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Coatings for Graphite Fibers

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SUMMARY

Several approaches for applying high resistance coatings continuously to graphite yarn were investigated. Two of the most promising approaches involved (1) chemically vapor depositing (CVD) SiC coatings on the surface of the fiber followed by oxidation and (2) drawing the graphite yarn through an organosilicone solution followed by heat treatments. In both methods, coated fibers were obtained which exhibited increased electrical resistances over untreated fibers and which were not degraded. This work was conducted in a previous program.

In this program, the continuous CVD SiC coating process used on HTS fiber was extended to the coating of HMS, Celion 6000, Celion 12000 and T-300 graphite fiber. Electrical resistances three orders of magnitude greater than the uncoated fiber were measured with no significant degradation of the fiber strengths. Graphite fibers coated with CVD Si_3N_4 and BN had resistances greater than 10^6 ohm/cm.

Lower pyrolysis temperatures were used in preparing the silica-like coatings also resulting in resistances as high as three orders of magnitude higher than the uncoated fiber. The epoxy matrix composites prepared using these coated fibers had low shear strengths indicating the coatings were weak.

1.0 INTRODUCTION

1.1 Background

Over the past several years, graphite fibers have been used to produce low density high strength composites for many aerospace structures. The interest in these composites has been growing steadily especially for use in aircraft structures. Because of this growing interest, it became of concern to both composite users and manufacturers when it was announced that the release of carbon fibers from composites due to fire or explosions could have serious effects on electrical and electronic equipment (Refs. 1,2).

1.2 Objectives

In order to solve this problem, NASA looked at several approaches to either prevent the release of fibers or to make the fibers nonconductive so they would not short circuit electrical equipment. A summary of these approaches was discussed at a NASA workshop in Hampton, VA on March 23-24, 1978 (Ref. 3).

1.3 Summary of Results from Previous Studies

The approach taken on this NASA program to solve the fiber conductivity problem was to coat the graphite fibers with a layer which would increase the resistance of the fiber. Hercules HTS graphite fibers were selected for use in the development of electrically resistant coatings because of the wide range of programs for which this fiber was being used. A preliminary study was first conducted on drawing graphite fiber through glass, dipping the fibers in colloidal silica, drawing fiber through organo-silicones and chemical vapor depositing (CVD) coatings of SiC and B or B alloys. This was followed by a more detailed study of the most promising methods which were the CVD SiC coating and organo-silicone approaches using graphite fibers. This work was reported in NASA CR-159078 (Ref. 4).

In the CVD SiC coating studies, it was shown that HTS graphite fibers could be coated continuously without degrading the fibers. The electrical resistance was highest (1000 ohms compared to 2 ohms for the untreated yarn) when a reactor temperature of 1398 K was used, a drawing rate of 30 cm/min and an in-line oxidation temperature of 773 K. For the organo-silicone method of coating HTS graphite fiber, the best conditions were as follows: concentration of ethyl-silicate 2.5 wt %, drawing rate 0.91 m/min and pyrolysis temperature of 1093-1173 K in a nitrogen atmosphere. The resistance of these fibers was 14 ohms vs 2 ohms for the untreated fiber and no degradation of the fiber was observed.

This program reported herein extended the CVD SiC coating studies to HMS, Celion 6000, Celion 12000 and T-300 graphite fibers. The organo-silicone coating approach was further studied using the Celion 6000 graphite fiber as the reinforcement and new coating materials were investigated. Additional studies were initiated on CVD silicon nitride and boron nitride coated graphite fibers. CVD silicon nitride and boron nitride have very high electrical resistances, but presented some problems in deposition since it had to be done at very low pressures. Therefore, the objective of this part of the program was to evaluate the CVD silicon nitride and boron nitride processes for forming coatings on graphite fiber to increase the resistance of the fiber while not decreasing its strength.

2.0 EXPERIMENTAL PROCEDURES

2.1 Coating Apparatus and Procedures

2.1.1 Continuous CVD SiC Apparatus

Continuous deposition of the SiC CVD coating of the graphite fibers was carried out in the apparatus shown in Fig. 1. Argon gas seals at both ends of the reactor kept the reactant gases within the chamber and minimized the introduction of outside air into the hot zone. An rf induction coil was used to heat the graphite susceptor which was placed within a double walled water cooled silica chamber. The inner graphite susceptor was separated from the silica walls with aluminum oxide spacers. An in-line oxidation furnace was placed between the exit part of the reactor and the take-up spool.

The reactant gases were introduced into the reactor after the graphite yarn had been brought to the desired temperature. The reactant gas flow rates were nominally 0.015 ℓ/min of methyldichlorosilane, 0.110 ℓ/min of hydrogen and 0.110 ℓ/min of methane. The methyldichlorosilane vapor needed for the SiC deposition process was obtained from a liquid evaporator. A schematic of this evaporator is shown in Fig. 2. The constant temperature of the water jacket together with the pressure within the supply tank was measured so that calculations could be made to determine the amount of methyldichlorosilane which was being introduced into the reactor during deposition experiments.

2.1.2 Static CVD Si_3N_4 Coating Apparatus

Two apparatus were used for the static chemical vapor deposition of silicon nitride. In one, mixtures of silicon tetrafluoride and ammonia were introduced into a large cylindrical hot reaction chamber. The graphite fiber to be coated was suspended within this chamber. A photograph of the graphite resistance furnace used in the initial experiments is shown in Fig. 3 and a schematic drawing of this apparatus is shown in Fig. 4. The reactant gases were brought into the furnace separately and mixed immediately before passing over the hanging graphite yarn. The pumping system capacity was adjusted to remove the exhaust gases at such a rate that there was always a supply of fresh reactant gas around the graphite yarn.

Deposition temperatures of from 1673 to 1873 K have been used to form CVD Si_3N_4 in this apparatus. For this program an initial deposition temperature of 1723 K was chosen since preliminary UTRC research on coating graphite yarn showed that this temperature yielded a good coating without visible degradation of the graphite fibers. Similar reasoning was used to choose the mole ratios of reactant gas and the pressure within the reactor to conduct a series of experiments in which graphite fiber was statically coated.

Another apparatus consisted of a double walled water cooled silica jacket with appropriate glass fittings for vacuum and low pressure operation. A graphite cylinder was placed within the water cooled silica tube and rf induction heating was used to bring this graphite cylinder up to the desired deposition temperature. The graphite yarn to be coated was suspended in the center of the heated tube and provisions were made for the introduction and exhaust of the gases. In this apparatus a 35 kW rf induction unit was used to heat the graphite cylinder in which the graphite yarn was suspended. In Fig. 5 is shown a photograph of this apparatus.

2.1.3 Static CVD BN Coating Apparatus

The static chemical vapor deposition of boron nitride was carried out in the same large cylindrical hot reaction chamber that was previously described for the Si_3N_4 experiments and shown in Fig. 3. In this case BF_3 and NH_3 were used as the reactant gases.

2.1.4 Organo-Silicone Coating Apparatus for Continuous Process Studies

A description of static experiments and results were given in NASA Contractor Report 159078 (Ref. 4). Two apparatus designs were used for continuous fiber coating. The first continuous fiber coating apparatus was also described in the referenced report.

The second apparatus was a modification of the first design, to provide for several improvements in operation and control of the coating process. These improvements include separation of the drying and hydrolysis chamber into two separate chambers, (1) to provide improved drying of the fiber after solution impregnation of the graphite yarn, (2) a separate hydrolysis chamber to prevent contamination of the coating solution by water, and for increased hydrolysis temperatures. In the previous design, a portion of the coating solution was under the drying and hydrolysis chamber, causing some contamination of the solution by water. Additional improvements were made in the drying chamber after hydrolysis, an increased number of temperature sensors for temperature control, and Teflon pulleys to prevent yarn crossover.

Coating studies of two systems from the static test coating results and from the first continuous coating results were continued in the modified continuous coating apparatus shown in Fig. 6. These were silicone resin GE, SR-355 and prepolymer ethyl silicate (ES), the Ranson & Randolph Co, R&R silicate binder #18. In addition, Owens-Illinois glass resins 100 and 650 and tri-n-butylborate were also investigated using the modified continuous process equipment.

2.2 Fiber Test Procedures

2.2.1 Electrical Resistance Measurements

A technique for obtaining the relative, but only approximate, resistance of one coated yarn compared to another involved laying out the coated fiber on an insulator. Two copper blocks 2.5 x 7.5 x .6 cm thick were then placed across the tows 2.5 cm apart. A sketch of the copper blocks in a measurement position is shown in Fig. 7. Care had to be taken so that about the same area of fiber was contacted each time and the contact pressure of the resistance measurement leads was the same. A volt-ohm microammeter which had a nominal input impedance of 100 K ohms per volt DC was used to record the resistance. The resistances of fibers coated using the organo-silicone approach were also measured by this technique.

