

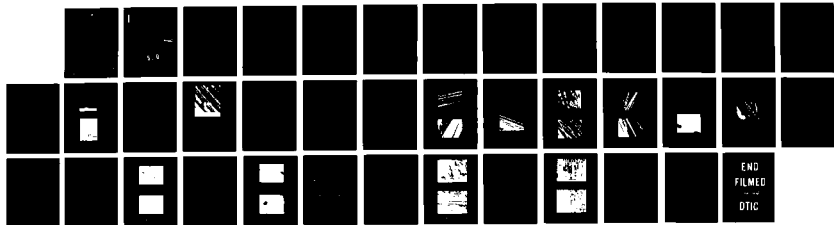
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IMPROVED OXIDATION RESISTANCE OF 3-D CARBON/CARBON
COMPOSITES(U) PHASEX CORP LEXINGTON MA
V KRUKONIS ET AL. 14 JAN 94 AFOSR-TR-94-0081

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Final Report

**Improved Oxidation Resistance
of 3-D Carbon/Carbon Composites
F49620-92-C-0036**

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14 January 1994

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SUMMARY

Carbon fiber reinforced silicon carbide matrix composites (C/SiC) were made by a process termed Supercritical Fluid Infiltration. A preceramic polymer, e.g., a polycarbosilane which can pyrolyze to form SiC, is dissolved in a supercritical fluid, the solution conveyed into a tightly woven preform of carbon fiber, and the preceramic polymer caused to deposit in the interstitial volume surrounding the fibers. Subsequent pyrolysis of the polymer forms the SiC matrix and fiber coating. Supercritical propane at conditions of 140°C, 4000 psi dissolves polycarbosilane to a concentration level of 30% (w/w), a level that results in substantial infiltration and deposition of the polymer. The yield of SiC from the parent polymer upon pyrolysis was determined to be about 50% (w/w); the polymer was fractionated using supercritical propane (in a process termed increasing pressure profiling), and it was found that some of the low molecular weight fractions gave extremely low yields of SiC (<25%) whereas some of the high molecular weight fractions yielded over 80% SiC. When the parent polymer was used for the infiltration studies the deposited material was modular in appearance suggesting that the liquid low molecular weight portion of the polymer was predominately and adversely influencing the uniformity. The high molecular weight fractions were later exclusively employed in carrying out the infiltration and composite formation studies.

The deposition/infiltration conditions were first determined using carbon tow and woven mats of carbon fiber. After the best combination of conditions as concerns maximum infiltration of preceramic polymer was found, 3D carbon preforms were used for subsequent testing. Initially a very thin layer of polymer was deposited on the fibers in the preform in order to improve the oxidation resistance. (These improved oxidation resistant preforms could then have been used for subsequent carbon/carbon production.) The SiC coated carbon preforms were measured for resistance relative to uncoated 3D preforms. At 1250°C for 4 hours in air, both materials lost essentially the same weight about 40%. The coating of SiC on the carbon fibers was not uniformly deposited and therefore did not impede attack by oxygen.

The experimental effort was then directed to more complete filling of SiC in the 3D carbon fiber preform. In the best tests multiple cycle infiltration/pyrolysis tests (similar to pressure-infiltration-carbonization cycles for carbon/carbon composites) specimens were made with 90% of theoretical density. These specimens exhibited enhanced oxidation resistance; in 48 hour exposure tests at 1250°C in air the SiC-infiltrated carbon preforms suffered about 10% weight loss, and the control (uninfiltrated) 3D specimens were essentially completely oxidized. Scanning Electron Microscopy analysis of the infiltrated and air-exposed specimens should that there was some shrinkage, i.e., oxidation of the surface, of some of the carbon fibers. In bend fracture testing the infiltrated specimens averaged 12,300 psi and after oxidation 8,600 psi.

I. INTRODUCTION

Topic AF92-016 sought developments in many areas of materials and advanced technology application. PhaseX Corporation proposed the application of a process termed Supercritical Fluid Infiltration to the improvement in oxidation resistance of advance carbon fiber/carbon matrix composites. Specifically, silicon carbide precursor polymers such as poly silanes and poly carbosilanes were to be infiltrated into carbon fiber mats or 3-Dimensional preforms, the polymer deposited so as to coat the fibers and partially fill the void structure, and the polymer pyrolyzed to silicon carbide coating, the silicon carbide providing the oxidation resistant coating.

Carbon/carbon (C/C) composites are the current state of the art material for extremely high temperature applications such as missile nose cones, rocket engines, and aircraft thrust reversers. However, even C/C composites suffer from some limitations, viz., the presence of microcracks in the matrix and/or fiber matrix debonded regions. In a high temperature atmosphere, especially, for example, in the bow shock of a reentry vehicle, oxygen (and especially atomic oxygen) can "burrow" into the microcracks and debond regions and accelerate oxidation attack of the fibers and matrix.

It is informative to discuss the C/C composite manufacturing process to show how voids and microcracks can derive. The manufacturing process is termed Pressure-Infiltration-Carbonization (and referred to by the acronym PIC). A preform of carbon fibers, e.g., either a 2D mat lay up or a 3D orthogonal knitted or pierced preform is placed into an autoclave, the autoclave evacuated, and hot pitch (or some other carbon forming resin) hydrostatically forced into the preform; hydrostatic pressure is typically 10-20,000 psi. The pitch infiltrated preform is then subjected to high temperature (2000°C), inert atmosphere carbonization. The pyrolysis reactions convert the resin to carbon, and concomitantly, the gasification of some of the pitch causes voids and fissures. The resulting structure is re-infiltrated to fill the macro cracks and macro voids, and repyrolyzed. At the end of the fourth PIC cycle the material is referred to as ACC-4 (Advanced Carbon Composite, 4 cycles of PICing). At the end of the fourth cycle the microcracks, now of the order of a few microns in width, are so small that the hydrostatic pressure of 10,000 or 20,000 psi is not sufficient to force the hot resin into the interstitial regions to reduce microcracks because of surface tension limitations.

Supercritical fluids, i.e., liquids and gases above their respective critical points, exhibit no surface tension limitations, and thus, at least, conceptually, a carbon forming polymer dissolved into a supercritical fluid can be conveyed into the micropores of the composite, the polymer deposited and subsequently pyrolyzed. Such a concept was the basis of a previously funded program (AFOSR/DARPA) Contract F49620-85-C-0053 to Babcock & Wilcox under which PhaseX Corporation carried out the SFI tests, and insofar as the results on that program were the basis of a variant suggested to AFOSR in response to AF92-016, a brief summary of the findings will be presented before describing the research and results of the current Phase I program.

In the proposal the technology, viz., supercritical fluids processing that was to be applied to the development of the SFI process, was described; a brief background on supercritical fluid solubility phenomena is also presented in the next section for its relevance to the development of the SFI process and its application to the formation of improved C/C composites.

II. BACKGROUND ON SUPERCRITICAL FLUID SOLUBILITY BEHAVIOR

A. Historical Development

Many compounds and materials can be dissolved by gases and liquids at conditions above their respective critical points. The first report of the phenomenon was in 1879 by two Scottish researchers, Hannay and Hogarth. They found that a supercritical fluid could dissolve compounds and that the dissolving power is a function of pressure; at high pressure a supercritical fluid dissolves a material to a larger extent than at low pressure.

An example of the pressure dependent dissolving power of supercritical fluids is given in Figure 1, which shows the solubility of naphthalene in two gases, carbon dioxide and ethylene. Curve A is the solubility of naphthalene in ethylene at 35°C (26°C above the critical temperature ethylene); the data show that at about the critical pressure (50 atm) a further increase in pressure causes the solubility to rise quite dramatically. Curve B shows the solubility of naphthalene in carbon dioxide at 45°C (14°C above its critical temperature); as for the ethylene case at about the critical pressure of carbon dioxide (73 atm) the solubility of naphthalene rises as pressure increased. Two points on the ethylene/naphthalene curve, viz., 1 and 2, point out how the solubility data can be extended to the development of a process to separate materials. A compound (in this case naphthalene) can be dissolved and extracted from some mixture at conditions of Point 1 (200 atm, 35°C) and the pressure can subsequently be reduced to Point 2 (100 atm) resulting in the precipitation of naphthalene; the ethylene can be recompressed to 100 atm and recycled to the extractor to dissolve more naphthalene.

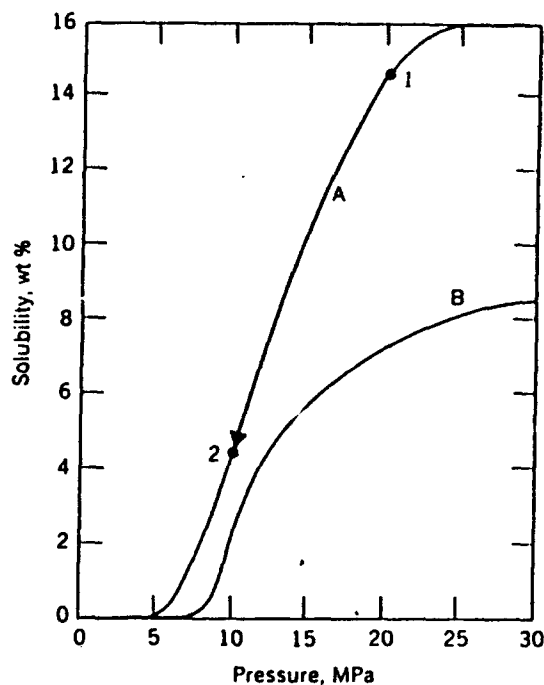


Figure 1. Solubility of Naphthalene in Ethylene and Carbon Dioxide

Applying a similar concept to Supercritical Fluid Infiltration, then, the compound to be dissolved at a high pressure would be the polycarbosilane, and the polymer would be deposited into the dense fiber matrix when the pressure was lowered.

Although some of the details of, for example, equipment configuration are different for the infiltration process compared to an extraction process, supercritical fluid processing has been in operation in the food and flavors industries on a large scale for over fifteen years, and thus the technical and engineering facets of this technology are fully optimized. It is of value to describe, first, a typical industrial extraction process (which might be the extraction of the flavoring agents from hops or decaffeination of coffee beans) to point out how the pressure dependent dissolving power of a supercritical fluid is advantageously applied to the infiltration of a polymer into a carbon fiber preform.

