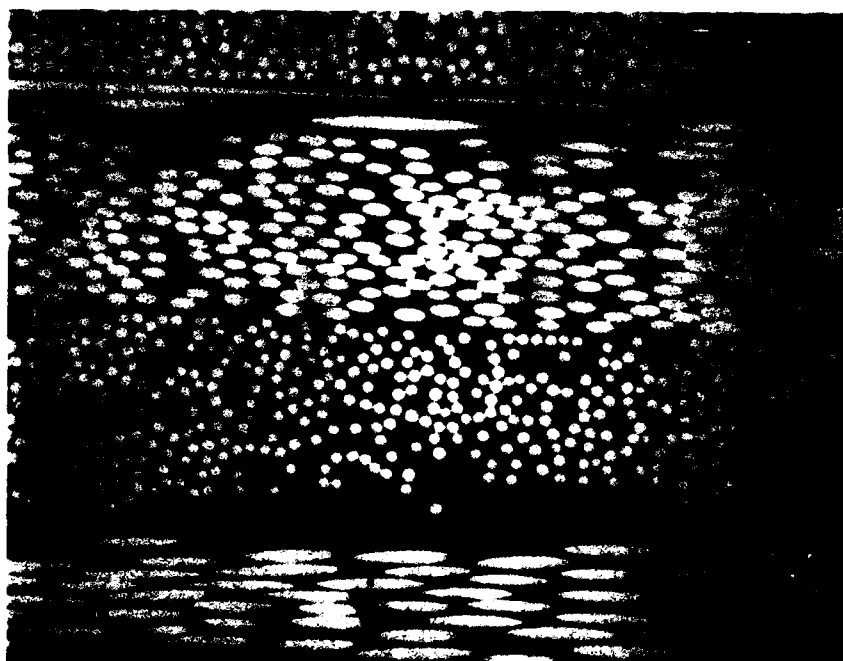
TEM/SAED MICROGRAPHS OF FRACTURED EDGE OF DOW CORNING SiC FIBER



**MICROSTRUCTURE OF UTRC-200 LAS MATRIX/UBE TYRANNO (LOX M) FIBER
COMPOSITE #49-90 (0°/90°)**



200μm



100μm

**FRACTURE SURFACE OF UTRC-200 LAS MATRIX/LOX M TYRANNO SiC FIBER
COMPOSITE #49-90 (0°/90°)**

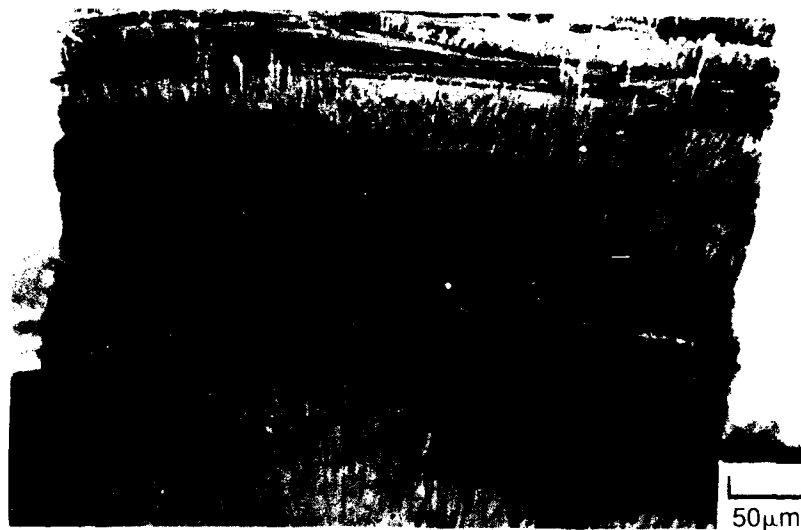
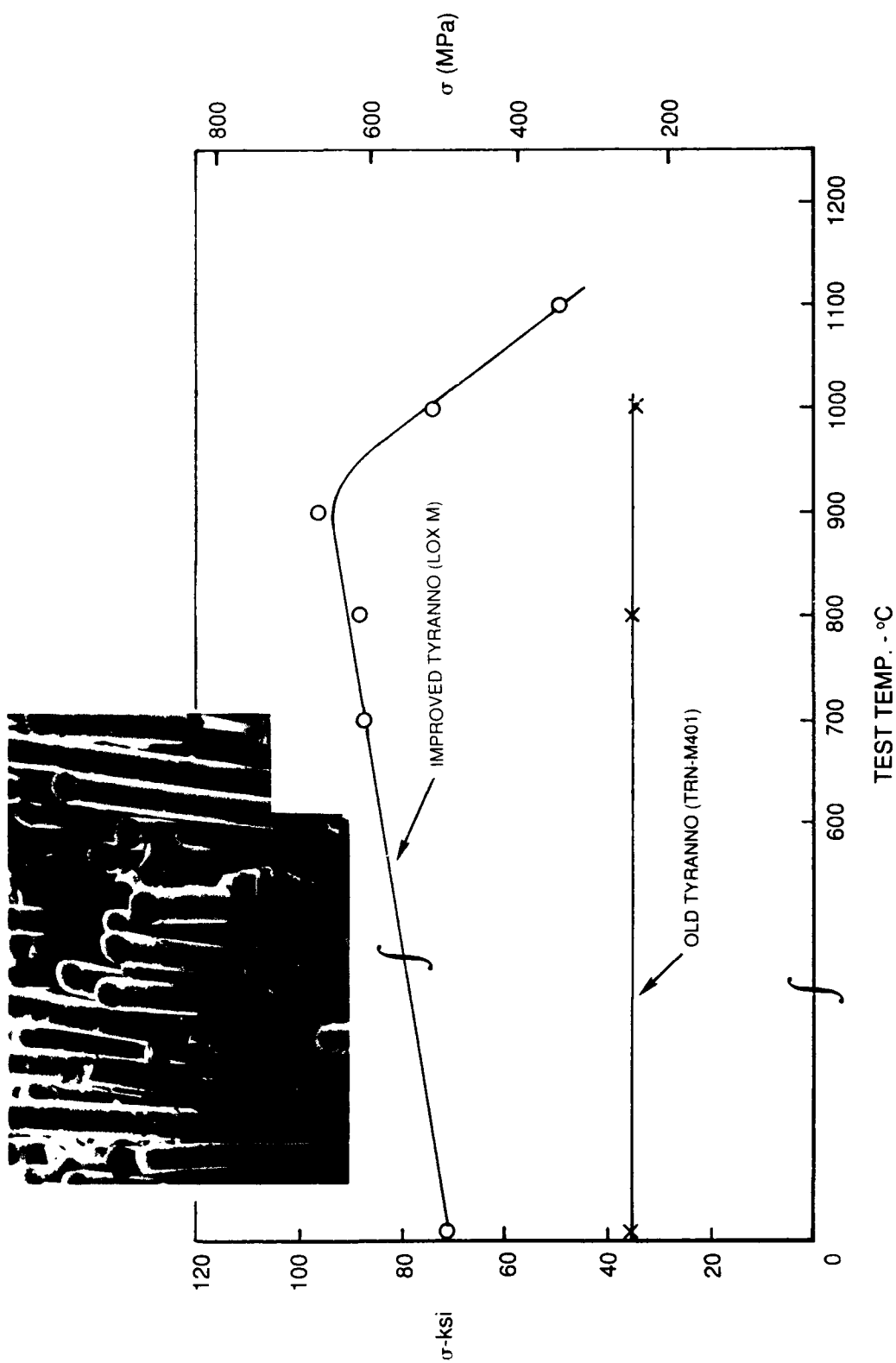
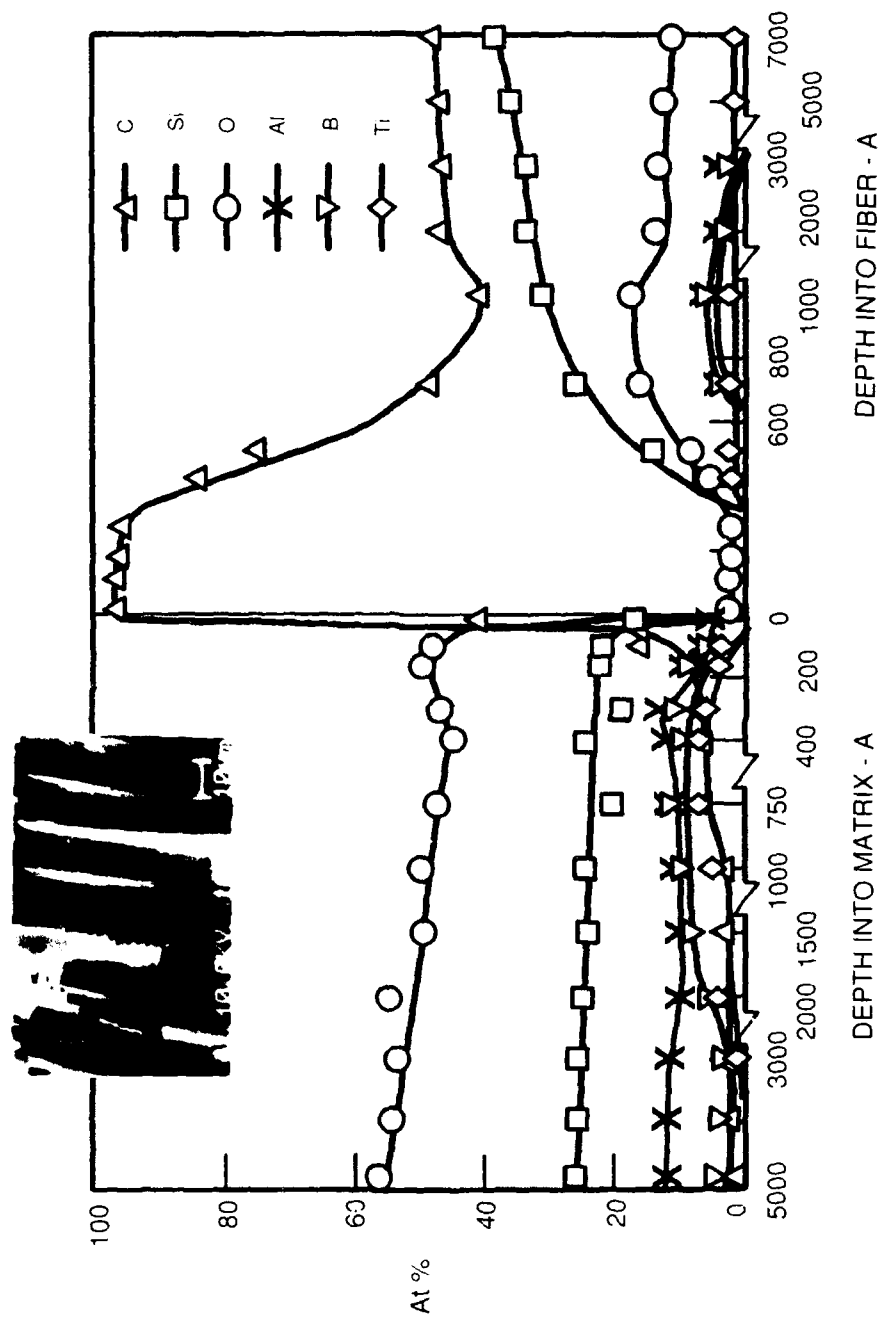