Another method of resistance measurement was developed to provide a continuous monitoring of yarn resistance for the CVD SiC coating process. This was done by passing the coated yarn over two electrically isolated copper rods after it exited from the in-line oxidation furnace and before the yarn was collected on the take-up drum. The copper rods were offset in the vertical plane to assure a constant tension sliding contact. A photograph of the CVD SiC coating apparatus with the continuous resistance measuring copper electrodes in place is shown in Fig. 8.

2.2.2 Arcing Tests

An open circuit test was used to determine if the CVD coated graphite fibers would arc when placed across open electrical leads. In this apparatus, two copper electrodes were placed in the bottom of a Teflon lined Lucite box and the output of a 120 VAC Variac with an in-line voltmeter was connected to these copper electrodes. An experimental setup is shown in Fig. 9. The tube that can be seen between the copper plates in the photograph is a piece of aluminum oxide used to prevent accidental contact between the bare copper electrodes. To observe the benefit of a CVD coating, an oxidized coating or one that had been in-line oxidized, a 6 cm length of the yarn to be evaluated was placed across the two bare flat copper electrodes. The spacing of the electrodes was maintained at 1.3 cm. The voltage was increased from 0 to voltage breakdown.

2.2.3 Ultimate Tensile Strength Measurements

2.2.3.1 Single Filament Tests

The tensile strength and modulus of individual fibers were measured for the uncoated, CVD coated, and oxidized CVD SiC coated yarn in a UTRC test apparatus (Ref. 5) which had been developed for fine filament testing. This technique

involved the extraction of single filament from a multi-filament bundle for attachment to the test apparatus. Careful calibration of the load cell and crosshead movement allowed for the calculation of both ultimate tensile strength from the breaking load and modulus from the elastic portion of the stress-strain curve. A photograph of the apparatus is shown in Fig. 10.

A minimum of ten fibers which broke in the gage length were used to determine the average tensile strength of the fibers. The area of an individual fiber which was used in the calculation of tensile strength was initially obtained from the average of 50 planimeter measurements. These measurements were made from 1000X photomicrographs of mounted cross sections of the yarns being tested.

2.2.3.2 Yarn Tests

There is no ASTM accepted standard for measuring tensile loads or strengths of high modulus graphite yarns. Tensile measurements of graphite fiber coated using the organo-silicone approach were made using the whole yarn. The specimens were prepared by impregnation of the graphite yarn with a 45 w/o solution of epoxy resin (Epon 828/Sonite 21, 100g/19g) in methylethylketone. The resin impregnated yarn bundle was pulled taut, fixed in this position and allowed to cure at room temperature overnight. The cured resin impregnated yarn was cut into 13.9 cm specimens (or 10.9 cm specimens) and placed on an aluminum plate. Each end was reinforced with 4.2 cm pieces of the same impregnated yarn by bonding it with epoxy resin (described above), at the same time as 2.5 cm square cellulose tabs were bonded to the ends, using Epon 907 adhesive.

Yarn tensile specimens were measured on a 890N Instron using pneumatic air driven grips to hold the specimens, at a crosshead speed of 0.05 cm/min. A specimen gage length of 2.5 cm or 5 cm was used.

2.2.4 Coating Thickness Measurements

An initial goal of this program was to obtain coating thicknesses on individual fibers of approximately 0.10μm. These coatings were too thin to measure accurately even at 1000X with conventional metallography. Preparations of mounted cross sections were then examined in the SEM with both chemical etchant and ion milling used to obtain edge relief. Specimens were also prepared and examined with an electron microscope.

2.2.5 X-ray Diffraction Analysis

The coated graphite fibers were formed into twisted yarn samples approximately 2.5 cm long and mounted in a standard Debye camera having a radius of 117.5 mm. Copper kα radiation was used at 40 kV and 20 ma. settings. An 8 hr exposure was typical for all samples in this series. During exposure, the yarn sample was

rotated to insure all possible planes within the specimen were presented to the X-ray beam. After the development of the film direct comparisons were made of each film with a standard SiC, Si_3N_4 or BN X-ray diffraction pattern. In the case of the fibers coated by the organo-silicone process, no pattern except that of the graphite fiber was ever observed, so it was assumed that the coating on these fibers was amorphous.

2.3 Composite Test Procedures

2.3.1 Epoxy Resin Flexural Strength Measurements

A resin formulation containing MY720, epoxy Novalac DEN 438, and curing agent 4,4'-diaminodiphenyl sulfone (DDS) in the weight ratios, MY720/DEN 438/DDS of 4.5/1.0/2.25 was developed for use as a resin matrix in graphite/epoxy composites. The epoxy resin system was designated UTRC-89Z. Flexural specimens were prepared and measured according to ASTM procedure D790-71. The specimen dimensions were 10 cm x 1.25 cm x .47 cm.

2.3.2 Fabrication of Graphite/Epoxy Prepreg Tape

Forty-five weight percent solution of the UTRC resin in a 50:50 weight percent of methylethylketone and cellusolve was prepared for impregnation of untreated graphite fiber and SiC coated graphite fibers. The objective in the initial coating process was to obtain a resin coated graphite yarn containing 33-35 w/o resin, in order to obtain a fiber volume percent of approximately 60% in a finished composite. Using the above solution, a graphite tape containing 43 w/o resin was produced and a composite with a fiber volume of only about 48% was formed. In order to decrease the resin content to 33 w/o in the graphite prepreg, the concentration of the impregnation solution was reduced to 35 w/o.

Resin impregnated tape 8.8 cm wide was prepared by passing the untreated or coated yarn through the resin solution via pulleys and then winding onto a 45 cm diameter drum. The tape was allowed to stand at room temperature in a hood to remove solvent. It was then cut into the appropriate size for fabrication into a composite, and placed in an oven at 298 K for 1 hr to remove excess solvent.

2.3.3 Fabrication of Graphite/Epoxy Composites

The solvent free precut tapes are stacked one over the other to yield layered composites 3.75 cm x 20 cm x .25 cm or 8.8 cm x 16.3 cm x .5 cm. The uncured lay-up was sealed in a nylon bag for vacuum molding. The bag was evacuated and the temperature was raised to 398 K, and maintained at this temperature for 1 hr. Pressure (690 Pa) was applied after 1 hr at 398 K. The temperature was raised to 423 K, and held at this temperature and pressure (690 Pa) for 1 hr. The composite was cured for an additional hour at 453 K, while at 690 Pa.

2.3.4 Flexural Property Measurement

The specimens used in determining flexural properties had a nominal size 8.8 cm long x .63 cm wide x .25 cm thickness, and were measured either by a 3-point or 4-point method at a span-to-depth ratio of 32/1 or less, according to ASTM procedure D790-71.

2.3.5 Shear Strength Measurement

The specimens used in determining the interlaminar shear strength had a nominal size of 1.5 cm long x .63 cm wide x .25 cm thick, and were measured at a span-to-depth ratio of 4/1.

3.0 DISCUSSION AND RESULTS

3.1 CVD SiC Coating Approach

The CVD deposition apparatus as modified for continuous monitoring of yarn resistance was also used to demonstrate the feasibility of coating graphite yarns. These yarns chosen for the CVD SiC process were HMS, Celion 6000, and T-300. Celion 12000 was also selected when during the course of this program unsized Celion 6000 yarn was no longer commercially available. Although individual filament diameters within different graphite yarn bundles were all about the same, the number of filaments per tow varied considerably. The HMS graphite yarn was composed of 10,000 filaments, T-300 graphite yarn contained 1400 filaments per tow and Celion 6000 and Celion 12000 contained 6000 and 12000 filaments per tow respectively.

Since the final task of this program was to supply NASA with epoxy resin composites containing the highest electrical resistance and reasonable strength CVD SiC coated graphite yarn of each of the above types of graphite tows, experiments were conducted which were directed toward achieving this goal. A range of drawing rates from 15 cm/min to 122 cm/min and the in-line oxidation furnace off or at a temperature of 773 K or 873 K were chosen as the overall matrix of operating parameters to bracket those conditions that would possibly yield the highest CVD SiC coated yarn resistance. This matrix is shown in Fig. 11.