B. Extraction Process Operation

A schematic diagram of a process which uses a supercritical fluid as a pressure-dependent solvent to extract an organic substance is given in Figure 2a. Four basic elements of the process are shown, viz., an extraction vessel, a pressure reduction valve, a separator for collecting the material dissolved in the extractor, and a compressor for recompressing and recycling fluid. (Ancillary pumps, valving, facilities for fluid makeup, and heat exchange equipment are omitted from the figure for clarity and ease of presentation.) Figure 2b shows extensive data on the solubility of naphthalene in carbon dioxide as a function of temperature and pressure, and the solubility "map" provides information for the selection of parameters for carrying out an extraction.

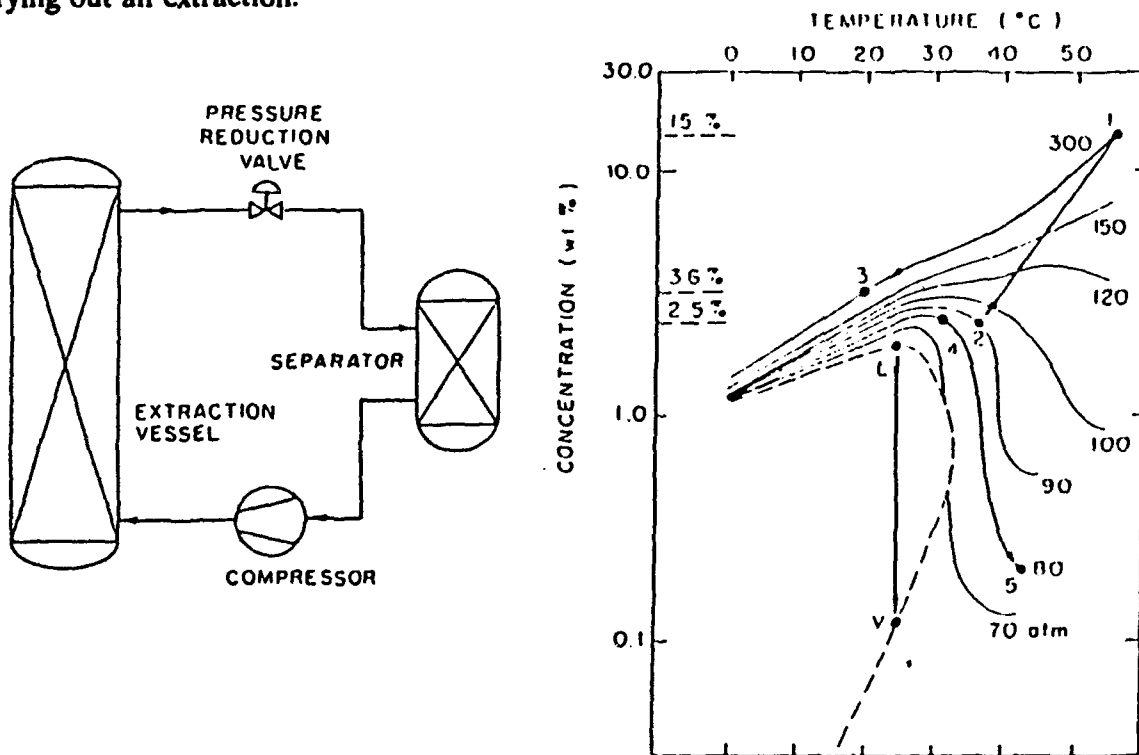


Figure 2. Schematic Diagram of Extraction Process and Data Used to Explain Operation and Recycle of Gas.

Reference to Figures 2a and 2b is made in explaining how a supercritical fluid process operates. Some process operating parameters are indicated on two solubility isobars in Figure 2b: 1 represents conditions in the extractor, e.g., 300 atm, 55°C, and 2 the conditions which exist in the separator, 90 atm, 32°C. The extractor vessel is assumed to be filled with naphthalene mixed with another material, which for purposes of this discussion, is assumed to be insoluble in carbon dioxide. Gas at condition 1 is passed through the extraction vessel wherein it dissolves and extracts the naphthalene from the insoluble material. The carbon dioxide-naphthalene solution leaving the extractor is expanded to 90 atm through the pressure reduction valve as indicated by the directed path in Figure 2b. During the pressure reduction step, naphthalene precipitates from the solution because as Figures 1 and 2a show, the dissolving power of carbon dioxide is low at low pressure. The precipitated naphthalene is collected in the separator, and the carbon dioxide leaving the separator is recompressed and returned to the extractor. This recycle process continues until all the naphthalene is dissolved and extracted. The directed line segment 1-2 in Figure 2b and its reverse on the solubility diagram represent the process.

Even though solubility data for naphthalene in carbon dioxide have been used to explain the operation of a supercritical fluid process, the solubility behavior shown in Figure 2b is very general. Any solid material and many liquid materials that dissolve to a modest extent in any supercritical fluid behave in this manner. The differences among various materials is only one of degree, e.g., the solubility of some other material in carbon dioxide may be higher or lower than that of naphthalene, but the pressure-temperature-concentration curves will exhibit similar characteristics. Many polymers, pitch, silicones, and silicon carbide precursor polymers that are used to create a silicon carbide matrix, and still other materials will behave similarly to the solubility isobars shown by Figure 2b.

In addition to the unique pressure-dependent dissolving power properties of supercritical fluid solvents, they possess very attractive transport properties, and these properties reinforce their value in the application of coating and forming a silicon carbide matrix on carbon mats carbide and 3-D preforms with ceramic precursor polymers. Table 1 compares the diffusivity, viscosity, surface tension, and density of typical organic solvents such as hexane and toluene to typical supercritical solvents like carbon dioxide and ethylene.

Table 1. Comparison of Properties of Supercritical Fluids and Organic Solvents

<u>Solvent</u>	<u>Diffusivity</u> (cm ² /sec)	<u>Viscosity</u> (cps)	<u>Density</u> (g/cc)	<u>Surface Tension</u> (dynes/cm)
Supercritical Fluid	10 ⁻³	0.02-0.05	0.6-1.0	0
Organic	10 ⁻⁵	1	0.8	20-50

As the table shows, the diffusivity of a solute diffusing through a supercritical fluid is two orders of magnitude higher than in a liquid solvent; a high diffusivity equates to high extraction rates of a component from liquid and solid surfaces. The viscosity of a supercritical fluid is much, much lower than that of a liquid, and a low viscosity and a zero(!) surface tension (zero

because there is no gas-liquid interface) make possible the extraction of materials from pores and cell structures with dimensions of less than one micron. The zero surface tension also is important for the reverse of extraction, viz., infiltration of materials into small pores; supercritical fluid solvents and solutions in supercritical fluids have the ability to penetrate into pores and channels of dimensions much less than one micron. The combined solubility and transport features of supercritical fluids strongly suggested their advantageous use in this proposed silicon carbide matrix coating and deposition process.

It is the zero surface tension and very low viscosity properties of a supercritical fluid that are most attractive for the proposed research. These properties allow small pores around fibers in a tow or woven mat to be penetrated for depositing a material. On the previous DARPA/AFOSR program this innovative process has already been shown to be technically superior to other impregnation processes for improving the oxidation resistance of fully-formed carbon/carbon composite parts such as ACC4. As related in the Introduction the process was to be tested for coating preforms (i.e., not already infiltrated and carbonized composites).

C. Results of Previous Work that Suggested Application of Supercritical Fluid Infiltration to C/C composites.

As related in Section II. B. previous work on Supercritical Fluid Infiltration had been carried out on an AFOSR/DARPA funded program; the goal of the program was to improve the oxidation resistance of C/C composites by coating the internal voids and external fissures with SiC precursor polymer, then pyrolyzing the polymer to SiC.

Figures 3 and 4 are cross sections of ACC4 that has been processed by SFI. Supercritical propane was used to dissolve the polycarbosilane and the solution depressurized to precipitate the polymer in the microvoids of the composite before the polymer was subsequently pyrolyzed to SiC.

Figure 3 is a scanning electron microgram (SEM) of a cross section of 2D C/C composite and the light grey regions designate the presence of SiC. Figure 4 is an Energy Dispersive Spectrogram (EDS), often referred to as an elemental "dot map", of the same region as that shown in Figure 3; the white "dots" are the signal for Si (from SiC). A comparison of the location of the light grey regions in Figure 3 and the Si dots in Figure 4 confirms that the microvoids in the composite have been filled (or coated) with SiC. In addition to filling the voids with SiC an improved high temperature oxidation resistance was a goal of the program. ACC4 composite test specimens, as produced and infiltrated, exposed to an oxygen atmosphere at 900° F, and the weight loss measured.



Figure 3. Scanning Electron Micrograph of Cross Section of SiC Filled C/C Composite



Figure 4. Energy Dispersive Spectrogram of Cross Section of Figure 3 Showing Population and Density of Silicon Atoms

Figure 5 compares the weight loss for the respective samples, and it is seen that the SiC infiltrated specimens are much more resistant to oxidation.