FIG. 19

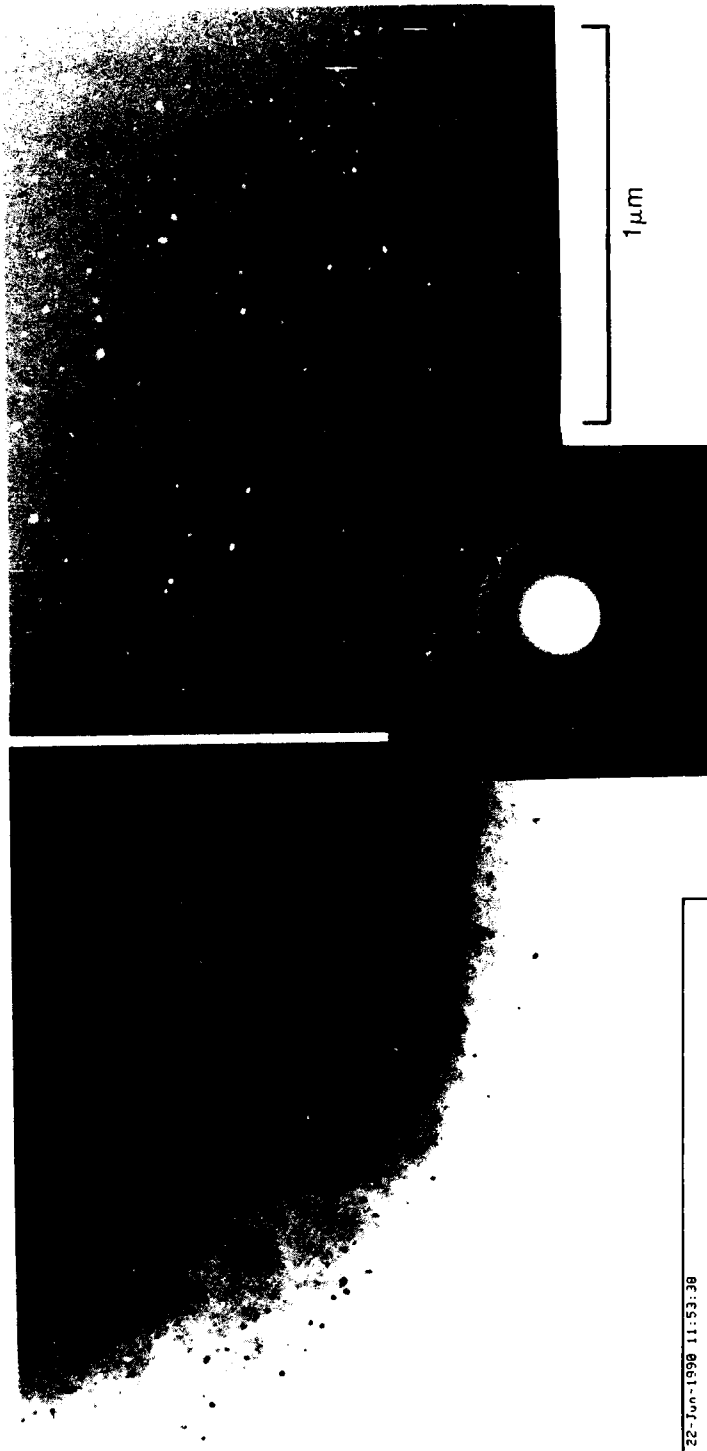
FLEXURAL STRENGTH (3-PT) VS TEMPERATURE IN AIR FOR UTRC-200 LAS
MATRIX/UBE TYRANNO FIBER COMPOSITES (0°/90°)



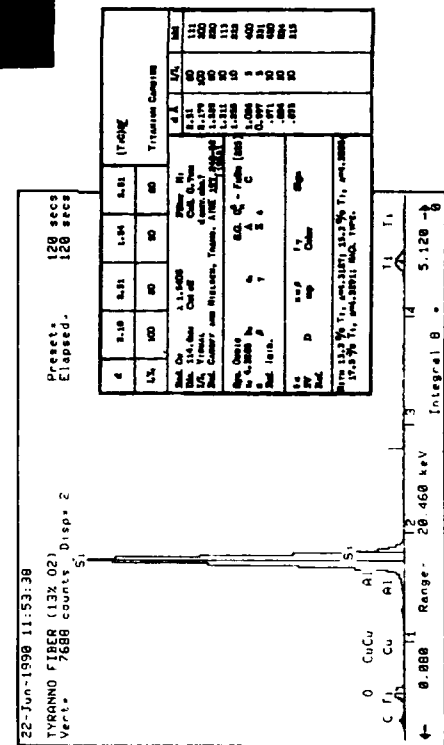
SAM DEPTH PROFILE
INTERFACIAL CHEMISTRY OF UTRC-200 LAS MATRIX/LOX M TYRANNO
SiC FIBER COMPOSITE #49-90