In Tables 1, 2 and 3 are listed the experimental runs for Celion 6000 graphite yarn, T-300 graphite yarn, and HMS graphite yarn for this drawing rate and in-line oxidation furnace temperature matrix. There are two sets of resistance values for each run which is listed in these tables. The first set was taken immediately after the run was made and the second set was made on the same length of coated yarn at a different time to determine the repeatability of the measurement. For most runs both these sets of resistance measurements did not differ greatly. From examining the overall resistance data in the three tables, it appears that fibers prepared at the higher drawing rates (90 cm/min and 122 cm/min) are not affected by in-line oxidation temperature levels. This is probably due to the extreme short residency time of the CVD SiC coated graphite yarn within the oxidation furnace at these high rates. The electrical resistance of the coated yarn does appear to increase with decreasing drawing rate. However, the results at the slowest drawing rate, 15 cm/min are not consistent. In general, these graphite yarns seem to run best through the reactor at speeds greater than 15 cm/min. This is particularly true for yarns in-line oxidized at the higher temperature of 873 K. The Celion 6000 graphite yarn and the T-300 graphite yarn under these conditions of low drawing rates and high in-line oxidation temperature continually clogged inlet and outlet reactor parts so severely that no coated yarn could be collected at these conditions. In the mid-speed drawing range the coated HMS and Celion yarns had higher resistances than the T-300 coated yarn.

Individual fiber tensile tests were made on the CVD SiC coated HMS and CVD SiC coated Celion 6000 graphite yarn from these runs. The results of these tests are listed in Table 4 for the Celion graphite yarn and Table 5 for the HMS graphite yarn. The pretwist of the as-received T-300 graphite yarn made it too difficult to extract individual fibers long enough for tensile testing. For the CVD SiC coated Celion graphite yarn at an in-line oxidation temperature of 773 K the ultimate tensile strength appears to peak (2333 MPa) at 30 cm/min and then taper off (1736 MPa) as the drawing rates increase to 122 cm/min. Examining similar data (Table 5) for the CVD SiC coated HMS yarn the in-line oxidation temperature of 873 K yields the more consistent (2200 MPa) ultimate tensile strength.

Comparing electrical resistance, reasonable tensile strength, and taking into account qualitative information such as smoothness of reactor operation, amount of yarn fraying during processing and handleability during evaluation, the following operating parameters were chosen for each graphite yarn. For the CVD SiC coated Celion 6000 graphite yarn an in-line oxidation temperature of 773 K at 30 cm/min resulted in a combination of an ultimate tensile strength average of 2333 MPa (339) and an electrical resistance average of 1.5 K ohms. The parameters chosen for the HMS graphite yarn were drawing rates of 30 cm/min and an in-line oxidation temperature of 873 K. These conditions yielded CVD SiC coated HMS graphite yarn which had an average individual fiber tensile strength of 2145 MPa (311 ksi) and a relatively high electrical resistance of 2.7 K ohms. For the T-300 graphite yarn deposition conditions of 30 cm/min with an in-line oxidation temperature of 773 K was chosen. For these conditions the CVD SiC coated T-300 graphite yarn had electrical resistances as measured with the copper block technique of 750 ohms.

Toward the completion of this program and before all the coated graphite yarn had been produced for complete composite evaluation the future availability of Celion 6000 graphite yarn became questionable. The same manufacturer was only able to supply unsized graphite yarn in a 12000 filament tow form, Celion 12000. CVD SiC coating experiments were made with this yarn at only one drawing rate, 30 cm/min. The in-line oxidation furnace was used at 773 K and 873 K. The resistance data for these runs are listed in Table 6. Individual filament tests were made on extracted fibers from this series of runs and these results together with tests on fibers extracted from the untreated graphite yarn are listed in Table 7. From the data in these two tables, the in-line oxidation temperature of 773 K was chosen as yielding the best combination of strength, 2355 MPa (342 ksi) and average resistance, 1.4 K ohms. These deposition conditions were used to produce enough Celion 12000 coated yarn for composite fabrication.

The parameters for the four types of graphite yarn along with reactor gas input and temperature of deposition are listed in Table 8. These chosen conditions were used to produce enough coated yarn of each type for incorporation into deliverable composites for NASA.

3.2 CVD Si_3N_4 Coating Approach

The chemical vapor deposition of silicon nitride onto HTS, HMS and Celion 6000 graphite yarn was investigated. The deposition of CVD Si_3N_4 involves the following gaseous chemical reaction:

$$3SiF_4 + 4NH_3 \rightarrow Si_3N_4 + 12\ HF$$

At UTRC it was found that this reaction when conducted at temperatures of approximately 1723 K and pressures of approximately 1 torr produces a dense, impervious, high resistance silicon nitride coating on bulk graphite substrates. In the large cylindrical deposition apparatus previously shown in Fig. 3, HTS graphite yarn was suspended in the center of the hot zone and CVD Si_3N_4 experiments were run for 5, 10, 15, 30, 45 and 60 min durations. Since only a 20 cm length of yarn was coated at one time, multiple experiments had to be made to obtain sufficient coated material for evaluation. In Figs. 12 and 13 are shown cross sections at 1250X for CVD Si_3N_4 coated HTS graphite yarn selected from runs of duration 5, 30, 45 and 60 min. From these figures it can be seen that the thickness increases with time and after extended periods (Fig. 13) the coatings become so thick that the reactant gas can no longer penetrate the yarn bundle. It was encouraging to observe that even in Fig. 13, individual fibers are still completely coated before fiber bridging occurs.

Successive X-ray diffraction patterns of the silicon nitride coated HTS graphite yarn were taken and are shown in Fig. 14. As would be expected, the strongest X-ray patterns were obtained from those HTS yarns which were run for the longer duration hence heavier silicon nitride coatings. A standard α Si_3N_4 pattern is also shown in this figure for comparison.

Another apparatus (that was shown in Fig. 5) which was much smaller in volume was developed for graphite yarn deposition. This new apparatus decreased pump down time, time to cool after deposition, etc. Initial runs with HTS yarn were made to assure the same quality of coating would be obtained in this apparatus as was previously achieved in the large CVD coating apparatus. In Table 9 are shown some individual fiber ultimate tensile strength and modulus data from extracted fibers from CVD Si_3N_4 HTS coated graphite yarn coated in the large and in the smaller apparatus. Included in this table are results from two HTS yarns which were exposed to 15 min deposition cycles in each apparatus except that no reactant gas was introduced for these yarns. These initial ultimate tensile strength data indicate that the large deposition furnace environment appears to cause slightly more degradation to the as-received yarn properties than does the smaller deposition apparatus.

SEM studies of these runs listed in this table were then conducted to observe the surface of the silicon nitride coatings. In Figs. 15, 16 and 17 are shown CVD Si_3N_4 coated HTS graphite fibers from deposition runs at 1673 K for 5, 10 and 15 min durations. In Figs. 18, 19 and 20 are shown fibers made at 1593 K deposition temperature again for times of 5, 10 and 15 min durations. For comparison purposes, a SEM photograph of the surface of as-received HTS yarn is shown in Fig. 21. In Figs. 15 through 17 the coating can be seen to be developing in thickness for longer deposition times. The surface differences in Figs. 18 through 20 are probably due to the lower deposition temperature. In Figs. 18 and 19 can be seen the start of bridging of the coating between two fibers. The surface debris shown in Fig. 20 could be due to the longer deposition times at this lower than normal deposition temperature.

To determine if excess SiF_4 in the reaction chamber was causing a loss in tensile strength of the CVD Si_3N_4 coated HTS yarn experiments were made with the SiF_4 gas flow input constant and varying amounts of ammonia introduced. For this series of runs the deposition times were of 10 and 20 min duration and deposition temperatures of 1593 K and 1673 K. In Table 10 are listed the results of individual fiber tensile tests on these coated yarns. The reason for the slightly lower tensile test results from these deposition conditions than those reported in the previous table is not known.

Resistance measurements (except to establish resistances of greater than 10^6 ohms) via the copper block technique developed for the CVD SiC coated graphite yarns could not be used for the CVD Si_3N_4 coated graphite yarns since the resistances of the Si_3N_4 coated yarns are too high to be in the range of the volt-microammeter used for that technique.

The qualitative arcing apparatus was used on lengths of coated yarn from each of these runs. The results of the arcing tests are given in Table 11. In general no experimental run of 20 min duration showed evidence of arcing with an open circuit voltage of 120 VAC. Thus the behavior of each pair of runs does indicate that the longer CVD Si_3N_4 coating runs do protect the graphite yarn better than the shorter runs. Data for an untreated HTS yarn are included in this table for comparison of its arcing behavior.

Static CVD Si_3N_4 experiments were made with HMS graphite yarn at four ammonia to silicon tetrafluoride ratios of 1.93, 3.72, 6.01, and 8.45 for deposition temperatures of 1523 K, 1623 K, and 1723 K. All of these runs were of 20 min duration. In Table 12 are listed the gas flows, NH_3/SiF_4 ratios, and the results of ultimate tensile tests on individual fibers extracted from the coated HMS tows. From examining the ultimate tensile test results in this table, there were three conditions which showed no decrease in tensile strength and three more in which the decrease in strength was less than 15% of the as-received tensile strength. The first three deposition conditions were at temperatures of 1623 and 1523 K but the second set included a deposition condition of 1723 K (Run SN-44).