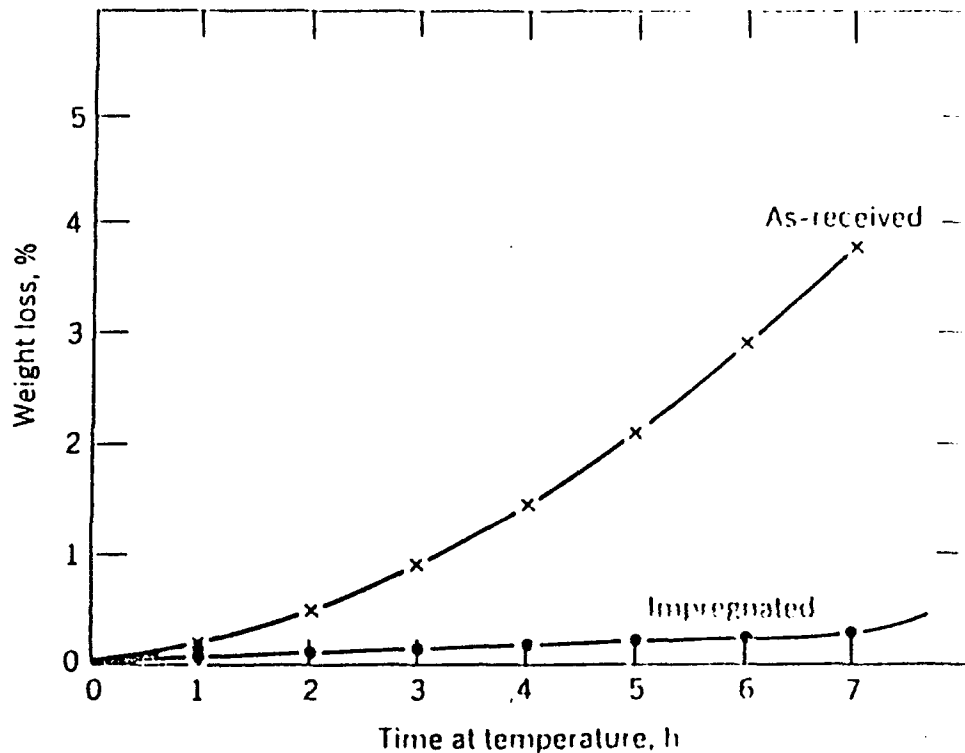


Figure 5. Comparison of Composite Weight Loss; the Lower the Weight Loss the Greater the Oxidation Resistance

Several other filtration tests were carried out on the program using carbon tow as the substrate; the goal of the tests was to deposit a thin film (a "flash") of polycarbosilane polymer on the carbon fibers. Figure 6 is a high magnification SEM that shows the extent of coverage of the surface of the fibers. The small "islands" of discontinuity are probably a result of fiber/fiber contact, but it is to be noted that the coverage of the fibers by the deposited and pyrolyzed polymer is quite complete.

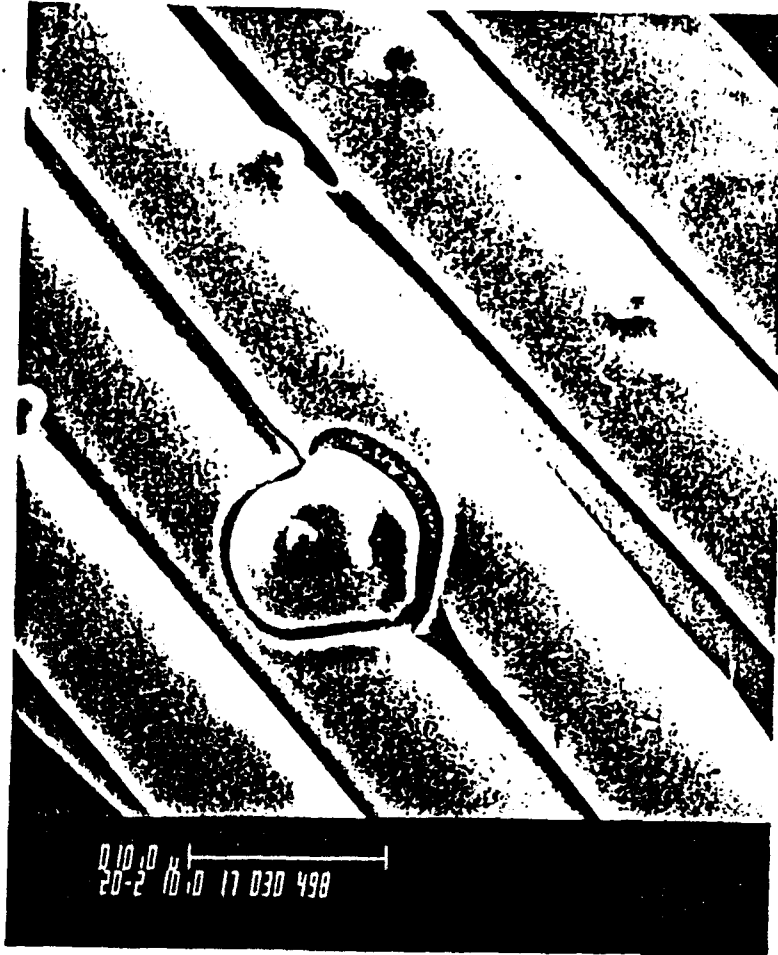


Figure 6. High Magnification SEM of Surfacing Coating of Carbon Fibers in a Tow

It was on the basis of the AFOSR/DARPA program results that the infiltration of SiC precursor polymer into mats or preforms of carbon fiber was suggested as a technically viable process for forming improved oxidation resistant C/C composites. If the carbon fiber is coated with thin "flash" of SiC, it is quite probable that oxidation resistance can be improved.

III. EXPERIMENTAL PROGRAM AND RESULTS

The program had several technical objectives, viz.,

1. To infiltrate into dense 2D and 3D preforms of carbon fibers a solution of polycarbosilane in a supercritical fluid (such as propane, for example).
2. To determine conditions to deposit the polycarbosilane in the preform, either onto the fibers as a thin coating or as a continuous coherent matrix of silicon carbide (after pyrolysis).
3. To convert the polycarbosilane to SiC.
4. To determine the properties of the composites formed by the overall process of infiltration, deposition, and pyrolysis.

A. Experimental Procedure

The experimental apparatus used for solubilizing and depositing the SiC precursor polymer is shown in Figure 7. The particular configuration is the solubilizing (or extraction) system for determining the solubility of compound in a gas. The important components are shown, viz., a gas compressor, extractor vessel, pressure letdown and flow control valve, flow rate indicator, and volume integrator. Heaters, temperature and pressure measurement, and control functions are not included in the figure for simplicity of discussion.

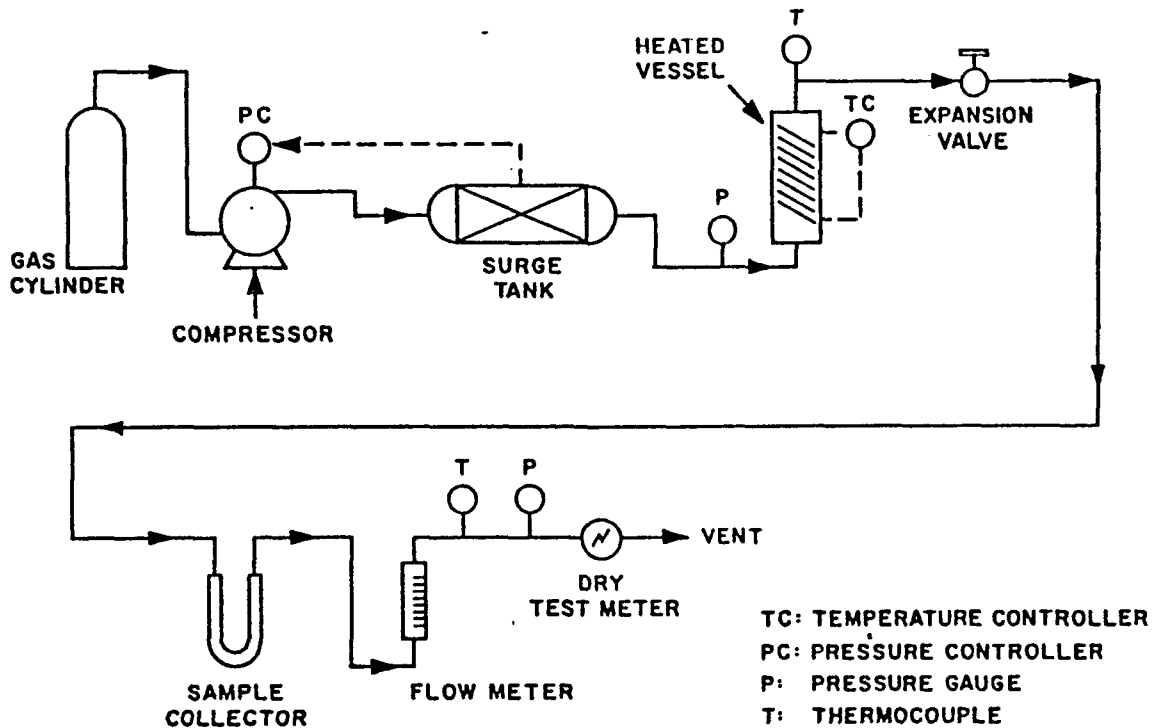


Figure 7. Schematic Diagram of Laboratory Supercritical Extraction/Deposition Apparatus

Later in this report the fractionation of the polymer into narrow molecular weight cuts is discussed, and the same apparatus is used to carry out the fractionation as follows: a charge of polymer is loaded into the vessel as described above, the system conditions are brought to the desired temperature, and gas at initially a low pressure is passed through the charge of polymer. At the particular combination of conditions, especially the low pressure, the lowest molecular weight species are dissolved; the amount of material that is dissolved at this condition is collected in the U-tube, and the gas is raised to a higher pressure to dissolve the next highest molecular weight fraction. The previously filled tube is changed for a fresh one, and the higher pressure - higher molecular weight fraction is collected. The step wise increase in pressure is continued until all the material is dissolved. The entire procedure is termed increasing pressure profile fractionation.

Finally the same apparatus is used to carry out the infiltration tests with the modification of the addition of another vessel above the extraction vessel that was shown schematically in Figure 7.

For the infiltration/deposition tests two vessels in series are employed as shown in Figure 8. In preparation for a test the SiC precursor polymer is charged to the first (bottom) vessel, the carbon substrate to be coated to the second, and the two-vessel system and associated valving connected to the high pressure piping shown previously in Figure 1. Temperature of both vessels (which can be controlled independently at either identical or different temperature) is adjusted to the desired level(s), and with Valves 1 and 2 open and Valve 3 closed pressure is brought to the desired level via the compressor section shown in Figure 1. For this program propane is the gas solvent used; carbon dioxide (used industrially in the coffee, hops, and spice extraction processes) can dissolve (some of) the polycarbosilane polymer, but very high pressure is required; propane can dissolve the polymer completely at lower pressure, and it is felt now that propane represents the better choice as concerns economics of the process. Phasex recognizes that advanced technology must be balanced with reasonable economics if the process is to be translated to government or commercial reality.