TEM/EDX/SAED THIN FOIL ANALYSES OF THE LOX M TYRANNO SiC FIBERS IN
UTRC-200 LAS MATRIX COMPOSITE #200-90



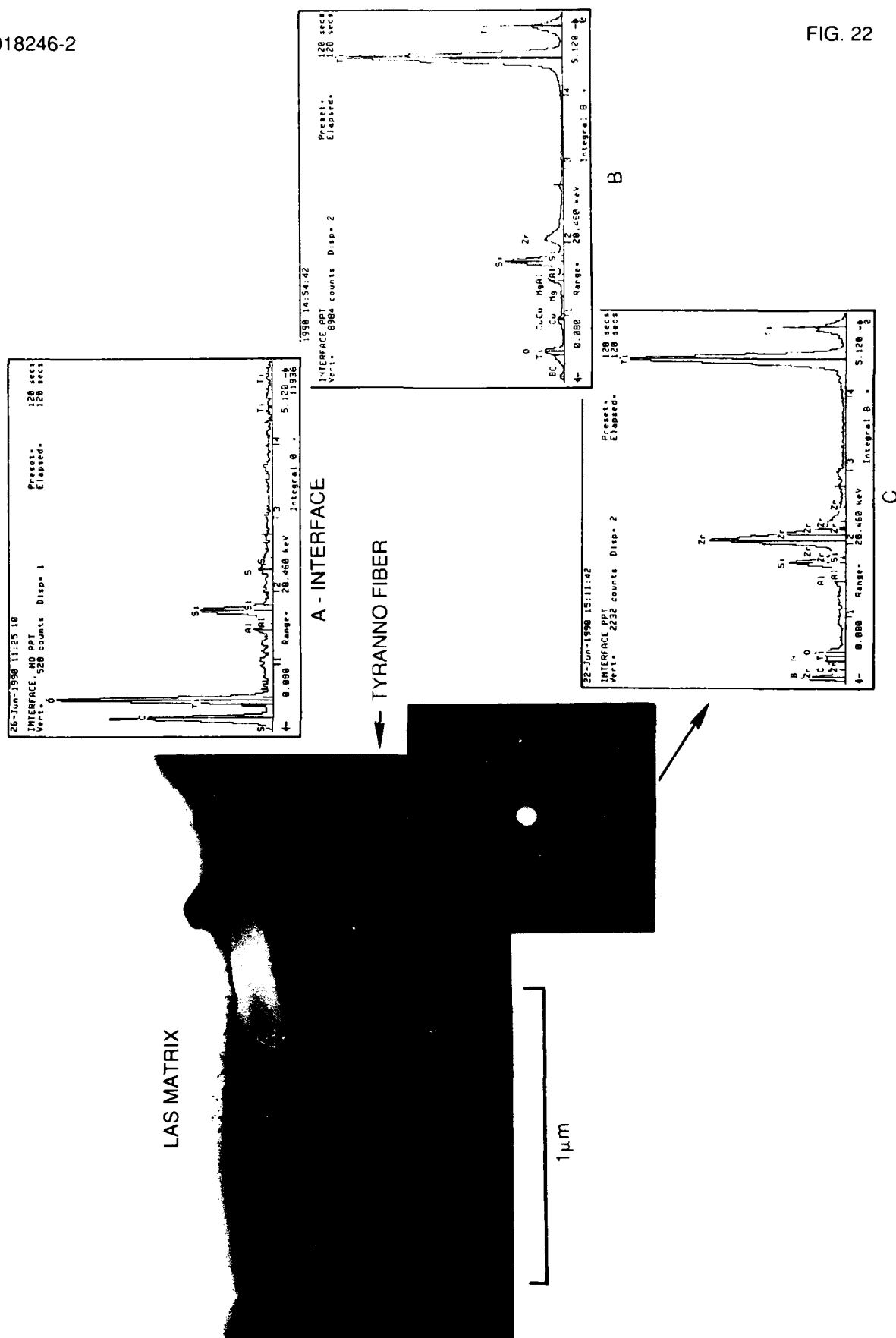
1 μm

 β -SiC+TiC

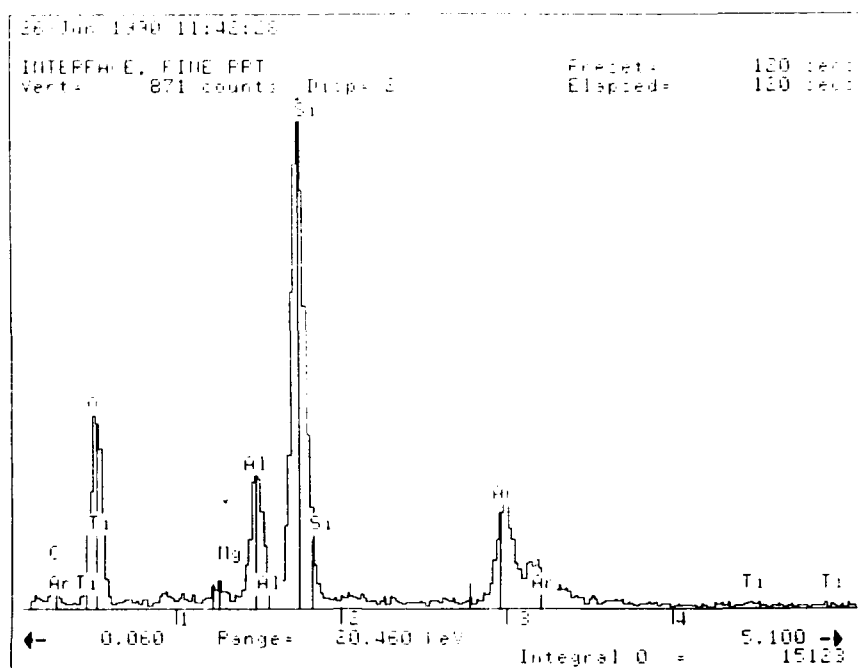
TEM/EDX/SAED THIN FOIL ANALYSES OF THE INTERFACIAL REGION IN AS-PRESSED COMPOSITE #200-90 (UTRC-200 LAS MATRIX/LOX M TRYANNO FIBERS)

R91-918246-2

FIG. 22



**TEM/EDX THIN FOIL ANALYSES OF THE INTERFACIAL REGION IN AS-PRESSED
COMPOSITE #200-90 (UTRC-200 LAS MATRIX/LOX M TYRANNO SiC FIBERS)**

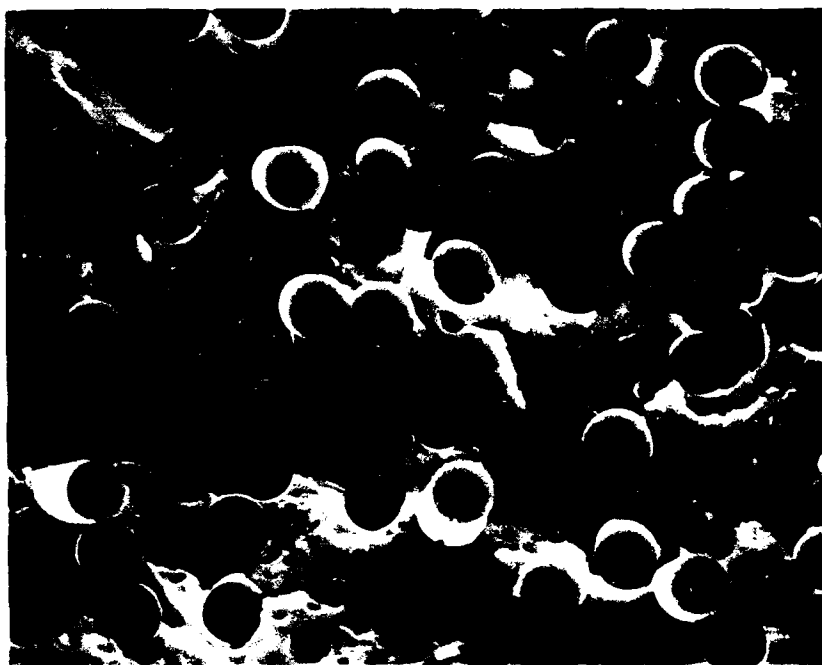


0.25 μm



0.25 μm

**INTERFACIAL FRACTURE CHARACTERISTICS OF LAS MATRIX/DOW CORNING SiC
FIBER (9217-57C1) COMPOSITE #414-90**



A)

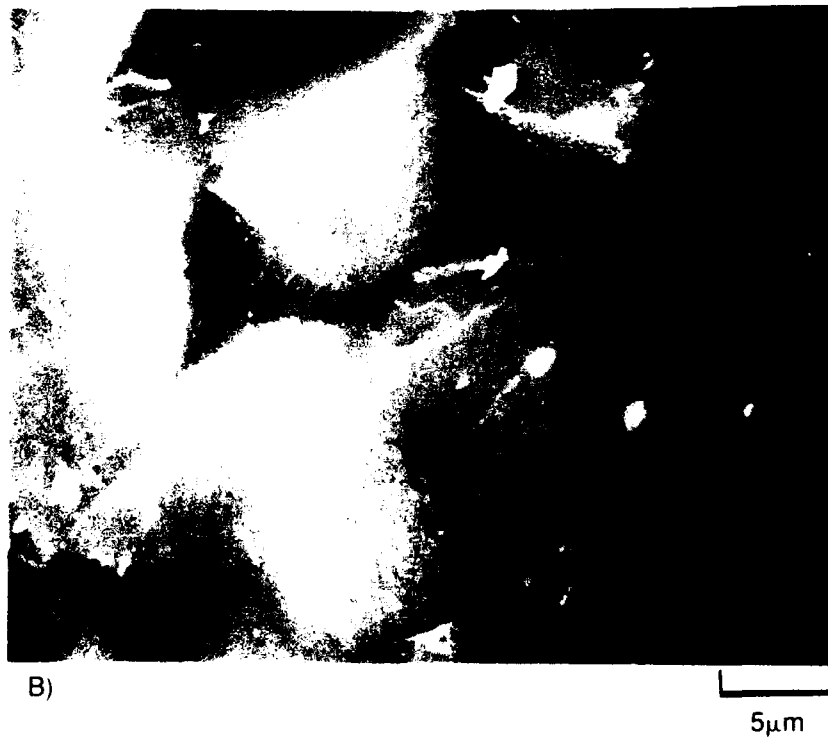
10 μm



B)