In an attempt to develop a correlation of thickness with time and gas input flow ratio combinations of experimental runs were made at flow ratios of 3.72, 6.01, and 8.45 for 5, 10 and 30 min durations. All these runs were made at a deposition temperature of 1723 K. In Table 13 are listed the operating parameters for these runs. Photomicrographs of the cross section of CVD Si_3N_4 coated HMS yarn for all three ratios for the 5 min duration experiments are shown in Fig. 22. The 10 min deposition experiments are shown in Fig. 23 for the 30 min deposition experiments in Fig. 24. The thickness of the silicon nitride coating can be seen to be increasing with increasing times of deposition. The long deposition time tends to start producing clusters of coated fibers (Fig. 24). The elongated appearance of the graphite fibers in some of these photomicrographs is due to off-axis specimen mounting during metallographic preparation. No clear correlation with coating thickness and NH_3/SiF_4 ratio could be extracted from these photographs. Individual fiber ultimate tensile tests were attempted on these runs but no filaments could be extracted from the longer duration runs (SN 78, SN 72, SN 80) and only short pieces could be tediously extracted from the remaining runs listed in Table 13.

To obtain coated HMS yarns which could be more readily tested, the same gas flow ratios and deposition temperature were used but the times of deposition were 1, 3 and 5 min. Individual filaments from these runs (except for run SN 95) could be extracted from the CVD Si_3N_4 coated HMS yarn bundle for testing. The results of the tests made on this series of runs are listed in Table 14. From this table it can be seen that runs SN 93 yielded values as high as 2458 MPa (357 ksi) and run SN 100 was also in excess of 2400 MPa (350 ksi).

These CVD Si_3N_4 coating experiments were conducted with one suspended tow in the chemical vapor deposition apparatus for each run. To make a composite of CVD Si_3N_4 coated HMS yarn the yield of each deposition experiment was increased by suspending 15 tows at one time in the center of the hot zone. Modifications had to be made to the inlet gas flow path to accommodate this increase of suspended tows to prevent blockage of the gas flow path by these larger number of tows in the reaction chamber. The reactant gas was introduced at the bottom center of the vertical cylindrical chamber, and as such the end of the tows nearest the gas inlet had the thicker silicon nitride coatings. The top left photograph in Fig. 25 was taken from the bottom end of the suspended tow and the Si_3N_4 coating is fairly thick. The upper right and bottom two cross section photographs in this figure were taken from vertical locations of the CVD Si_3N_4 coated HMS graphite yarn which was used to fabricate a composite panel. It can be seen from these cross sections that the CVD Si_3N_4 coating thickness of lengths that went into composites from these runs was less than 0.5 microns.

Static experiments with Celion 6000 graphite yarn were made at 1723 K deposition temperature and various times and reactant gas ratios. In Table 15 are listed the parameters for these runs which were made for 5, 10 and 30 min durations. Photomicrographs of cross sections of the CVD Si_3N_4 coated Celion graphite yarn made in the runs listed in this table are shown for the 5 min duration in

Fig. 26 for the 10 min experiment in Fig. 27, and for the 30 min experiment in Fig. 28. The behavior of the Celion 6000 graphite yarn in the deposition chamber was similar to that of the HMS graphite yarn except at the longer deposition times the corresponding thickness of CVD Si_3N_4 coating appears greater with the Celion 6000 graphite yarn. As was previously shown with the CVD Si_3N_4 coated HMS graphite yarn (Fig. 25), at the longer deposition times bridging of the coating across Celion 6000 fibers also occurs (Fig. 28).

These fairly thick Si_3N_4 coatings on the Celion 6000 graphite yarn presented difficulty again similar to the HMS coated yarn in that single filaments could not be easily extracted. For this reason the CVD Si_3N_4 experiments with Celion 6000 were repeated for the shorter (1, 3 and 5 min) run times. The deposition parameters and ultimate tensile test results for this series of experiments are listed in Table 16. Even with these shorter deposition times, single filaments from runs SN 115 and SN 121 could not be extracted for testing. Both these runs were of 5 min duration. Although the tensile strengths with CVD Si_3N_4 coated Celion graphite yarn are not as high as those obtained with the CVD Si_3N_4 HMS graphite yarn (see Table 14), values of 1860 to 2020 MPa (270 to 290 ksi) for runs SN 116 through SN 118 are considered acceptable. These three runs were all made at ammonia to silicon tetrafluoride ratios of 6.01.

The Celion 12000 graphite yarn which was discussed earlier in this report as having been received toward the end of this program was not completely evaluated for CVD Si_3N_4 coating. In Fig. 29 is shown a cross section of CVD Si_3N_4 coated Celion 12000 graphite yarn that was run for 20 min at NH_3/SiF_4 ratio of 6.01 and a deposition temperature of 1723 K. From this and other preliminary experiments it is felt that, other than any problems associated with handling 12000 filament tows as opposed to the 6000 filament ends in previously available Celion 6000 graphite yarn, this new yarn should present no difficulties in the CVD Si_3N_4 coating process.

3.3 CVD BN Coating Approach

The chemical vapor deposition of boron nitride onto HMS and Celion 6000 graphite yarn was investigated. The reactant gases used for this deposition process were boron trifluoride and ammonia. The reaction equation can be expressed as:

$$BF_3 + NH_3 \rightarrow BN + 3HF$$

Previous work at UTRC had shown that bulk pyrolytic BN could be formed on graphite substrate at temperatures of 1873 K under reduced pressures. These same conditions therefore were used in the first experiments with HMS graphite yarn. Two 20 cm lengths of the HMS tow were suspended in the center of the large vapor deposition apparatus that was shown in Fig. 3. Temperature of

deposition was held constant at 1873 K while experiments were run for various times of from 5 min to 180 min. Another series of experiments were made in which the time of deposition was held constant at 30 min and temperature of deposition lower in 25 K increments from 1873 K down to 1748 K. These runs are listed in Table 17. A plate of graphite was also placed in the deposition chamber for these last series of runs. This plate was used to measure the rate of weight gain per unit area and rate of thickness growth. From the weight gain measurements, it was felt that the deposition temperature of 1748 K was too low to initiate formation of measurable amounts of BN. Electrical resistance measurements with the copper block technique indicated that at least 10 min of deposition time at 1873 K was needed to obtain an open circuit reading ($>10^6$ ohm) on the CVD BN coated HMS graphite yarn. For the 30 min experiments all except the 1738 K run had tow resistances too high to measure.

3.3.1 CVD BN Celion 6000 Graphite Yarn

Celion 6000 graphite yarn was used as the substrate in the CVD BN apparatus. The temperature of deposition was held constant at 1873 K and runs of from 1 to 45 min were made. The CVD BN coating runs for Celion 6000 graphite yarn are listed in Table 18. The shorter duration runs listed in this table (1 to 5 min) were made to produce coated tows from which individual fibers for tensile testing could be extracted. Sections of coated yarn were taken from the runs listed in this table for studying growth rate. In Fig. 30 are shown runs of 1 and 10 min duration. In Fig. 31 are shown cross sections of the 20 and 45 min experiments. The effect of longer deposition times can be seen by comparing the CVD BN thickness as shown in these two figures. The CVD BN coated yarn from the 45 min duration experiment was brittle and contained many areas of individual fibers clumped together.

The extraction of single coated fibers for tensile testing on deposition runs of longer than 10 min was not possible. The 1 min duration runs were not a problem but difficulty was encountered with the 10 min deposition experiments. The results of ultimate tensile strength and modulus tests on the extracted CVD BN coated Celion graphite yarn are given in Table 19. The lower measured tensile strength of 1180 MPa for BN 19 compared with 2200 MPa of the untreated Celion 6000 graphite yarn was probably due to the exposure of the graphite yarn to the deposition temperature of 1873 K at low pressures rather than the presence of the CVD BN coating. This effect of temperature can be seen with the results of BN 16 which indicated a tensile strength of only 830 MPa after having been exposed to 10 min at 1873 K compared with the 1 min exposure of BN 19.