When the pressure has reached the desired level, gas flow through the two vessels is initiated, and flow is continued until some polymer is seen to collect in the U-tube downstream of the pressure reduction valve. Observation of the precipitation of polymer there ensures that the polymer in Vessel 1 has been dissolved and has been transported (through Valve 2) into Vessel 2. The flow is stopped immediately upon observation of the precipitation of polymer in the U-tube, Valves 3,2,&1 closed (in that order), and the system held at pressure and temperature for a selected period of time to allow diffusion and homogenization of the polycarbosilane polymer to obtain. The pressure and temperature are then lowered along a constant volume profile path to cause the polymer to nucleate and deposit. As related earlier heterogeneous nucleation is desired, and nucleation is a function of initial concentration (e.g., whether the polymer/gas initially solution is saturated), initial temperature, pressure, and, very importantly, the rate of attainment of supersaturation which directly affects (and effects) the deposition of polymer from the gas phase onto the carbon fiber substrate).

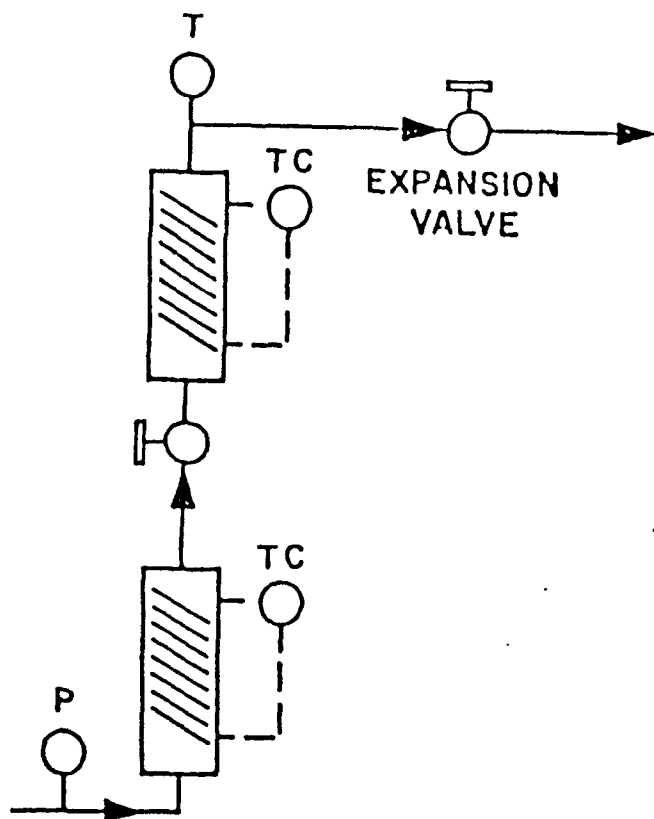


Figure 8. Two Vessel Configuration for Infiltration/Deposition

B. Infiltration into Single Layer Mats.

Tests with deposition of the polymer onto carbon fiber woven mats or sections of separated carbon fiber were carried out first because of their simplicity of analyses by optical microscopy, and the results are most facilely presented in the form of photomicrographs. For the most part in the first series of tests the tightly woven mat is first separated into looser fiber bundles for the infiltration/deposition tests; separation is done for two reasons, viz., ease of microscopy examination and for quantitative evaluation of the uniformity of coating on individual fibers that might otherwise be impeded if all the fibers were contiguous. Later in this program tightly woven mat and preforms (made from several layers of mat) were tested. Figure 9 is a photomicrograph of a few fibers from the uncoated mat; the scale marker on the photograph shows that the carbon fibers are about $7-8\mu$ in diameter. A lower magnification photomicrograph of a section of uncoated carbon fibers separated from the dense mat is given in Figure 10.

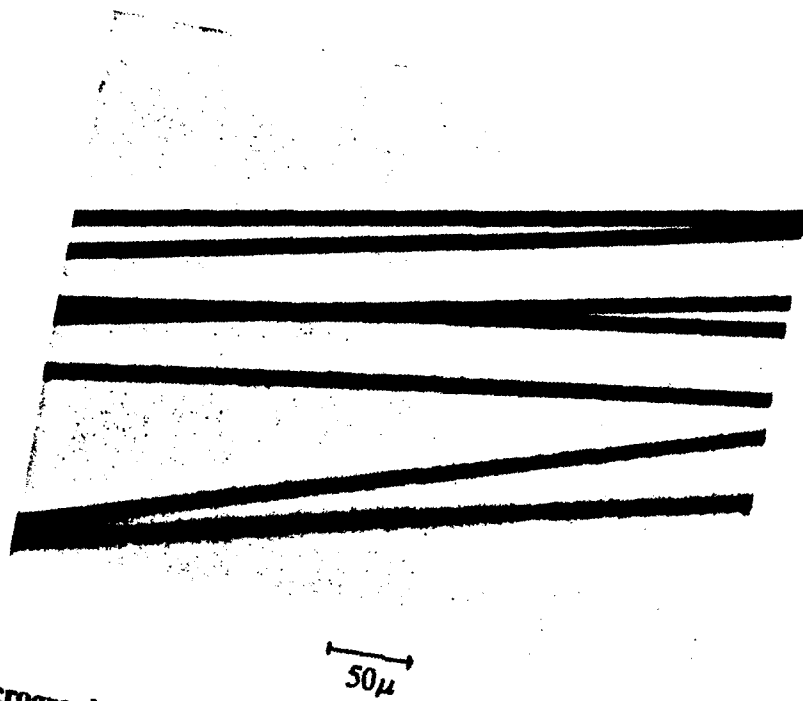


Figure 9. Photomicrograph of Uncoated Carbon Fibers Separated From Woven Carbon Mat

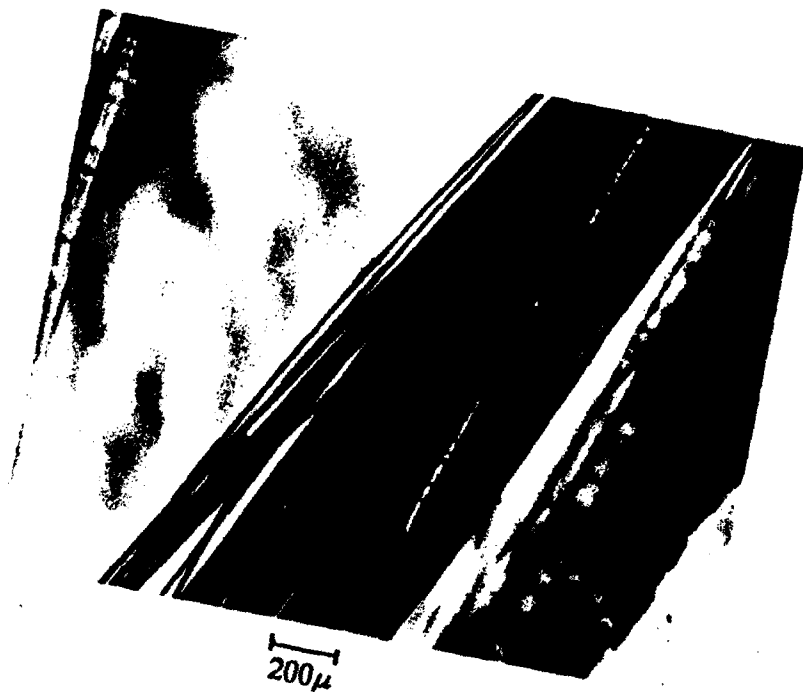


Figure 10. Lower Magnification Photomicrograph Showing Carbon Fibers at Edge of Mat

Many deposition tests were carried out during the early period, and some selected samples are presented to show how the early work progressed toward the goal of producing uniform adherent coatings of precursor polymer in the fibers and also to show some of the problem areas that were to be resolved. For ease of presentation the photomicrographs presented below accent only a few fibers (out of a group of tens or scores), but usually the photomicrographs shown are representative of the sample. Several different types of coatings, e.g., beads, powdery, rough, etc., have been formed on the fibers during the testing of parameters and are discussed below.

Figure 11 shows carbon fibers coated from supercritical propane solution using the parent polycarbosilane polymer. "Beads" of polymer have been deposited. At the infiltration deposition conditions of 4000 psi, 140°C the parent polymer is liquid, and it is postulated that the beads that have formed on the carbon fibers are a result liquid polymer surface tension forces and phenomena.

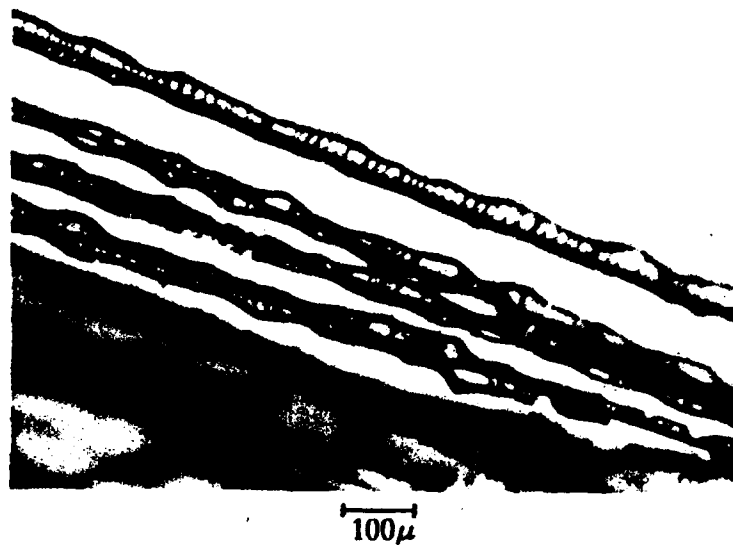


Figure 11. Photomicrograph of Carbon Fibers Infiltrated with Parent Polymer

At other deposition conditions, viz., at 100°C, which is near the critical temperature of propane (96°C), beads also resulted using the parent polymer as shown in Figure 12.