5 μm

**INTERFACIAL FRACTURE CHARACTERISTICS OF LAS MATRIX/DOW CORNING SiC
FIBER (9217-41C) COMPOSITE #1-91**



**INTERFACIAL FRACTURE CHARACTERISTICS OF BMAS MATRIX/DOW CORNING SiC
FIBER (9217-57C1) COMPOSITE #462-90**



A)

5μm



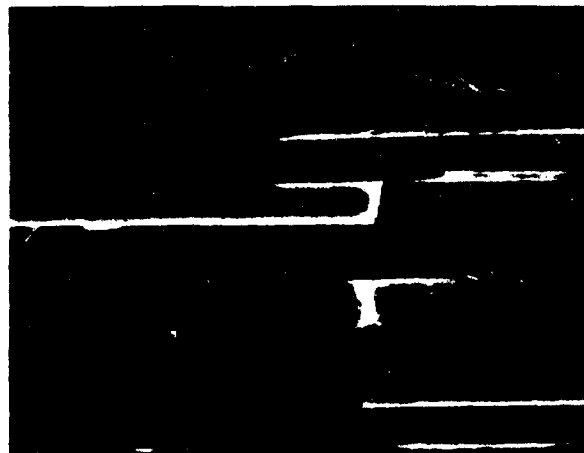
B)

5μm



C)

10μm



D)

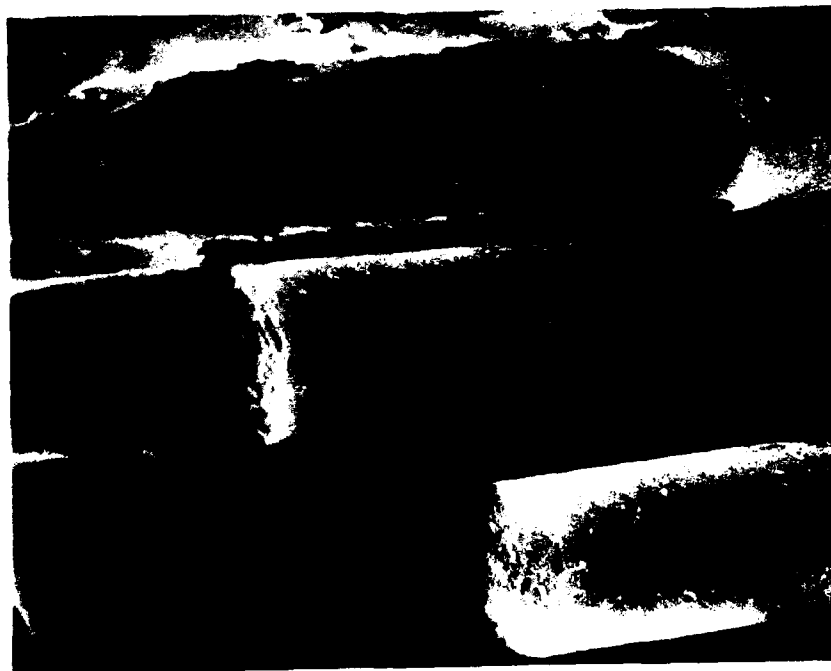
10μm

**INTERFACIAL FRACTURE CHARACTERISTICS OF BMAS MATRIX/DOW CORNING SIC
FIBER (9217-41C) COMPOSITE #2-91**



A)

5 μ m

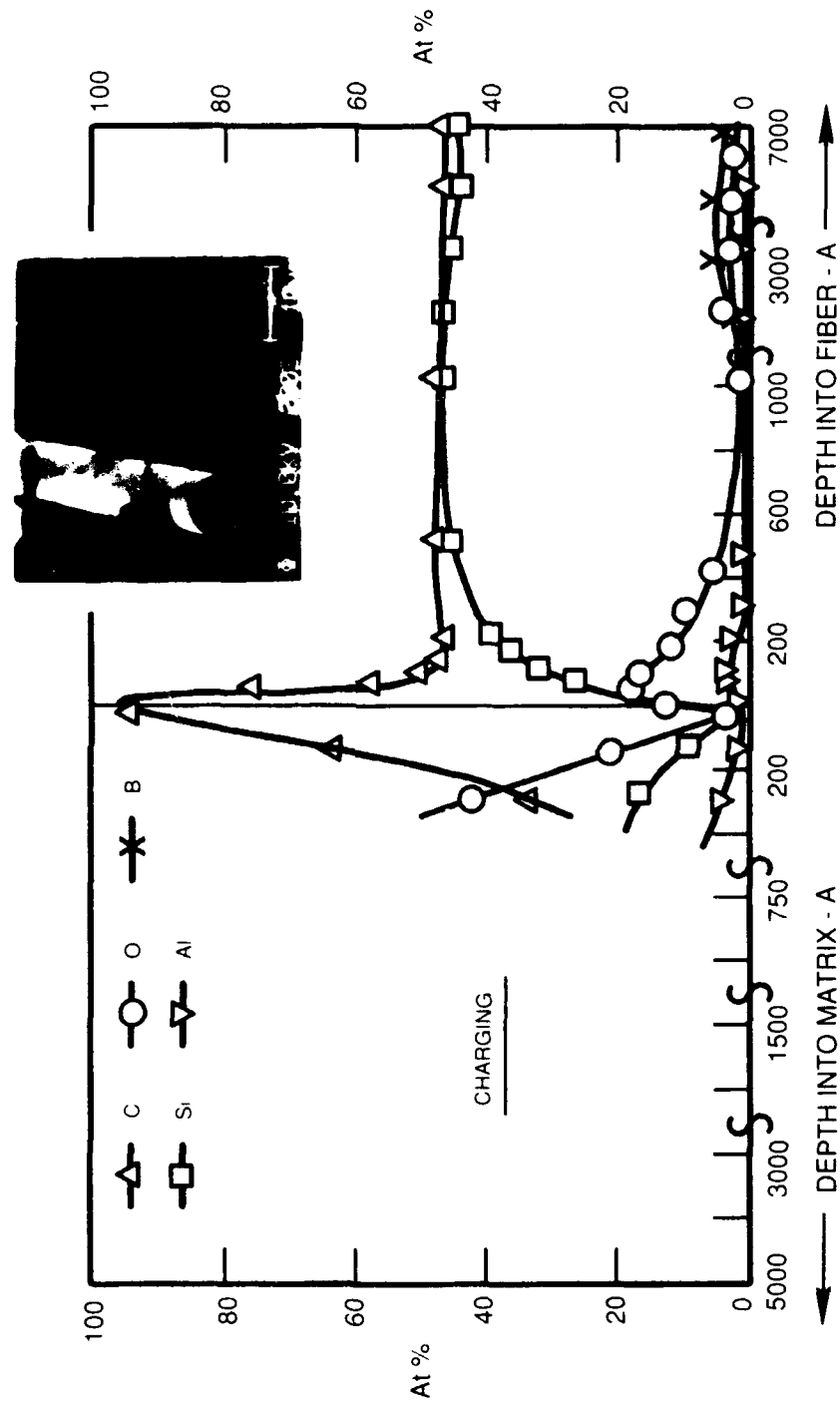


B)