3.4 Evaluation of CVD SiC Coated Graphite Yarns in Composites

Large composite panels of untreated and CVD coated graphite yarn were required to be made and shipped to NASA at the completion of this program. The graphite yarn for these panels was: HMS graphite yarn, Celion 6000 graphite yarn, T-300 graphite yarn, and Celion 12000 graphite yarn. The CVD processing conditions for each graphite yarn were chosen to produce the highest electrical resistance with the least decrease in mechanical properties of the untreated graphite yarn and were shown in Table 8. The epoxy resin required for these panels was to be in all cases the MY720 containing UTRC 89-Z resin. To evaluate the UTRC method of in-house impregnation of yarn, tape fabrication, lay-up, and laminate cure cycles, that were to be used to fabricate these deliverable composites, small composites were made. These small composites were unidirectional 6 to 12 layers thick, 3.8 cm wide by 7.62 cm long. Specimens were cut from these panels for three point modulus of rupture and short beam (s/d 4:1) testing. Along with the UTRC 89-Z resin, PR-286 and PR-288 epoxy resins were used as matrices for the HMS graphite yarn series. For the remaining graphite yarns only PR-288 and the UTRC 89-Z resins were used for these small composites.

3.4.1 Summary of Previous Studies with CVD SiC Coated Graphite Yarn Composites

At the conclusion of the previous program composite panels were made consisting of three types of HTS graphite yarn. These three types were: untreated HTS graphite yarn, CVD SiC coated HTS graphite yarn, and CVD SiC in-line oxidized coated HTS graphite yarn. Each panel was composed of 16 layers of unidirectional yarn 7.64 cm x 7.64 cm with a minimum 60% volume fiber content. The resin used in these panels has been given the notation UTRC 89-Z. This resin was composed of MY720, DEN 438 and DDS and was previously described on page 8 of this report. Flexural properties of the resin are listed in Table 20. The composite specimens were numbered 212-6, 212-7, and 212-8. The first was the laminate made with untreated HTS graphite yarn, the second contained CVD SiC coated HTS graphite yarn, and the third contained CVD SiC coated HTS graphite yarn which had been given an in-line oxidation treatment of 773 K. Test specimens were machined from these panels with s/d of 4:1 for short beam shear tests.

The results of these tests are listed in Table 21 and the averages show that the untreated HTS graphite yarn panel had a shear strength of 39.6 MPa (5.75 ksi). The CVD SiC coated HTS graphite yarn panel had a shear strength of 76 MPa (11.0 ksi) and the CVD SiC coated HTS graphite yarn that had been given an in-line oxidation treatment at 773 K had a shear strength of 101 MPa (14.6 ksi). The latter shear strength values indicate that the oxidation step treatment of the CVD SiC coated HTS graphite yarn promotes bonding in the UTRC 89-Z resin.

3.4.2 CVD SiC Coated HMS Graphite Yarn/Epoxy Composites

The untreated HMS graphite yarn was initially used with both the PR-286 and PR-288 resin systems to make the small evaluation composites. Test results from these composites are listed in Table 22. The average flexural strength, modulus of elasticity and shear strength for each composite can be compared with the last entry in this table which was taken from Hercules data sheets. This comparison would indicate that the in-house impregnation of yarn, tape fabrication and lay-up, and composite cure cycle can produce acceptable finished composites. The untreated HMS graphite yarn was then used to prepare small composites with the UTRC 89-Z resin. The results for the mechanical tests of specimens cut from two of these panels are listed in Table 23. The overall average of 756 MPa (110 ksi) for the flexural strength and 42.5 MPa (6.2 ksi) for short beam shear are both lower than similar values obtained in the PR-286 and PR-288 resins.

The CVD parameters were chosen to produce the highest electrical resistance coated and oxidized HMS graphite yarn. This CVD SiC coated HMS graphite yarn was then used to make small composites in UTRC 89-Z resin. The results for the mechanical tests of specimens cut from two of these panels are listed in Table 24. From this table it can be seen that for the UTRC 89-Z resin the CVD SiC coated HMS graphite yarn produces an improvement of from 42.3 MPa (6.1 ksi) up to 62.8 MPa (9.1 ksi) in shear strength. The flexural strength of the coated yarn also shows a slight improvement of from 756 MPa (110 ksi) for the untreated yarn to 867 MPa (126 ksi) for the CVD SiC coated HMS graphite yarn.

3.4.3 CVD SiC Coated Celion Graphite Yarn/Epoxy Composites

Untreated Celion 6000 graphite yarn was used to make six small composites. Three of these employed PR-288 and the other three used UTRC 89-Z as the resin matrix. The mechanical test results of specimens cut from these six panels are listed in Table 25. In the PR-288 system, the untreated Celion 6000 graphite yarn yielded the highest combination of properties obtained with carbon-epoxy composites in this program. The averages of composites T62A, T62B, and T69 yielded 1850 MPa (268 ksi) for the flexural strength and 95.1 MPa (13.8 ksi) for the short beam shear strength. With the UTRC 89-Z resin the average flexural strength of 1638 MPa (238 ksi) was more than satisfactory but the average shear strengths were only 44.6 MPa (6.5 ksi) with this resin system for the untreated Celion 6000 graphite yarn.

CVD SiC coated Celion yarn that had been oxidized at the temperature that yielded the combination of the highest electrical resistance with the least decrease in individual fiber strengths was used to make five small composites. These five employed UTRC 89-Z as the resin matrix. The results of mechanical tests for this group are listed in Table 26. For the CVD SiC coated and oxidized

Celion 6000 graphite yarn in the UTRC 89-Z resin the averages of the five composites listed in Table 26 yield 833 MPa (121 ksi) for the flexural strength and 62.1 MPa (9.0 ksi) for the short beam shear strength. The average flexural strength for the coated yarn was less than that obtained with the untreated yarn 833 MPa (121 ksi) compared to 1638 MPa (238 ksi) in the UTRC 89-Z resin. The shear strength on the other hand was slightly higher, 61.2 MPa (9.0 ksi) compared to 44.6 MPa (6.5 ksi) for the untreated yarn.

3.4.4 CVD SiC Coated T-300 Graphite Yarn/Epoxy Composites

The T-300 graphite yarn because of its relatively small number of filaments per tow and twist present in the as-received yarn was the most difficult graphite yarn to handle in both the CVD process and in tape making procedures used for composite fabrication. Only five of the small composites for evaluation were made with T-300 graphite yarn. The mechanical test results of these five composites are listed in Table 27. The first three composites (T73, T77, T78) were made with untreated T-300 graphite yarn in the UTRC 89-Z resin. The last two composites listed in this table were T84 and T85 which were made with the CVD SiC coated and oxidized T-300 graphite yarn. In the UTRC 89-Z resin the untreated T-300 graphite yarn yielded averages of 1489 MPa (216 ksi) for the flexural strength and 56.6 MPa (8.2 ksi) for short beam shear strengths. Composites T78 in this series had values of 1654 MPa (240 ksi) for the flexural strength and 84 MPa (12.2 ksi) for the shear strength. This particular composite compares favorably with the optimum desired properties for this system combination.

The CVD SiC coated and oxidized T-300 graphite yarn was used to make only two small composites and these were both with UTRC 89-Z resin. The averages for these two composites were 673 MPa (97.6 ksi) for the flexural strength and 78.6 MPa (11.4 ksi) for the short beam shear strength. The flexural strength values are lower for the CVD SiC coated T-300 graphite yarn compared to the untreated T-300 graphite yarn in the same UTRC 89-Z resin but the average shear strengths for the coated yarn are higher 78.6 MPa (11.4 ksi) compared with 56.6 MPa (8.2 ksi) for the untreated T-300 graphite yarn. These lower flexural strength values are felt to be due in part to the difficulty encountered in making these composites. This difficulty was attributed to the previously discussed poor handleability of the CVD SiC coated T-300 graphite yarn.

3.4.5 CVD SiC Coated Celion 12000 Graphite Yarn/Epoxy Composites

The Celion 12000 graphite yarn as was discussed previously had become available late in this program. Because of this lateness only four small composites were made for evaluation. One of each of the following: untreated Celion 12000 graphite yarn in PR-288 resin (T91); untreated Celion 12000 graphite yarn in UTRC 89-Z resin (T95); CVD SiC coated and oxidized Celion 12000 graphite yarn in PR-288 resin (T93); and CVD SiC coated and oxidized Celion 12000 graphite yarn in UTRC

89-Z resin (T94). The test results of specimens cut from these four composites are listed in Table 28. The shear strengths for the PR-288 resin system of 110 MPa (16.0 ksi) and for the UTRC 89-Z resin system of 103 MPa (14.9 ksi) for both these untreated Celion 12000 graphite yarn composites are considered more than acceptable.