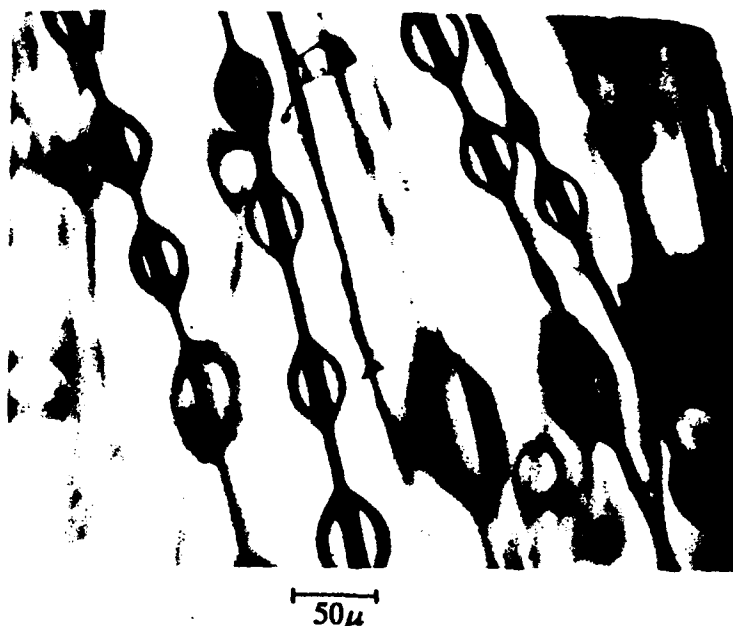


Figure 12. Photomicrograph of Carbon Fibers Infiltrated with Parent Polymer

At low pressure, where the solubility of the polymer is low, discrete beads were formed as shown in Figure 13; the discrete, small beads are probably the result of low concentration in the gas phase combined with preferred heterogeneous nucleation sites on the fibers.

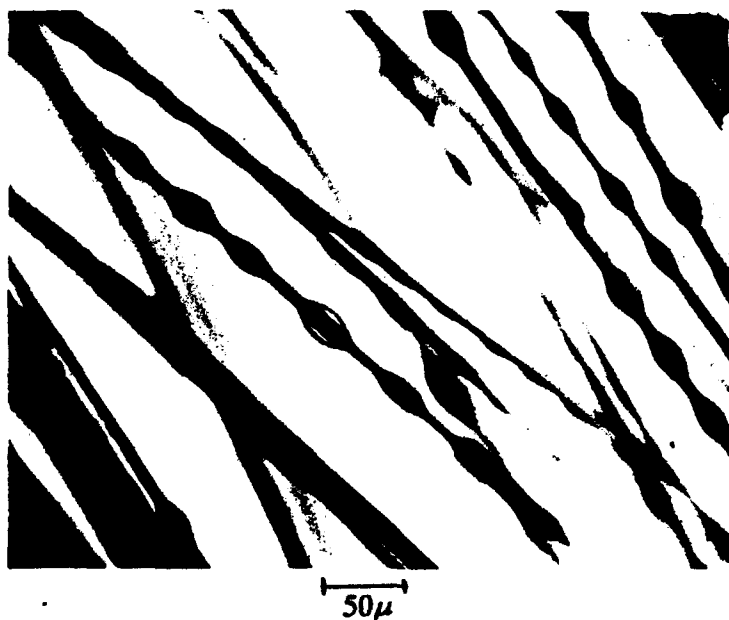


Figure 13. Photomicrograph of Carbon Fibers Infiltrated with Parent Polymer at Low Concentration in Propane.

Some of the parent polymer was fractionated so as to remove the low molecular weight (and liquid forming) material, and the highest molecular weight species were employed in subsequent infiltration/deposition tests. Figure 14 shows fibers from typical infiltration test using the higher molecular weight fraction. Figure 15 is a wider area micrograph showing many carbon fibers from a tow.

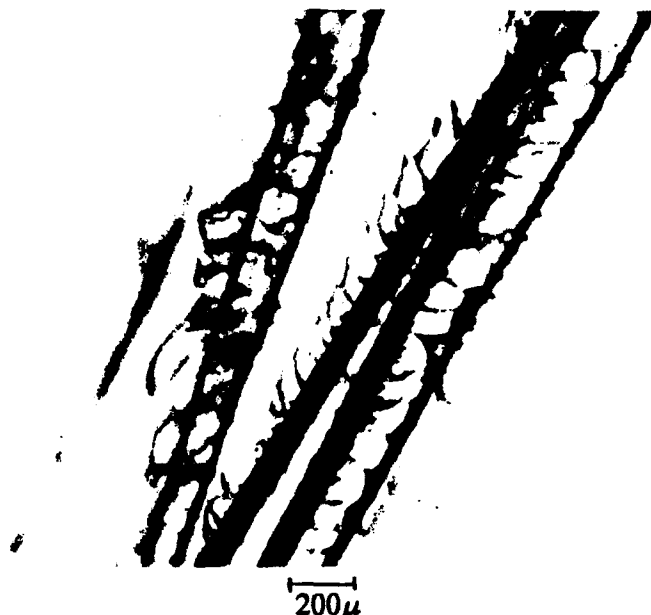


Figure 14. Carbon Fiber Infiltrated with Fractionated High Molecular Weight Polycarbosilane

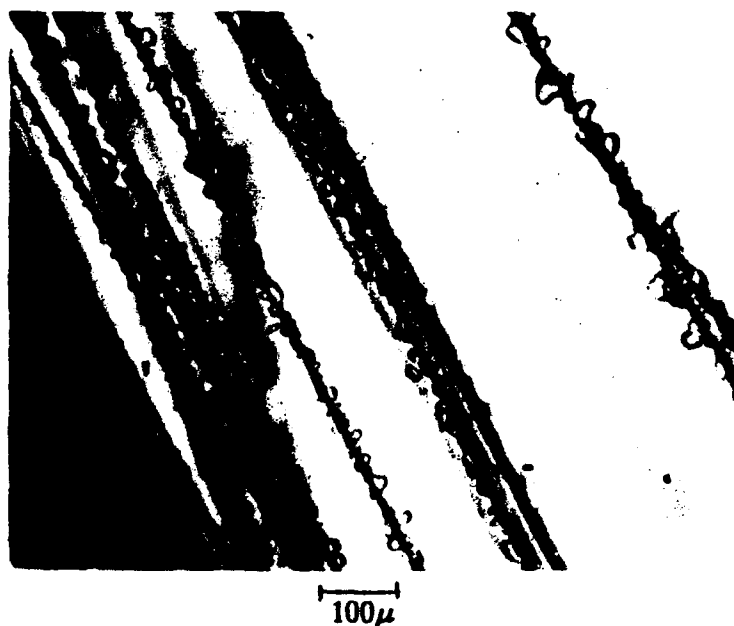


Figure 15. Low Magnification Photomicrograph of Other Infiltrated Unseparated Fibers Using Fractionated Polycarbosilane

Instead of a "beady" deposition that was seen with the parent polymer, the deposit seen in Figures 14 and 15 are more crystalline in appearance, a reflection that the low molecular weight and "runny" oligomers have been removed by the fractionation.

Some other infiltration tests with the low MW free species yielded deposits as shown in Figure 16. In Figure 16 the microscope focuses on many carbon fibers at the surface of the mat, the deposit that results from a rapid cooling/pressure decrease in the infiltration vessel. The deposit is very loose and appears to consist of agglomerates of particles. There may have been both homogeneous and heterogeneous deposition occurring here.



Figure 16. Photomicrograph of Carbon Fibers at Surface of Mat Infiltrated with Low Concentration of Fractionated Polycarbosilane

As with almost all early testing on exploratory research and development programs, there are occasional anomalies encountered. Figure 17 is a photomicrograph of separated carbon fibers from one test that employed the high MW polycarbosilane polymer, and both crystalline and "beady" deposits were seen; the reason for the appearance of the bead which previously had been thought to be a result of the presence of low MW and low melting oligomers, is not explainable; on the other hand, it was seen only once out of literally hundreds of specimens that were examined by optical microscopy.

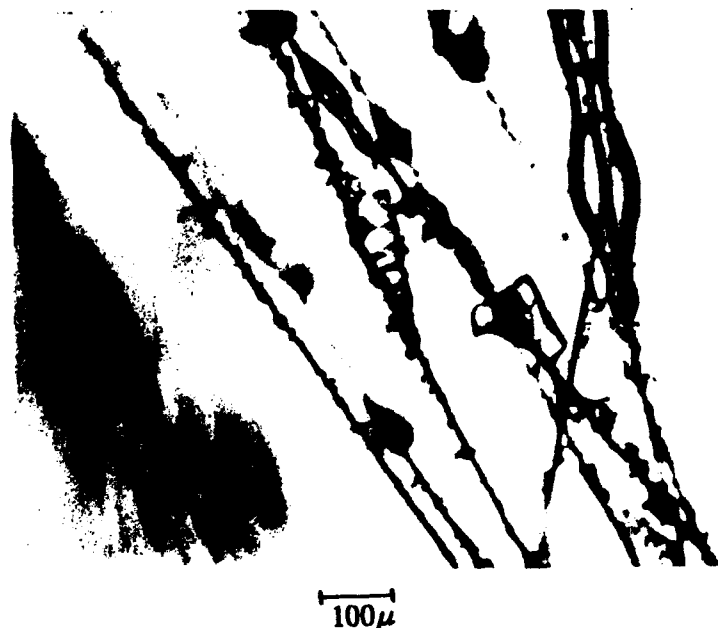


Figure 17. Photomicrograph of One Anomalous Infiltration and Deposition Result; Both Crystalline and Beady Deposits Are Seen

The high MW fractions that were used in the infiltration and deposition tests were obtained by a process that Phasex has termed supercritical Fluid Fractionation, and the conduct of a laboratory fractionation test was explained briefly in the Experimental Procedure, III.A.

With reference to Figure 7 in the Experimental Procedure section a polymer is fractionated into low polydispersity cuts via a process called increasing pressure profiling. A charge of polymer (e.g., 100 or 1000g) is extracted over a range of pressures starting with a low pressure and raising the pressure sequentially. At the first (and low) pressure gas flow is passed through the charge and the lowest molecular weight species are extracted and collected. The collection vessel is changed to a new one, the pressure is raised to a new level and the remaining polymer extracted of the next lowest molecular weight species which are collected in

the second U-tube, and so on, until the entire charge has been dissolved. the fractions are analyzed by Gel Permeation Chromatography for number average molecular weight (M_n) and weight average molecular weight (M_w); polydispersity index (sometimes abbreviated as PDI) is the ratio M_w/M_n and the closer the value is to 1.0 the narrower the molecular weight distribution.

The molecular weight results of one large fractionation test are tabulated in Table 2 and the data for the parent polycarbosilane are included for comparison.