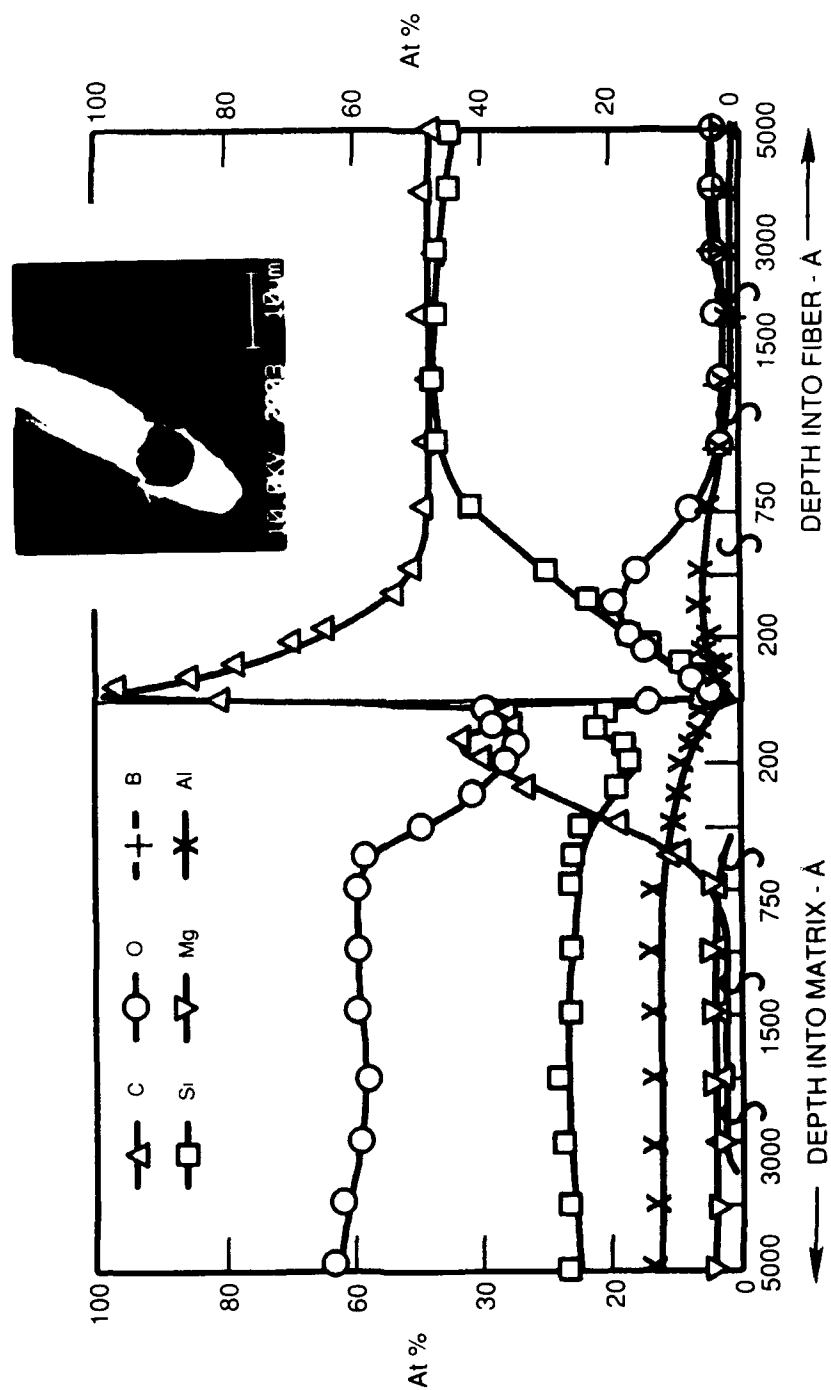
5 μ m

91-4-52-25

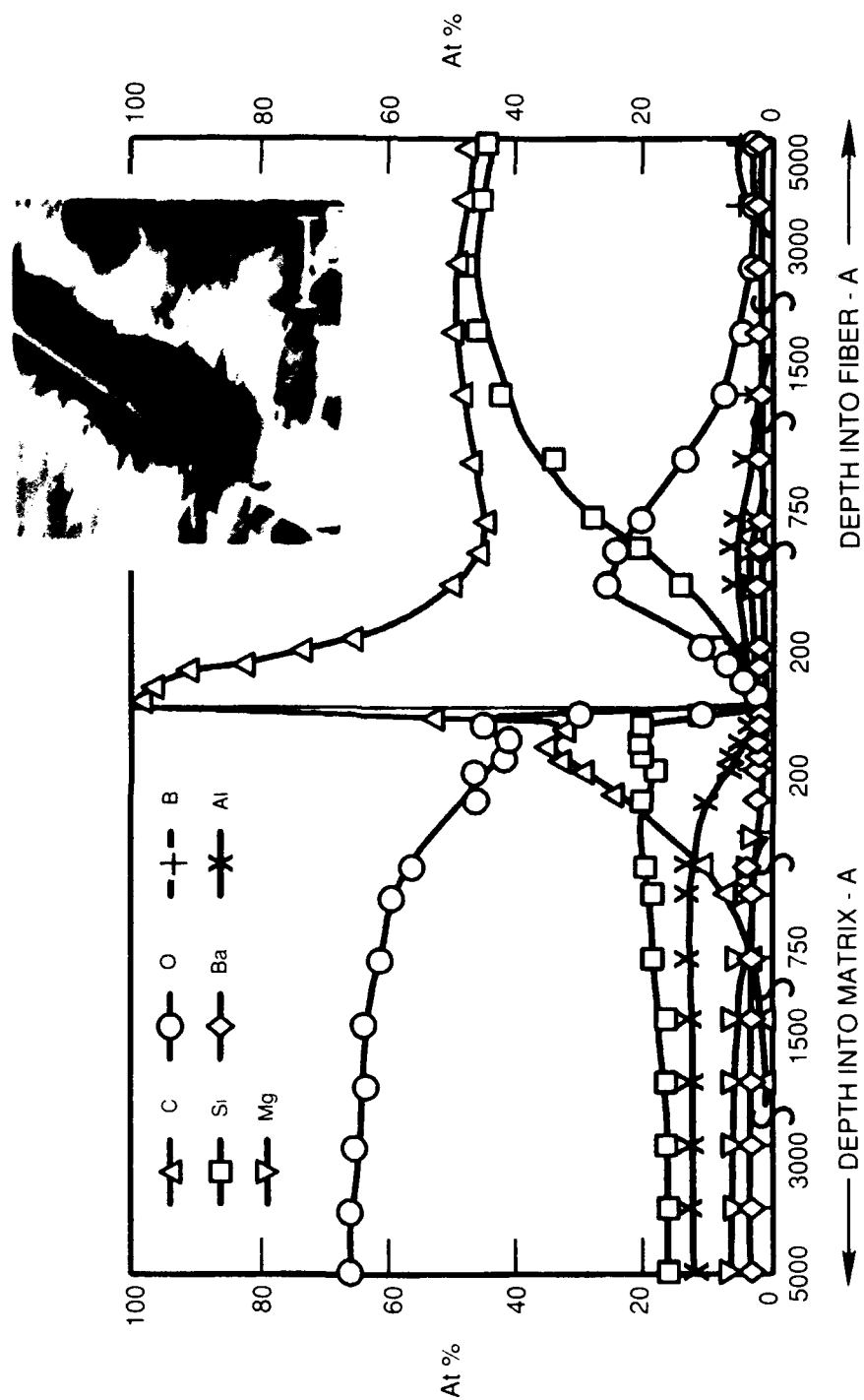
SAM DEPTH PROFILE
INTERFACIAL CHEMISTRY OF LAS MATRIX/DOW CORNING SiC FIBER
 (#9217-57C1, BLACK) COMPOSITE #414-90



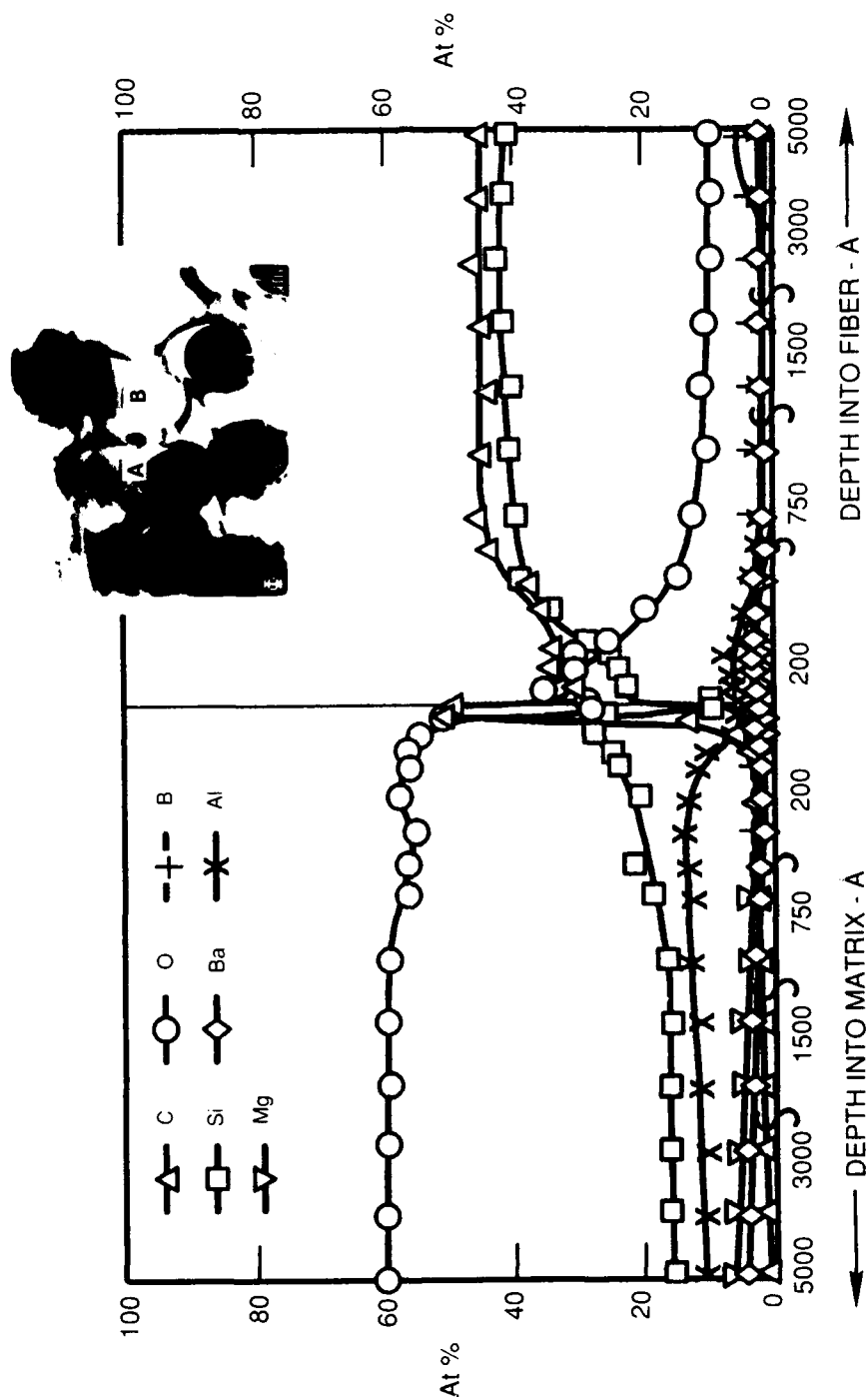
SAM DEPTH PROFILE
INTERFACIAL CHEMISTRY OF LAS MATRIX/DOW CORNING CRYSTALLINE
SiC FIBER (#9217-41C) COMPOSITE #11-91