The CVD SiC coated Celion 12000 graphite yarn in the PR-288 resin averages of 1288 MPa (187 ksi) for the flexural strength and 105 MPa (15.3 ksi) for the short beam shear strength compare favorably with those obtained with the CVD SiC coated Celion 6000 graphite yarn previously described. In the UTRC 89-Z resin, the CVD SiC coated Celion 12000 graphite yarn composite yielded averages of 1142 MPa (165 ksi) for the flexural strength and 73.1 MPa (10.6 ksi) for the short beam shear strength. These results are slightly better than what had been achieved with the CVD SiC coated Celion 6000 graphite yarn in this resin system.

3.4.6 Summary of CVD SiC Coated Graphite Yarn/Epoxy Composite Data

The test results from the small composites made for evaluation with UTRC 89-Z that have just been described are summarized in Table 29 for the various combinations of untreated and treated graphite yarns. From this table it can be seen that in general the flexural strength is lower for Celion 6000 and T-300 graphite yarns in the UTRC 89-Z resin system. The CVD SiC coated yarns in most cases when incorporated in the UTRC 89-Z resin yield shear strength results close to 68.9 MPa (10 ksi) which was correspondingly higher than those for composites containing the untreated yarns in this same resin.

3.4.7 Composites Delivered to NASA

Large composites 7.6 cm x 7.6 cm by 16 unidirectional plies were required by NASA from this program for burn tests. In Table 30 are listed these deliverable composite panels with a description of the graphite yarn and CVD SiC/O_2 treatment when used. All of these composite panels were made with the UTRC 89-Z resin as a matrix.

3.5 CVD Si_3N_4 Coated HMS Graphite Yarn/Epoxy Composites

CVD Si_3N_4 coated HMS graphite yarn from the multiple yarn deposition experiments were put into a composite panel with PR-288 epoxy resin. These composites were made by coating individual CVD Si_3N_4 coated HMS graphite yarn tows with resin and hand placing them in the small composite panel die. The results of mechanical tests of specimens cut from these small composites are listed in Table 31. The manual control of spacing improved as each composite was prepared (T88 through T90). Composite T90 was by far the most cosmetically acceptable panel and yet the modulus of rupture results of all three panels listed in Table 31 are fairly close.

The average of the Young's modulus of all three panels when compared to previous results with HMS graphite yarn indicate that the volume fraction of incorporated graphite yarn was slightly more than half of what had been previously achieved using continuous yarn-tape fabrication processes. These composites, due to the hand lay-up process, were resin rich. The average modulus of elasticity of these panels as listed in this table was 103 GPa whereas a 60% volume fraction HMS graphite yarn panel is typically 182 GPa (see Table 22). Normalizing the obtained flexural strength by the ratio of modulus of elasticity of 60% volume fraction to that obtained would yield flexural strengths of approximately 1096 MPa (159 ksi). These values are definitely in the range of HMS-epoxy composite results, and if this normalization is justified would indicate that the CVD Si_3N_4 coating process did not significantly degrade the HMS graphite yarn.

3.6 Discussion of Organo-Silicone Approach to Develop Coated Graphite Fibers with High Electrical Resistance

3.6.1 Results of Previous Studies - Static Test Runs

In the organo-silicone coating experiments, the objective was to determine if the graphite filaments could be coated with an organo-silicone precursor, and through pyrolysis convert the organo-silicone to a continuous coating of amorphous silica.

In the first year's effort, four types of silicone materials were selected for these experiments by the static method. Two of these were monomeric silanes, capable of forming a polymeric gel on the fiber surface, and two others were soluble silicone prepolymers. Another criteria of selection was that each material would be capable of undergoing decomposition to mostly silicon dioxide, containing little or no silicon carbide.

The silanes selected were methyltriethoxysilane (MTS) and vinyltriacetoxysilane (VTS). The prepolymers selected were GE silicone resin SR-355 and a commercial prepolymer of ethyl silicate (ES). The materials selected are listed in Table 33.

The procedure used to coat HTS graphite yarn by the static method and details of these static experiments were described in Ref. 4. As a result of the static tests, which are summarized in Table 33, one material, a commercial prepolymer of ethyl silicate (ES), was selected for studies in a continuous coating apparatus.

3.6.2 Results of Previous Coating Experiments in a Continuous Reactor

As mentioned above in the first year's effort, ethyl silicate prepolymer was selected for additional studies to coat HTS fiber on a continuous basis. Silica-like coated HTS fibers produced in this continuous reactor were evaluated for electrical resistance, oxidation resistance at 703 K for 8 hrs in static air, tensile strength, and for coherency of coating by SEM observations. Silica-like coated HTS fiber with optimum properties was selected for further evaluation in a unidirectional composite. The data were presented in the first year's report.

From the shear data in that report, it was concluded that the silica-like coating had caused a decrease in the adhesion of the epoxy resin to the coated fiber surface. This suggested: (1) that the coating layer was poorly wetted by the epoxy resin or (2) that the coating consisted of a mechanically weak boundary layer. The physical appearance of the fiber suggested that the coating produced a mechanically weak boundary layer. Experiments designed to improve the silica-like coating to increase the electrical resistance of the fiber and the shear and flexural properties in composites were carried out during the second year's effort. In addition to additional studies with ethyl silicate as a coating material, three other materials were evaluated in this program. These are Owens-Illinois glass resins 100 and 650, and tri-n-butylborate.

3.6.3 Studies Using Modified Continuous Coating Reactor

The continuous reactor used in the first year's effort was modified to carry out the coating studies during this period. The modified continuous coating reactor is shown in Fig. 6. Celion 6000 graphite yarn was used instead of HTS graphite yarn as was done in the previous work. As mentioned above, four materials were selected for evaluation as coating materials. They were ethyl silicate (ES), Owens-Illinois glass resins 100 and 650, and tri-n-butylborate. The results of these studies for each coating material are described below.

3.6.3.1 Ethyl Silicate Coating Studies

A series of coating studies was initiated with Celion 6000 graphite yarn instead of HTS graphite yarn as was done in the previous work. Ethyl silicate solution was used as the coating medium. The conditions of the coating runs and the effect on the fiber properties are listed in Table 34. The highest resistance generated from this series of runs in which the ethyl silicate concentration was varied from 2.5 to 10 w/o is 180 ohms. The conditions for this run (5 w/o, steam 393 K, drawing rate 0.91 m/min, pyrolysis temperature 1093-1173 K) were repeated several times. In each case, this resulted in a lower resistance

(27-95 ohms) than experienced in run #SC-16. The powder-like appearance of the coating on the surface suggested that the coating is easily removed causing this variation in resistance.

As indicated in Table 34, initial pyrolysis studies with the ethyl silicate system were carried out at 1093-1173 K in nitrogen. Therefore, a series of runs using ethyl silicate at two levels of resin concentration, 2.5 and 3.5 wt %, for application to Celion 6000 graphite yarn was carried out at a lower pyrolysis temperature to determine its effect on electrical resistance. The results of these tests are also listed in Table 34. It is clear from the run made at 473 K in steam that this low temperature treatment generated a coating with high electrical resistance, relative to the high temperature treatment (1093-1173 K). It is also apparent that steam treatment improves the resistance of the coating. The 573 K treatment also improved the electrical resistance of the ethyl silicate coating, relative to the 1093-1173 K treatment, but not nearly to the same extent as the 473 K treatment. Based on these results, ethyl silicate appeared to be an attractive candidate, as a coating material for increasing the electrical resistance of the graphite fiber surfaces.

3.6.3.1.1 Fiber Properties

The effects of the coating process on the tensile strength of coated fibers which showed good electrical resistance were determined. In addition, the weight percent coating on these coated fibers, and by calculation, the approximate thickness this coating would represent was also determined.

The weight percent coating and tensile loads for the ethyl silicate coated fibers are listed in Table 34. It should be pointed out that a 20 w/o increase in fiber weight is equivalent to about 15 v/o increase in the fiber volume, when the densities of the graphite fiber and silicon oxide coating are taken into consideration. If the diameter of the fiber increases from 8×10^{-4} cm to 9×10^{-4} cm, this would amount to a 26.5% increase in fiber diameter. This suggests that increases in fiber weight from 20 to 35.3 w/o correspond to coating thicknesses of 0.75 to 1.0μm. This is the range of fiber weight increases generated in coating of Celion 6000 graphite yarn with ethyl silicate at the concentration levels and drawing rate (0.91 m/min) used in these studies. Relative to "as-received" Celion 6000 graphite yarn, high electrical resistance yarns from runs SC-48, -49 and -50 exhibit the same tensile properties, indicating that the coating or coating process does not degrade the fiber. Silica-like coated yarn from the high temperature runs SC-19 and -20 appeared to have undergone degradation (560 to 467N vs 636N for "as-received" yarn).