Table 2. Fractionation Conditions and Molecular Weight of Fractions of Polycarbosilane Polymer. (Temperature = 130°C)

<u>Fraction</u>	<u>Pressure (psi)</u>	<u>M_n^*</u>	<u>M_w^*</u>	<u>Polydispersity Index, M_w/M_n</u>
Parent Polymer		980	2954	3.01
1	1200	312	456	1.46
2	1600	491	664	1.35
3	2000	584	826	1.41
4	2350	629	974	1.55
5	2550	831	1249	1.50
6	3400	1210	1712	1.41
7	4000	1550	2234	1.44
8	4500	3545	6138	1.73

* M_n and M_w are number average molecular weight and weight average molecular weight.

As the data in Table 1 show, there is a wide range of MW in the parent polymer.

As a pictorial example of the narrowness of the fractions, several selected GPC chromatograms are superposed on the parent and are reproduced in Figure 18 and 19. The GPCs of the fractions are all superposed onto the Parent GPC for clarity considerations. The narrowing of the polydispersity index is obvious from the superposition of the GPCs (and, of course, from the data given in Table 2.)

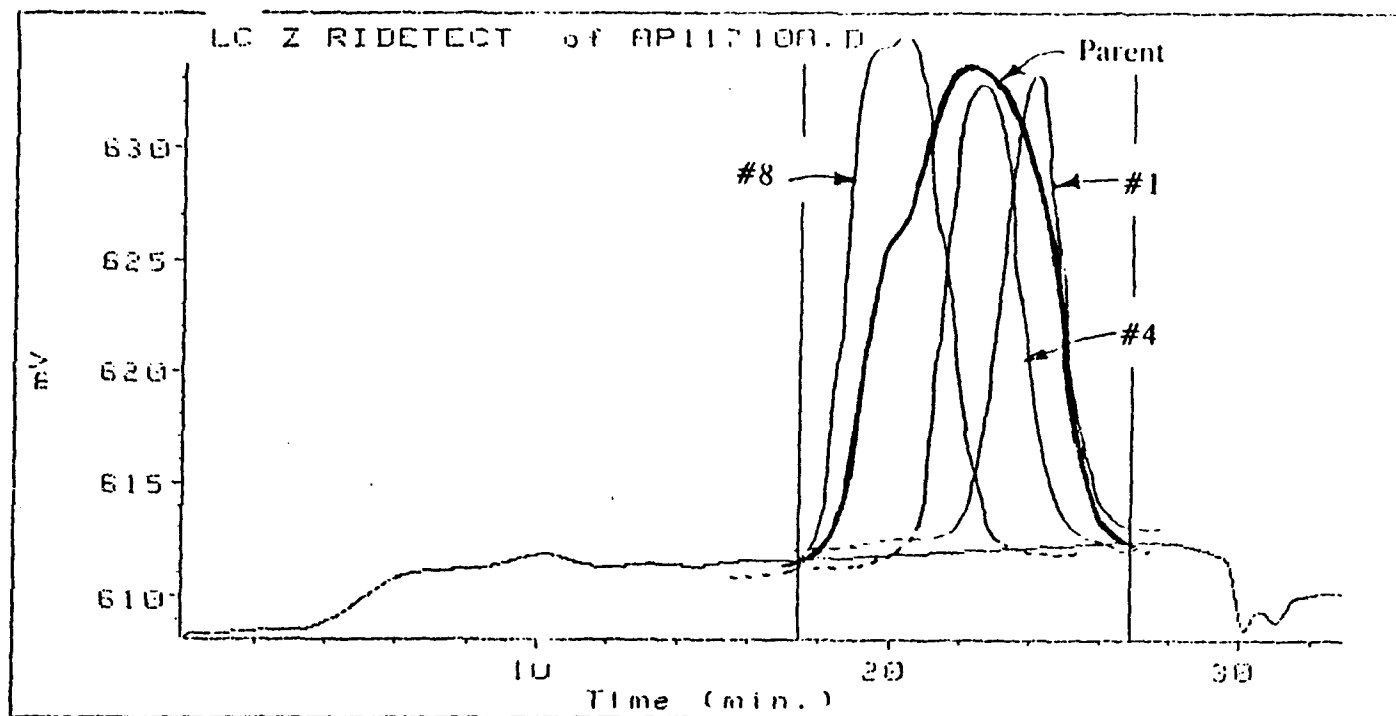


Figure 18. Comparison of GPC Chromatograms; Fractions 1, 4, and 8 Superposed on Parent Polymer

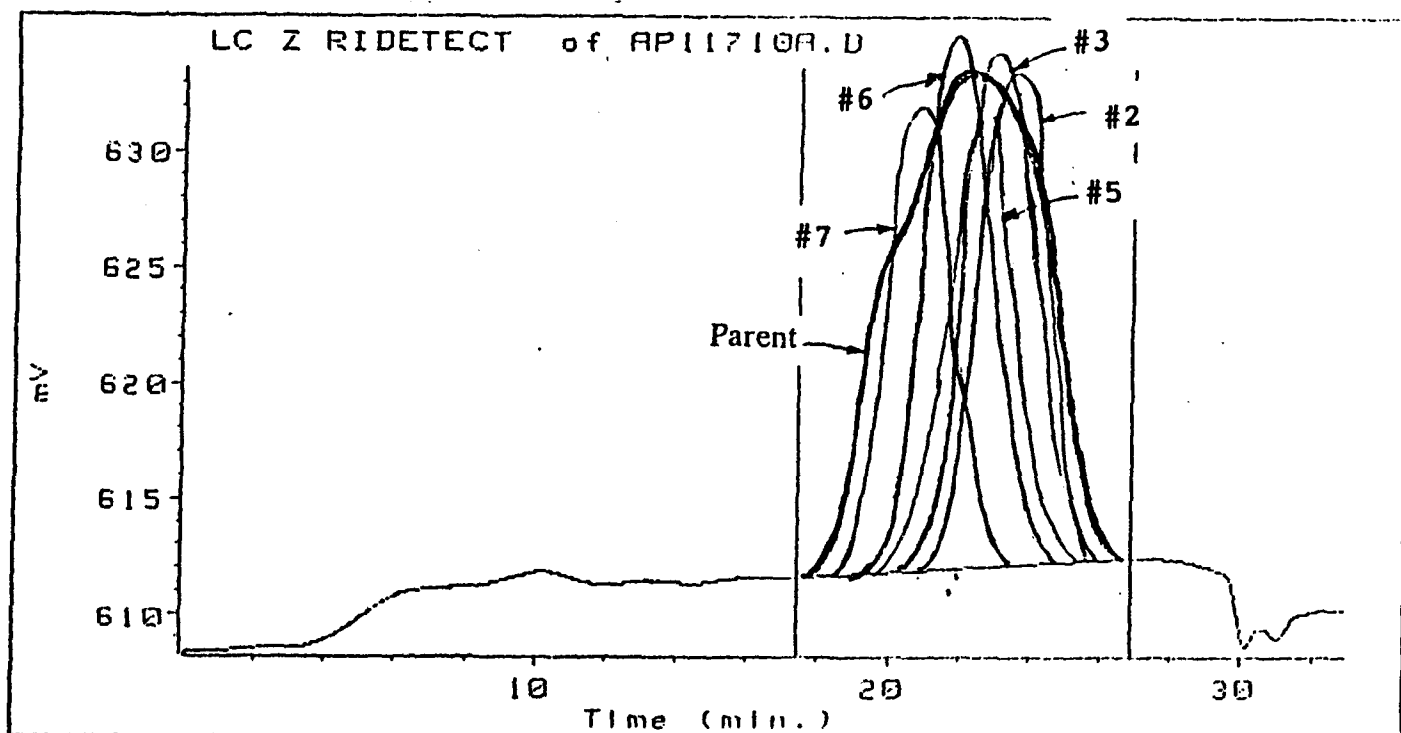


Figure 19. Comparison of GPC Chromatograms; Fraction 2, 3, 5, 6, and 7 Superposed on Parent Polymer

The amount of silicon carbide that is obtainable from the polymer when it is converted (pyrolyzed) to SiC is an important consideration. A portion of each fraction was pyrolysed at 900°C in an inert (argon) atmosphere, and it is informative to relate information about the physical characteristics of the respective fractions of precursor polymer and the yield of silicon carbide from the fractions as given in Table 3; silicon carbide yield is the amount of material (in percent by weight) that remains in the ceramic boat after the polymer is pyrolyzed.

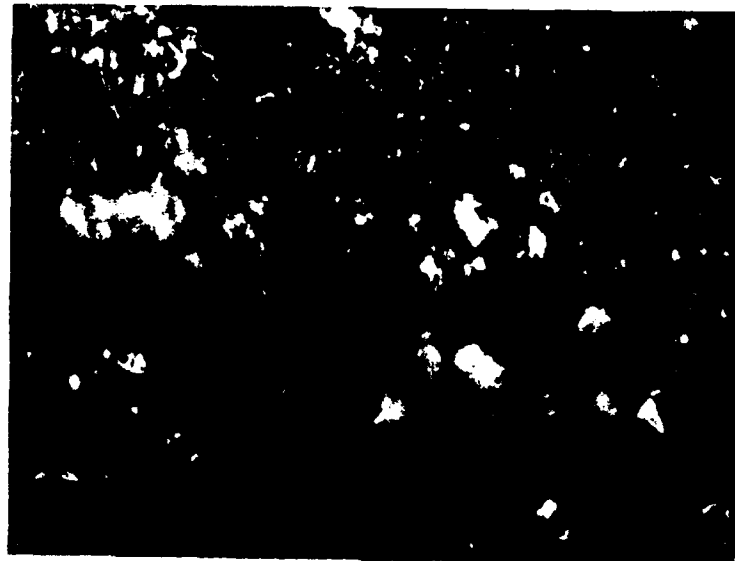
Table 3. Physical Properties of the Fractions and Silicon Carbide Yield after Pyrolysis of Fractionated Polycarbosilane

<u>Fraction</u>	<u>Physical Appearance of Polymer Fraction</u>	<u>Silicon Carbide Yield %</u>
Parent Polymer	Crystalline powder	57
1	thick liquid	6
2	semi solid	20
3	sticky powder	23
4	powder	27
5	powder	34
6	powder	65
7	fluffy powder	75
8	fluffy powder	84

As can be seen from the data given in Table 3 and from the curves in Figures 17 and 18, the polymer is composed of a wide molecular weight range of oligomers some of which are liquid (Fraction 1), semi solid and sticky powder (Fractions 2 and 3), and powder (Fractions 4 on). More relevant to this program than the physical appearance, molecular weight, and polydispersity index of the respective fractions the silicon carbide yield varies widely, from a few percent for the low molecular weight fractions, e.g., Fractions 1,2,3, and 4, to a yield much higher than the parent polymer. As was found in the early part of the program the nature of the infiltrated and deposited polymer was a function of the molecular weight of the precursor polymer.