SAM DEPTH PROFILE
INTERFACIAL CHEMISTRY FOR BMAS MATRIX/DOW CORNING CRYSTALLINE
SiC FIBER (#9217-41C) COMPOSITE #2-91



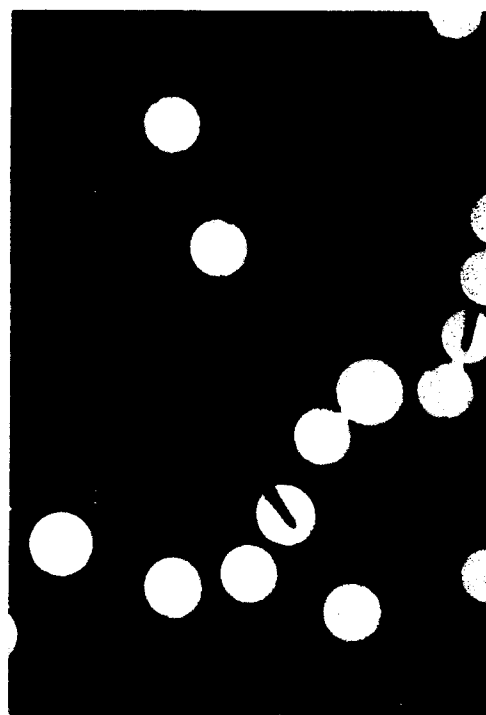
SAM DEPTH PROFILE
INTERFACIAL CHEMISTRY OF BMAS MATRIX/DOW CORNING CRYSTALLINE SiC
FIBER (#9217-57C1) COMPOSITE #462-90



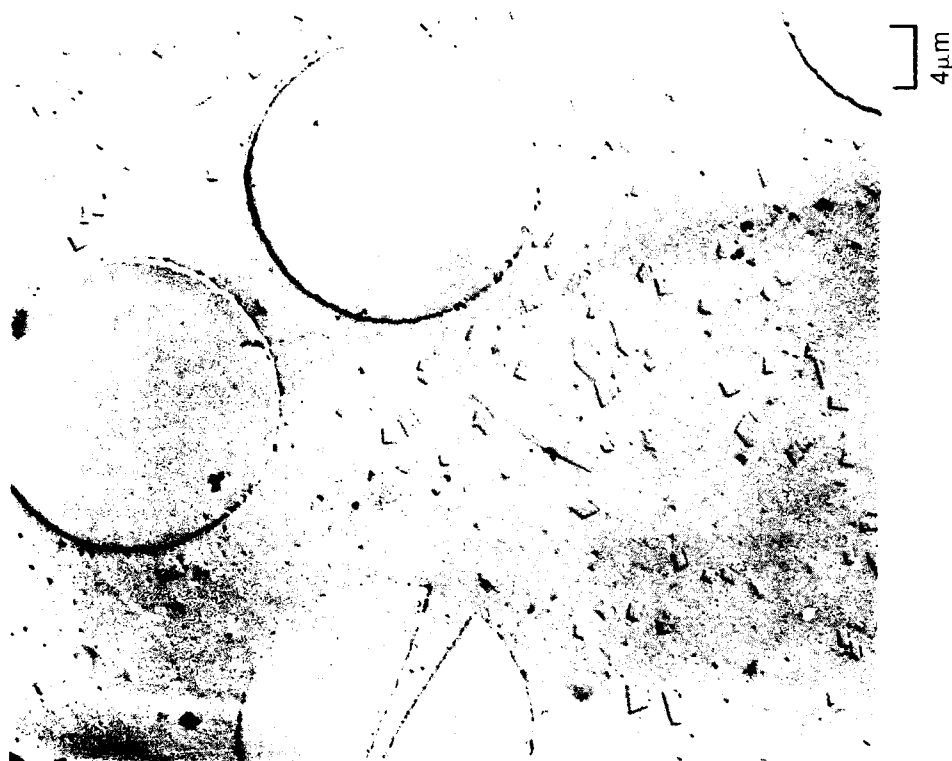
OPTICAL/TEM REPLICA CHARACTERIZATION OF LAS/DOW CORNING SIC FIBER
#9217-41C; AS-PRESSED, (COMPOSITE #1-91)



100 μm

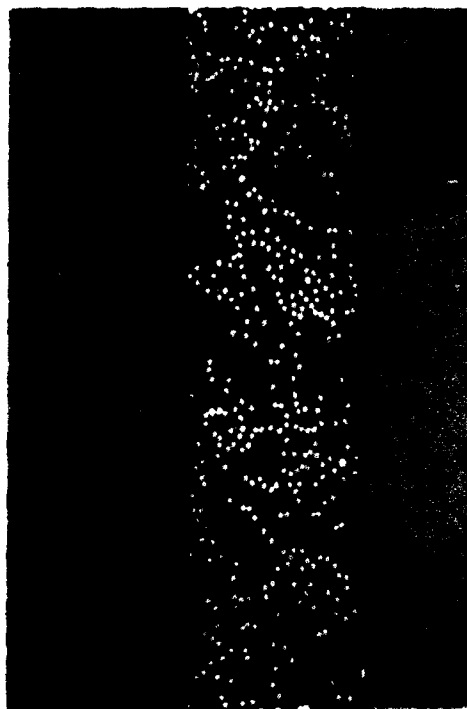


10 μm

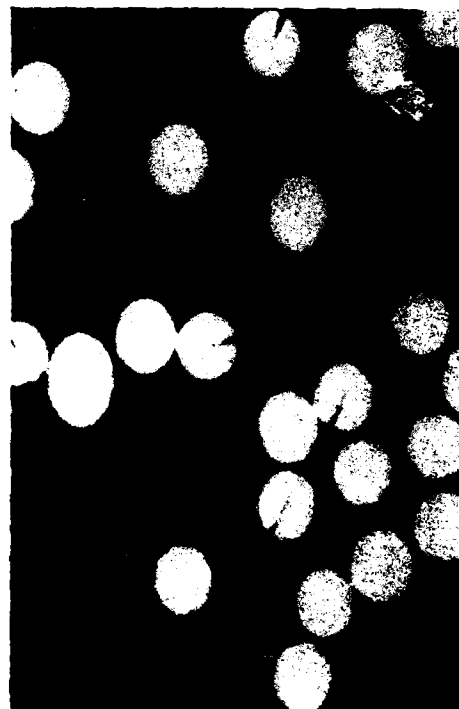


4 μm

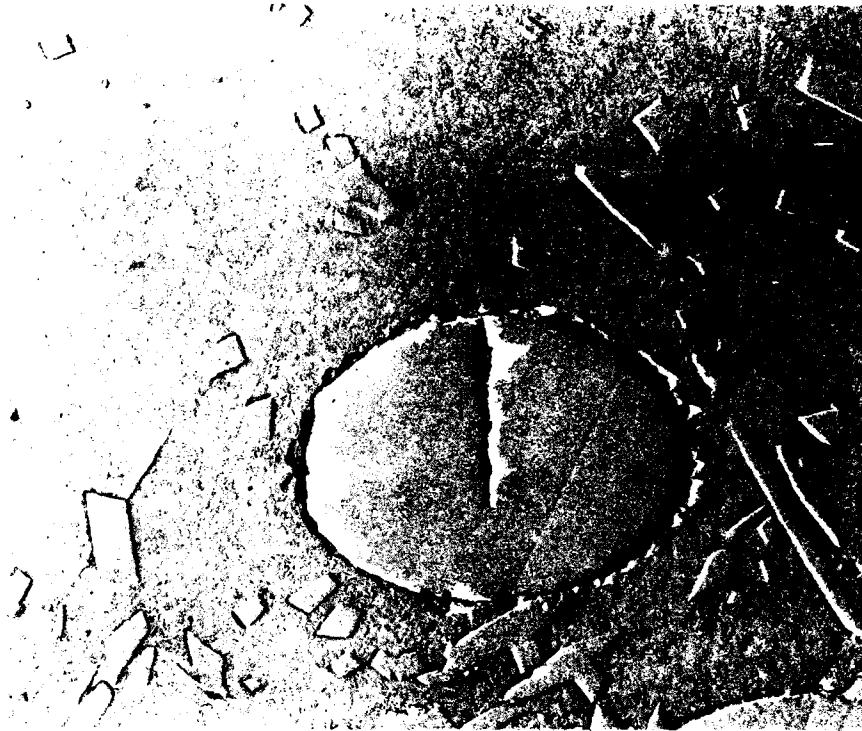
OPTICAL/TEM REPLICA CHARACTERIZATION OF BMAS/DOW CORNING SiC
FIBER #9217-57C1 (BROWN); (COMPOSITE #462-90)