3.6.3.2 Glass Resin 100 Coating Studies

Two novel silicone resin materials called glass resin 100 and glass resin 650 manufactured by Owens-Illinois were also investigated as coating materials. Initial studies were carried out at a low pyrolysis temperature, with and without steam treatment to determine the effect on electrical measurements. The results of these studies are listed in Table 35. Several points are obvious from these studies: (1) steam treatment is necessary to obtain high electrical resistance at the lower pyrolysis temperatures, 473 and 573 K, and (2) a pyrolysis temperature of 573 K is adequate in generating a coating with high electrical resistance, (3) this coating material appears promising in that an electrical of about 150C ohms was obtained and appears to be reproducible as shown by runs SC-22 and SC-36, (4) the highest electrical resistance was obtained by a 673 K pyrolysis temperature.

3.6.3.2.1 Fiber Properties

The weight percent increase and tensile loads for the glass resin 100 coated Celion 6000 are listed in Table 35. Here again, a range in weight percent coatings are generated in these coating studies. A weight increase of 17.3% (run SC-36) would cause an increase in fiber diameter of about 0.5μm. The coated fiber with the highest electrical resistance, run SC-37, represents 21.4% increase in fiber weight, or a diameter increase of 0.75μm. The tensile loads required to fracture these coated yarn samples (SC-36 and -37) are equivalent to the load required to fracture "as-received" Celion 6000 yarn. This indicates that the coating or coating process does not damage the fiber. Coated fiber from runs SC-21, -22, -23 and -24 appeared to have undergone about a 10% loss in tensile properties.

3.6.3.3 Glass Resin 650 Coating Studies

Owens-Illinois glass resin material 650 was also evaluated. A series of runs was made over a temperature range of 473 to 1173 K. The results of this study are listed in Table 36.

Every condition tested produced a coated fiber with much greater electrical resistance than uncoated fiber. The run made with steam followed by low temperature pyrolysis (473 K) produced an electrical resistance equivalent to runs made using Owens-Illinois glass resin 100 (1100 to 1500 ohm). However, in contrast with the high temperature runs with this latter resin, a run made at a pyrolysis temperature of 1173K yielded a coated fiber with a resistance of 6500 ohms. This result shows that both glass resin systems are capable of forming high resistance coatings on Celion 6000 graphite fibers.

3.6.3.3.1 Fiber Properties

Table 36 lists the weight percent coating on Celion 6000 fiber generated by coating with glass resin 650 and the tensile loads required to fracture the coated yarns. The range of weight increases due to the coating is 17.7 to 30.2%, similar to that experienced with glass resin 100 and ethyl silicate. The increase in coating thickness would be 0.5 to 7.5μm. Except for yarn samples from run SC-47, tensile loads required to fail the tensile specimens of coated yarn are equivalent to that required to fail "as-received" Celion 6000 suggesting that the coating or coating process does not degrade the tensile strength of the fiber. Apparently the 1173 K pyrolysis temperature used in run SC-47 produces a high electrical resistance coating, but causes a 56% loss in tensile strength.

3.6.3.4 Tri-n-butylborate Coating Studies

The promising results using Owens-Illinois glass resin 100 to yield silica-like coated Celion 6000 graphite yarn with a resistance of 1500 ohms suggested that other similar resin systems and coating materials should be tested. Therefore during this program, silica-like coating studies were discontinued temporarily to evaluate tri-n-butylborate as a coating material. The concept behind the use of tri-n-butylborate is the fact that it is easily hydrolyzed to hydrated boric acid, and the boric acid is converted to a glassy boron oxide.

$$B(OCH_2CH_2CH_2CH_3)_3 + 3H_2O \xrightarrow[\text{(steam)}]{} B(OH)_3 + 3\,HOCH_2CH_2CH_2CH_3$$

$$2B(OH)_3 \xrightarrow[\text{heat}]{} B_2O_3 + 3H_2O$$

A series of runs were made at several concentration levels of tri-n-butylborate in isopropyl alcohol. Table 37 lists the conditions of each run and the resultant resistance of the coated Celion 6000 graphite fibers. It is clear from the low resistance measurements that these concentration levels of tri-n-butylborate are ineffective in increasing the electrical resistance of Celion 6000 graphite fibers.

In experiments for runs SC-25 through -34, the coated fiber was hydrolyzed and then returned into the coating solution. This was repeated five times before the final pyrolysis step. In this approach, it was found that during the multiple coating operation the boric acid, $B(OH)_3$, produced in the hydrolysis step was being removed in the coating solution. This meant that only the last coating operation resulted in $B(OH)_3$ pyrolysis to glassy B_2O_3. The quantity of boron oxide produced on the surface must be extremely small since the coating was ineffective in increasing the electrical resistance of Celion 6000 graphite fibers.

Additional runs were made in which the borate ester coated fiber was hydrolyzed and subsequently pyrolyzed, followed by another dip into the coating bath. This process was repeated five times. Two runs made from a 2.5 w/o solution did not produce a boron oxide glass coating with improved electrical resistance over the uncoated yarn. Apparently, at this low concentration (2.5 w/o), even with five dips, the glass coating produced was extremely thin or is not a coherent coating. Additional studies were not carried out at higher concentration levels.

3.6.4 Evaluation of Silica-like Coated Celion 6000 Graphite Fibers in Epoxy Composites

3.6.4.1 Composite Properties

Composites of the highest resistance coated fibers of each coating material were fabricated and tested for shear and flexural strength and modulus. Two hundred feet of coated fiber for each system was required to fabricate 3.75 cm x 12.5 cm x .25 cm composites. The coated fiber was selected on the basis of high electrical resistance and excellent strength retention of the coated Celion 6000 fiber relative to untreated Celion 6000 graphite fiber. The results of the mechanical tests are listed in Table 38. The low shear strength values of about 35 MPa (5 ksi) for the coated fibers relative to what is usually obtained for untreated fiber, 115 MPa (15 ksi) clearly demonstrates that each coating material is poorly bonded to the graphite fiber. This is further illustrated by the poor flexural strength and modulus values. A typical flexural strength of a Celion 6000/epoxy composite is 1565 MPa (225 ksi) while these composites exhibited strengths of only 279 to 350 MPa (40 to 50 ksi).

A shear failure mode of the flexural specimens was noted for each case, a further indication of the poor bonding of the coating to the fiber. Higher treatment temperatures of the coatings result in lower resistances, but may produce stronger coatings. Future work should be directed toward obtaining these stronger coatings.

3.6.5 Conclusions of Organo-Silicone Coating Studies

For the organo-silicone coating approach, the best conditions established as a result of these studies are listed in Table 39 for each material.

4.0 GENERAL CONCLUSIONS

The CVD process for coating graphite yarns with SiC, Si_3N_4 or BN has been shown to be a method for increasing the electrical resistance of the as-received yarn. In the case of CVD SiC continuous process with HMS, T-300, Celion 6000 and Celion 12000 yarns an in-line oxidation furnace could be used to oxidize the surface of the SiC coating to further increase the electrical resistance of the coated yarn. This oxidation furnace temperature was varied from 700 to 873 K with either 773 K or 873 K found to be optimum for a particular graphite yarn. The temperature of the deposition chamber was also found to be an important factor in increasing the resistance of the coated yarn with 1398 K an optimum. The highest successful drawing rate for the CVD SiC process used was 122 cm/min but 30.5 cm/min was found to be optimum for all five types of graphite yarn studied in terms of yielding the highest increase in electrical resistance. It was found that on the average the CVD SiC continuous coating process with the in-line oxidation step did not degrade the mechanical properties of the untreated yarn. This was ascertained through individual filament testing of ultimate tensile strength.

Small composites were made from untreated and CVD SiC coated graphite yarns in both PR-288 epoxy resins and in UTRC 89-Z resins. The UTRC 89-Z resin contained the components of MY720/DDS. For the untreated and CVD SiC coated yarns the flexural strength (three point measurement) and short beam shear strength were lower in the UTRC 89-Z resin than in the PR-288 epoxy resin for corresponding conditions. All the CVD SiC coated yarns in the UTRC 89-Z resin for the most part had shear strengths of at least 68.9 MPa (10.0 ksi).

The CVD Si_3N_4 static coating process was used with HTS, HMS, Celion 6000 and Celion 12000 graphite yarns. An optimum temperature of 1723 K and an ammonia to silicon tetrafluoride ratio of 6.01 was found to produce consistently coated yarn that could withstand 120 VAC open circuit tests without signs of arcing for all the graphite yarns studied. This was a static CVD process in which 15-20 cm long tows were able to be coated at one time. Individual fiber tests indicated that the CVD Si_3N_4 process did not significantly degrade the mechanical properties of the as-received untreated yarn. The CVD Si_3N_4 coated HMS graphite yarn was used to make a composite panel with PR-288 epoxy resin as the matrix. Mechanical tests of these composites were made and the results after correction for low volume fraction were similar to untreated HMS graphite yarn in this epoxy matrix.