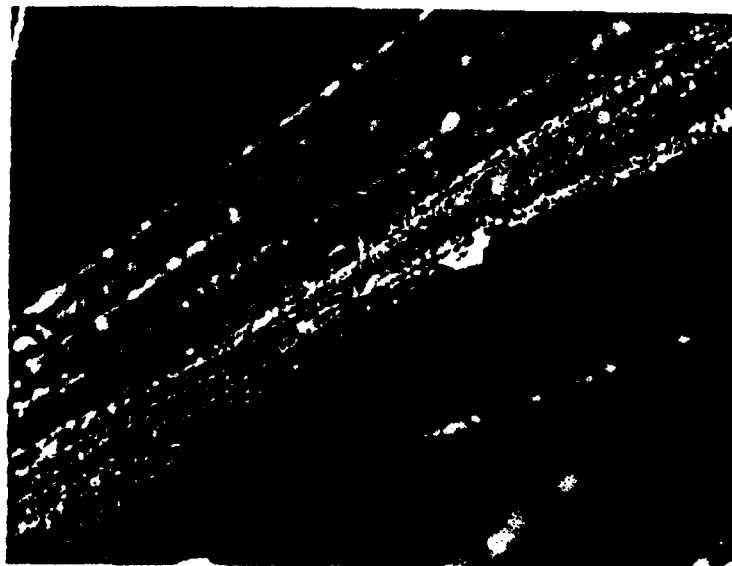
C. Infiltration into Multi Layer Carbon Mat Preforms

After the initial tests on small sections of mat infiltration tests next focused on larger assemblies of the woven fiber mat; the mat was tested as single layers and later in lay ups of several layers to test the potential for uniform infiltration under severe constraints of penetrability. Larger sections of mat were at first rolled into cylinders then later fabricated into simulated laid up preform specimens for infiltration. Figure 20 is a photomicrograph of one section from a rolled cylinder of mat that was infiltrated with polycarbosilane. The interior section (unrolled and lying flat) is shown in the figure, and it is seen that the deposition of polycarbosilane polymer (which is present as the white dots) is not very uniform.



100 μ

Figure 20. Photomicrograph of Infiltrated Carbon Fiber Mat from Interior Section of Rolled Cylinder



200 μ

Figure 21. Larger Area (lower magnification) Photomicrograph of Infiltrated Carbon Mat From Interior of Cylinder

Figure 21 is a lower magnification photograph showing a larger area from the interior of the cylindrical roll of fabric; the coverage is again seen to be non uniform. A section of infiltrated mat from the exterior of the cylindrical roll is shown in Figure 22; the coverage (identified by the dense white deposits) is substantially greater, and it was reasoned that an increased contact and diffusion period would increase penetration and deposition during the pressure/temperature decrease cycle. The hold time for most of the initial tests with small sections of mat was about five minutes. The flow of the polycarbosilane solution (in propane) through the vessel occurred within about 15 seconds (i.e., one vessel volume of gas and solution was passed through the carbon fiber mat situated in the infiltration vessel), but transfer into the tight mat probably required more time.

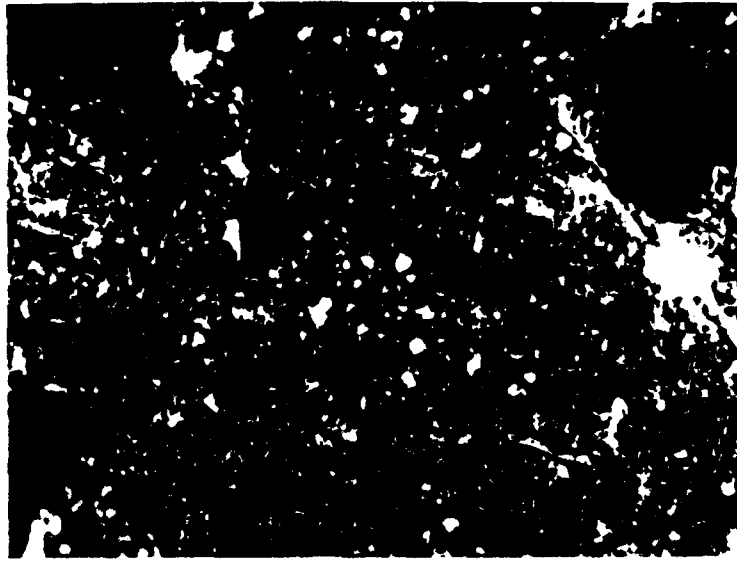
Infiltration tests with multi layer rolled cylinder of mats were carried out with 30 minutes hold times, and the results were immediately more dramatic; the infiltration/deposition is shown in the next two photomicrographs of sections taken from the tightly rolled cylinder. Figure 22 is of a section from the inside cylinder wall (and the mat is rolled flat in order to take the photomicrograph). Figure 23 is of a section of mat that was sandwiched in an interior layer in the cylindrical roll, and in spite of some polycarbosilane deposit that was dislodged when the layers of mat were pulled apart, there is still seen to be substantial coverage on and in the mat.

D. Infiltration into 3D Carbon Fiber Preforms

With most of the infiltration and deposition parameters worked out, the studies progressed to the next stage of infiltration of 3D carbon preforms. In analyzing what occurred with the 3D preforms during Supercritical Fluid Infiltration pictorial evidence (in the form of photomicrographs) was more difficult to obtain, and instead the weight gain (of deposited polymer) of the individual 3D carbon preforms was measured. Weight gains and then subsequent partial weight reduction when the polymer is pyrolyzed to SiC is given later in tabular form.

The 3D preform was supplied by Textron Systems Division (formerly Avco Missile Systems Division before it was acquired by Textron Corporation) by Arthur Traverna, manager of the carbon/carbon production department. The 3D carbon preform was fabricated from high strength, high modulus fibers in a piercing process, i.e., carbon fiber mat was laid up in 0°-90° orientation and then pierced with carbon fiber bundles perpendicular to the mats. The 3D preform was then infiltrated very lightly with pitch and the pitch carbonized. The amount of carbonized pitch was only a few percent by weight of the carbon preform, but it provided rigidity of the assembly for subsequent handling, either in the AVCO PIC process or at Phasex during this work on Supercritical Fluid Infiltration of preceramic polymer.

The large 3D preform sample was machined into $\frac{1}{2} \times \frac{1}{2} \times 1\frac{1}{2}$ " blocks for the infiltration tests. The first tests with the preforms were directed to the formation of a thin deposit of polymer for the purpose of providing oxidation resistance to the carbon fibers themselves (rather than relying on a Chemical Vapor Deposited layer of SiC on the exterior of the fully densified C/C composite). Tests with deposition extent of 1, 2, and 5% by weight were not successful in providing the desired resistance to oxidation. At the oxidation test temperature of 1250°C in air both the control blocks of carbon fiber preform and the infiltrated specimens lost weight to about the same extent; the rate of weight loss was over 40% in four hours. Although SiC was in fact deposited in the preform, the layers on the carbon fibers must not have been uniform, thus the oxygen attack on exposed fibers. Tests next focused on more extensive infiltration of polycarbosilane into the preform; machined 3D blocks of the same dimensions,



—
200 μ

Figure 22. Photomicrograph of Infiltrated Mat; Layer from Inside Diameter of Cylinder



2 3

Figure 23. Photomicrograph of Infiltrated Mat; Layer from Interior of Rolled Cylinder

viz., ½ x ½ x 1½", were used. In the 3D infiltration tests multiple blocks were placed into the top vessel (see Figure 8) for a dual purpose, one, merely to produce more than a single infiltrated specimen for subsequent pyrolysis and oxidation resistance testing, and two to determine the variation within the vessel of the extent of filtration of specimens so that uniformity considerations could be addressed.

In one test series several infiltration - pyrolysis cycles (similar to PIC cycles) were repeated with the blocks of 3D preforms, and Table 4 gives the results of weight gain after infiltration and weight loss after pyrolysis during multiple cycle infiltration.

Table 4. Gravimetric Analysis of Multiple Cycle Infiltration/Pyrolysis Cycles

Position and Initial Weight	Cycle 1		Cycle 2	
	After Infil.	After Pyrol.	After Infil.	After Pyrol.
1, 3.95g	5.66g	5.01g	5.91g	5.57g
2, 4.03	5.47	4.84	5.84	5.41
3, 3.61	5.35	4.65	5.45	5.13
4, 3.82	5.40	4.73	5.53	5.18
5, 3.65	5.36	4.71	5.27	5.06

Cycle 3		Cycle 4	
After Infil.	After Pyrol.	After Infil.	After Pyrol.
6.47g	6.13g	7.02g	6.68g
6.40	5.98	6.98	6.55
5.93	5.61	6.41	6.09
5.98	5.63	6.43	6.08
5.62	5.41	5.99	5.77

The first column in the table gives a position-in-the-vessel designation (top to bottom, Specimen 1 to Specimen 5) and the initial weight of the specimens. The other columns give, in pairs, the weight after the Xth cycle infiltration and pyrolysis. Thus in cycle 1, (the first infiltration/pyrolysis cycle) it is seen that the specimen at the top of the 12" long vessel (Specimen 1) was infiltrated with about the same percent fill as the middle and bottom specimens. Statistically over the course of the four cycles there was essentially no variation of infiltration with axial position.

For completeness of information here, the pyrolyses that was carried out at University of MA a Lowell, consisted of a slow heat up rate, viz., 100°C/hr in an argon atmosphere to a maximum temperature of 1100°C; this heat up rate and maximum temperature were suggested by the supplier of the polycarbosilane (and it also had been verified in other work carried out by Dr. Vasilos of the UMA/Lowell Materials department).