100 μm

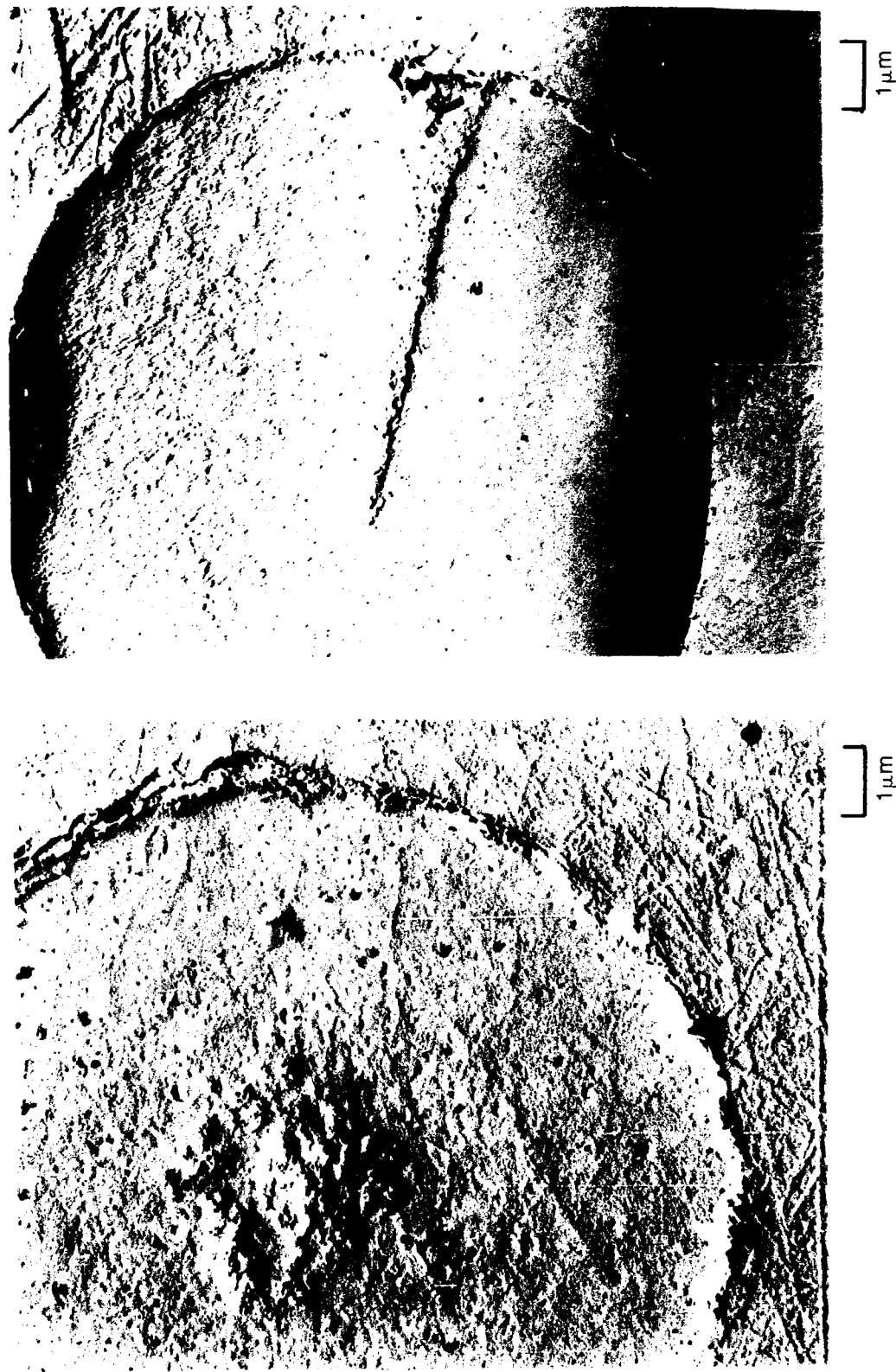


10 μm

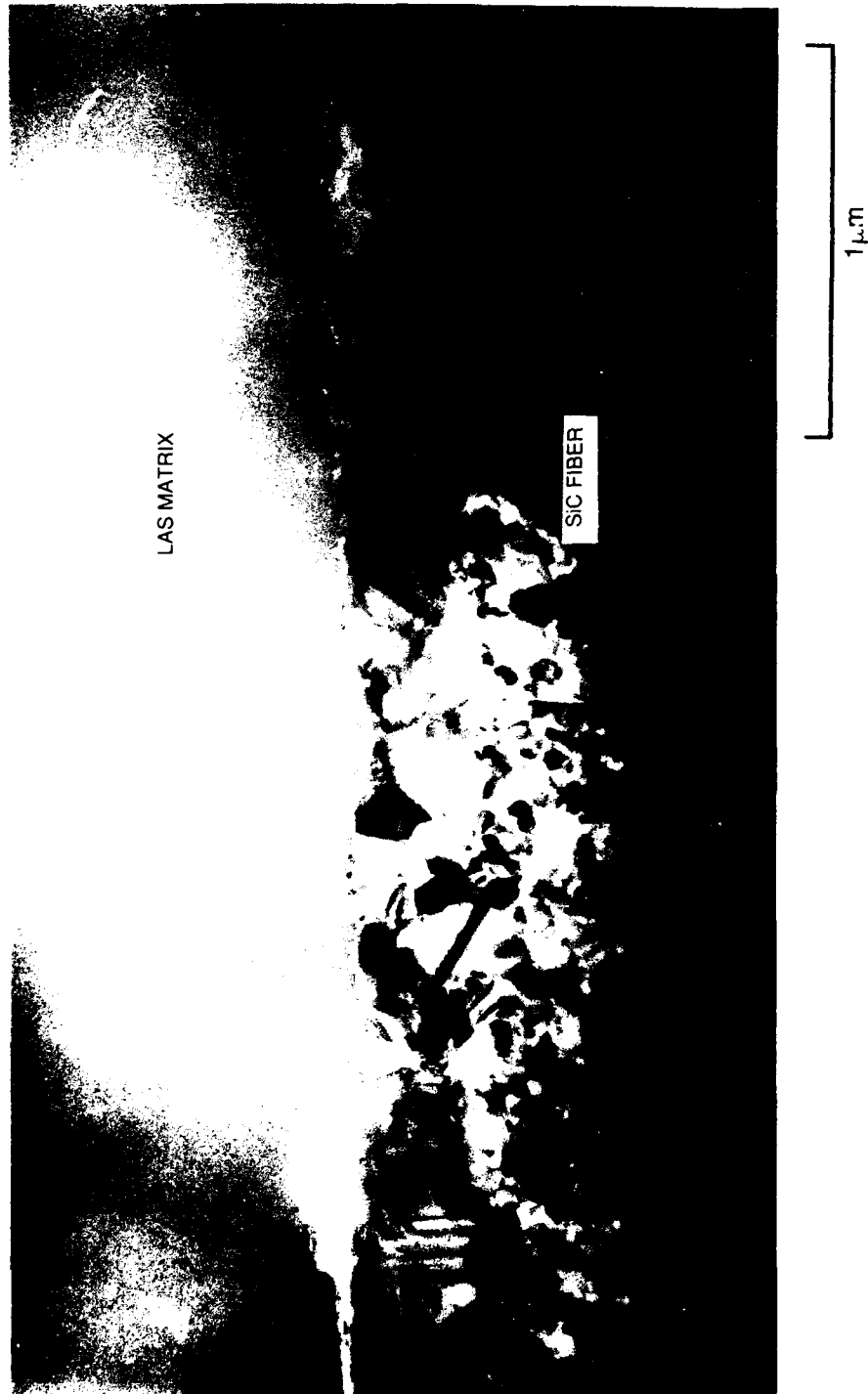


4 μm

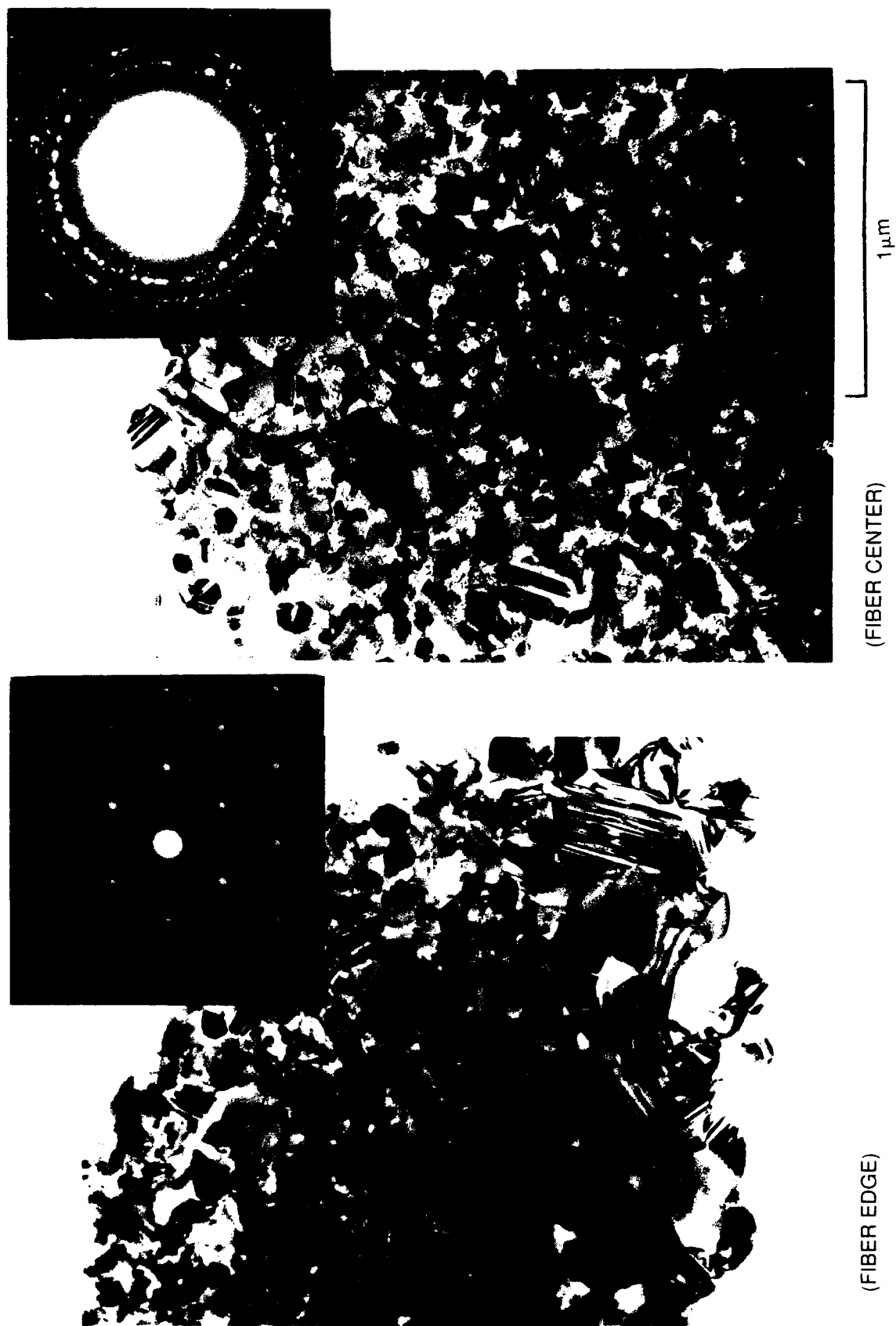
TEM REPLICA CHARACTERIZATION OF LAS/DOW CORNING SIC FIBER #9217-57C1
(BLACK); (COMPOSITE #414-90)



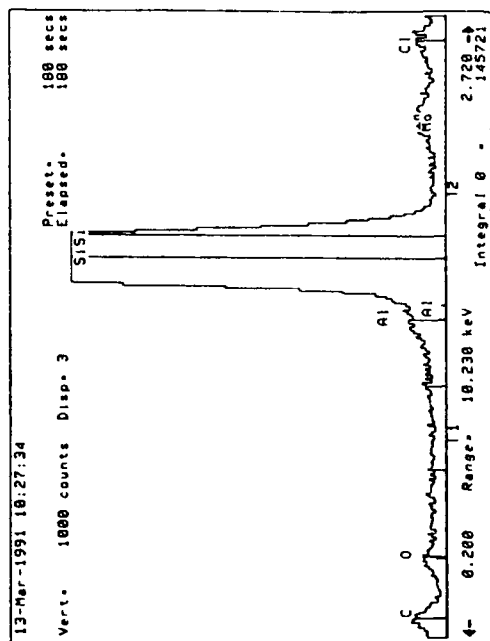
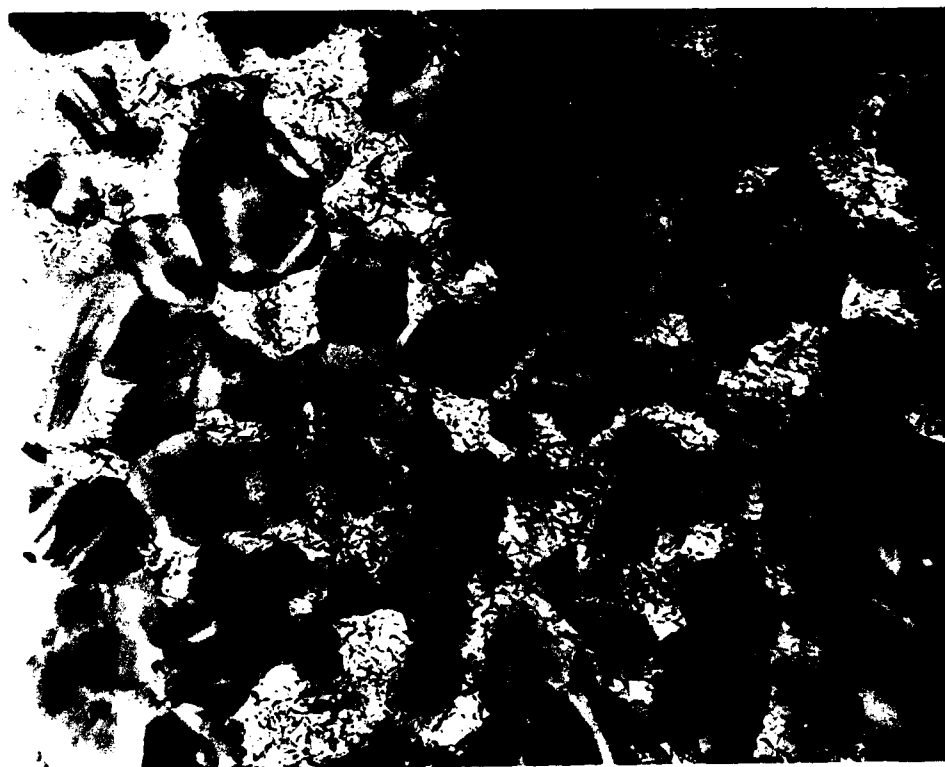
TEM THIN FOIL CHARACTERIZATION OF LAS/DOW CORNING SIC FIBER #9217-41C;
AS-PRESSED, (COMPOSITE #1-91)



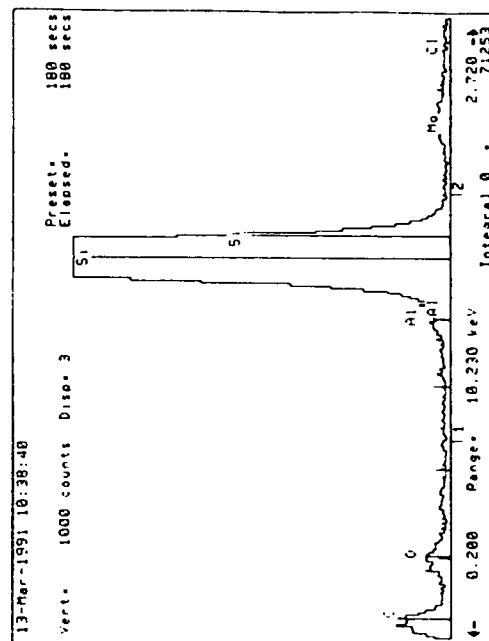
TEM/SAED THIN FOIL CHARACTERIZATION OF LAS/DOW CORNING SiC FIBER
#9217-57C1 (BLACK); (COMPOSITE #414-90)



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



FINE GRAIN PHASE



COARSE GRAINS