Figure 24 and Figure 25 (at higher magnification) are Scanning Electron Micrographs (SEMs) of interior surfaces of a typical infiltrated and pyrolyzed specimen that has been prepared for SEM examination by cutting with a diamond wheel. In the particular specimen whose SEM is shown in the figures the unfilled porosity was measured to be about 10% i.e., 90% of theoretical density. Of the specimens tested for porosity the range was from 78% to a high of 92%; the average was about 85%.

The cross section was obtained by sawing across the mats, i.e., parallel with the pierced (3rd dimension) of the 0-90°C mat; thus, the cut is also parallel with one direction of the mat and perpendicular to the other as is seen in the two figures. Some voids between layers of mat are evident and to a lesser extent voids between individual carbon fibers in a layer; penetration to the internal volume regions of the specimen has been reasonably well achieved.

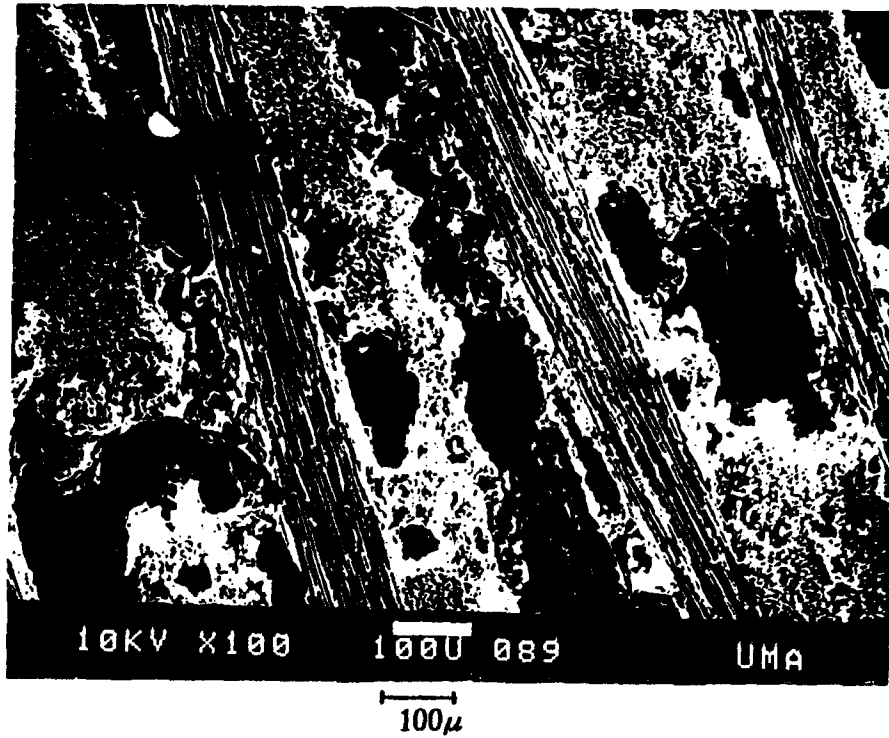


Figure 24. SEM of Cross Section of SiC Infiltrated Carbon Fiber Preform

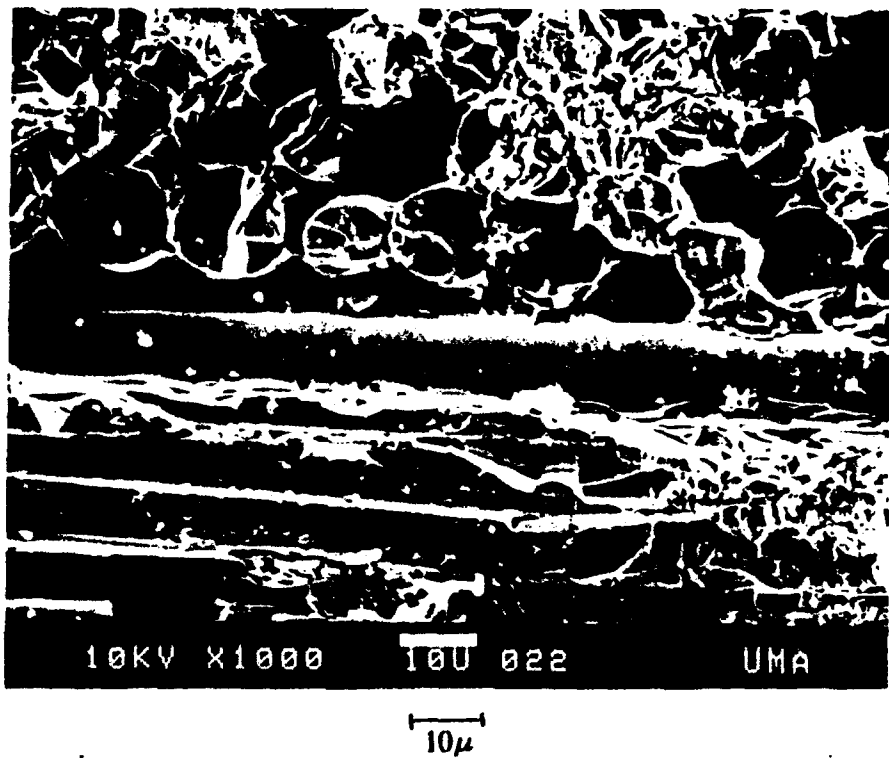


Figure 25. Higher Magnification of Specimen Shown in Figure 24

The infiltrated/pyrolyzed specimens were exposed to high temperature oxidation testing at 1250°C in air, this time for a period of 48 hours. Non infiltrated carbon preforms essentially disappeared during the exposure. The infiltrated specimens were much more oxidation resistant as would be expected from the deposition/formation of SiC in the specimens. As an average there was about a 15% loss in weight which was due to oxidation of individual fibers in the interconnected void regions. The range of loss was from 25% in poorly protected specimens to a low of about 10% weight loss; in all cases the loss was due to the oxidation of individual carbon fibers. Two SEMs of an oxidized specimen are shown in Figures 26 and 27 at two different magnifications. There is fiber fraying and what appears to be carbon fiber-SiC matrix debonding (or more likely carbon fiber diameter erosion) seen in the SEMs.

There were two tests carried out at UMA/Lowell on overlaying a sintered SiC coating on the specimens to reduce oxidation attack; they were not successful in accomplishing the desired goal.

Finally several specimens were tested in bend fracture. Specimens not subjected to oxidation averaged 12,300 psi and after oxidation (at the 48 hr, 1250°C exposure conditions) they averaged 8,600 psi, a reasonably good retention and demonstration considering the total effort on the Phase I program. The fracture made consisted of sequential fiber fracture and matrix (as might be expected from a fiber reinforced composite specimen) rather than the catastrophic fracture behavior displayed by monolithic brittle materials such as silicon carbide.

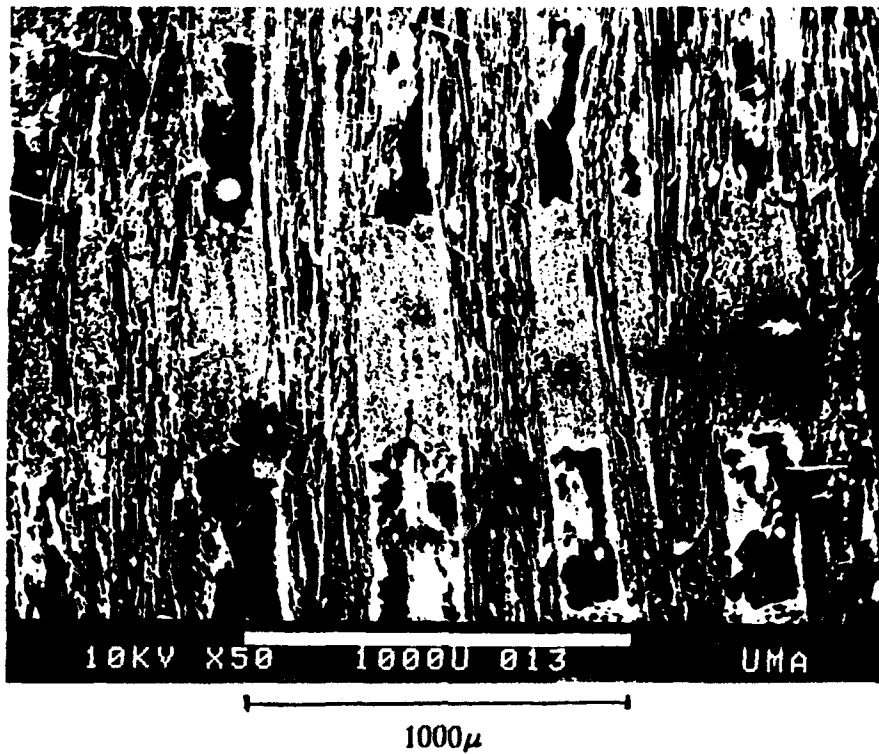


Figure 26. SEM of Cross Section of Oxidized Specimen



Figure 27. Higher Magnification of Specimen Shown in Figure 26

IV. CONCLUSIONS AND RECOMMENDATIONS

1. In the feasibility demonstrations on this program Supercritical Fluid Infiltration was shown to be technically capable of forming specimens of carbon fiber/SiC matrix composites.
2. The composite specimens were reasonably stable in air at 1250°C for 48 hours. The weight loss of the SiC-Coated preforms was 10%; the uncoated 3D carbon preforms completely oxidized.
3. The precursor polymer was shown to be composed of a wide range of molecular weight oligomers. The low molecular weight fractions provided very little (<20%) SiC matrix upon pyrolysis, and the high molecular weight fractions yielded much more (>80%); the parent (unfractionated) polycarbosilane had an average SiC yield of 50%.
4. Because the infiltration and pyrolysis steps are carried out at well below the temperature at which current CVI process is carried out, the Supercritical Fluid Infiltration (SFI) process has technical merit if a carbon fiber reinforced/SiC matrix composite is the desired goal.
5. Although full theoretical density of the preform was not achieved (the best value was 90% of full density), the oxidation/weight loss tests showed very substantial decrease in oxidation compared to the uninfiltreated preform. Because SiC matrix composites made by a number of processes are increasingly being investigated, further work to study and *optimize the process is recommended.*

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STINFO Program Manager**