A CVD BN static coating process for both HMS and Celion 6000 graphite yarns was investigated. Deposition temperature of 1873 K for times of 1 to 45 min duration were found to produce a BN coating on the individual graphite yarn. Deposition times of 10 min were required to produce CVD BN coated yarn which

could withstand a 120 VAC arcing test. Ultimate tensile strength measurements of uncoated single graphite fibers after exposure to the 1873 K thermal environment showed a considerable decrease in strength. Tests of single CVD BN coated fibers (after exposure to the 1873 K deposition conditions) gave this same low ultimate tensile strength. This low tensile strength of the CVD BN coated fibers is felt not to be due to the CVD BN process but to the thermal exposure effects of 1873 K on the graphite yarn.

For the organo-silicone coating approach the best conditions established as a result of these studies produced silica-like coated Celion 6000 graphite fibers with an electrical resistance ranging from 720 to 2950 ohms, compared with 4.0 ohms for "as received" Celion 6000 graphite fibers.

Composites fabricated from these coated fibers exhibited shear strengths of 33 to 45 MPa (4.80 to 6.59 ksi) and flexural strengths of 261 to 374 MPa (37.9 to 54.3 ksi). These values are considerably lower than can be derived from "as received" Celion 6000 graphite fibers, shear strengths of 102 MPa (15.0 ksi) and flexural strengths of 1530 MPa (225 ksi). The composites tested in flexure failed in a shear mode. Several reasons can account for these low shear and flexure values; (1) the pyrolyzed organo-silicone coating layer could be poorly wetted by the epoxy resin, (2) the coating could be a mechanically weak boundary layer, (3) the coating could be poorly bonded to the fiber surface, or (4) a combination of all three. The physical appearance of the coated fibers suggest that the coating may be a mechanically weak boundary layer. In order to improve the bonding of the silica-like coating to the fiber, a high pyrolysis temperature must be used.

5.0 REFERENCES

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Table 1

Resistance Data for CVD SiC Coating Runs on Celion 6000 Yarn

Run Number	Drawing Rate cm/min	Deposition Temp K	In-Line Oxidation Temp K	Resistance, Ohms Top	Middle	Bottom
N 714	15	1398-1453	none	3.5K	45K	7K
				3.0K	10K	125K
N 715	30			750	155	118
				450	210	220
N 716	60			300	160	390
				280	160	450
N 717	90			360	290	210
				200	90	110
N 718	122			55	110	1.5K
				220	110	200
N 719	15		773	80K	4.2K	29K
				10K	1.2K	55K
N 712	30			1.8K	1.8K	1.8K
				1.2K	1.1K	1.4K
N 713	60			1.8K	3.3K	5.8K
				1.4K	2.1K	4.4K
N 720	90			230	50	28
				220	70	55
N 722	122			75	155	300
				75	60	400
N 725	30		873	800	600	4.6K
				1.2K	1.0K	7.5K
N 724	60			900	2K	650
				1.0K	1.6K	250
N 723	90			200	300	800
				300	400	450
N 722	122			140	16	42
				13	17	18

Table 2

Resistance Data for CVD SiC Coating Runs on T-300 Graphite Yarn

Run Number	Drawing Rate cm/min	Deposition Temp K	In-Line Oxidation Temp K	Resistance, ohms Top	Middle	Bottom
N 727	30	1398-1453	none	400	500	300
				900	380	320
N 728	60			300	280	360
				260	200	400
N 729	90			210	90	90
				140	60	95
N 730	122			62	75	100
				62	50	150
N 732	30		773	1K	1.5K	400
				550	650	400
N 733	60			200	350	180
				550	130	80
N 734	90			70	65	86
				75	70	80
N 735	122			50	65	200
				68	80	155
N 739	30		873	550	280	6.2K
				900	270	3.6K
N 738	60			200	100	350
				140	150	210
N 737	90			60	55	50
				58	52	55
N 736	122			30	25	75
				50	30	200

Table 3

Resistance Data for CVD SiC Coating Runs on HMS Graphite Yarn

Run Number	Drawing Rate cm/min	Deposition Temp K	In-Line Oxidation Temp K	Resistance, ohms Top	Middle	Bottom
N781	15	1398-1453	none	15 K	15 K	18.5 K
				12 K	16 K	17 K
N777	30			3.8 K	5.4 K	3.5 K
				3.2 K	5.2 K	3.8 K
N778	60			73	220	600
				100	200	650
N779	90			2.6	3.2	3.0
				3.1	3.0	2.8
N780	122			2.5	4.4	3.5
				2.8	4.1	3.2
N782	15		773	15 K	12.5 K	7 K
				16.5 K	17.5 K	20 K
N765	30			925	1.1	490
				2.8 K	310	390
N766	45			45	320	500
				35	170	380
N768	60			80	92	170
				120	110	160
N769	90			65	90	32
				48	70	30
N770	120			5.5	3.8	3.2
				5.5	3.2	3.6
N783	15		873	95	170	500
				115	140	600
N773	30			1.3 K	4.4 K	2.4 K
				1.9 K	3.3 K	3.0 K
N774	60			70	19	40
				47	13	37
N775	90			65	12	25
				60	15	40
N776	120			4.6	2.7	2.1
				3.5	2.8	2.2

Table 4

Ultimate Tensile Strength and Modulus Results from Tests on Individual SiC Coated Celion 6000 Graphite Yarn

Run Number	Drawing Rate	In-Line Oxidation Temp	Ultimate Tensile Strength		Modulus	
	cm/min	K	MPa	(ksi)	GPa	(10^6 psi)
N714	15.0	none	1899	(276)	200	(29.0)
N715	30.5	none	1888	(274)	185	(26.9)
N716	61.0	none	2181	(317)	210	(30.4)
N717	91.5	none	2474	(359)	202	(29.3)
N718	122.0	none	2278	(331)	148	(21.5)
N719	15.0	773	1649	(239)	172	(25.0)
N712	30.5	773	2333	(339)	207	(30.0)
N713	61.0	774	2142	(311)	194	(28.1)
N720	91.5	773	1693	(246)	157	(22.8)
N721	122.0	773	1736	(252)	188	(27.3)
N725	30.5	873	2670	(387)	196	(38.4)
N724	61.0	873	1910	(277)	161	(23.3)
N723	91.5	873	1941	(282)	195	(28.4)
N722	122.0	873	2137	(310)	156	(22.5)
As Rec'd Celion 6000			2626	(382)	183	(26.6)
			2477	(359)	173	(25.1)

Table 5

Ultimate Tensile Strength and Modulus Results from Tests on Individual CVD SiC Coated HMS Graphite Yarn

Run Number	Drawing Rate cm/min	In-line Oxidation Temp K	Ultimate Tensile Strength MPa	(ksi)	Modulus GPa	(10^6 psi)
N781	15	None	1696	(246)	277	(40)
N777	30	↓	1755	(255)	305	(44)
N778	60	↓	2184	(317)	321	(47)
N779	90	↓	2116	(307)	263	(38)
N780	122	↓	2203	(320)	271	39
N782	15	773	1901	(276)	283	(41)
N765	30	↓	1999	(290)	278	(40)
N768	60	↓	2205	(320)	309	(45)
N769	90	↓	2077	(301)	270	(39)
N770	122	↓	2262	(328)	281	(41)
N783	15	873	2369	(344)	293	(43)
N773	30	↓	2145	(311)	305	(44)
N774	60	↓	2164	(314)	350	(51)
N775	90	↓	2310	(335)	274	(40)
N776	122	↓	2242	(326)	315	(46)
As Received HMS			2164	(314)	287	(42)

Table 6

Resistance Data for CVD SiC Coating Runs on C-12000 Graphite Yarn

Run Number	Drawing Rate cm/min	Deposition Temp K	In-Line Oxidation Temp K	Resistance, ohms Top	Middle	Bottom
N872	30.5	1398-1453	773	1K	1.85K	1.4K
N874	30.5	↓	873	1.6K	.9K	1.4K
N876	30.5	↓	none	.5K	1.2K	.4K

Table 7

Ultimate Tensile Strength and Modulus Results from Tests on Individual Filaments from C12000 Graphite Yarn

Fiber Condition	Oxidation Temp. K	Ultimate Tensile Strength MPa	(ksi)	Modulus GPa	(10^6 psi)
CVD SiC coated	none	2144	(311)	231	(33.5)
CVD SiC coated	773	2355	(342)	229	(33.2)
CVD SiC coated	873	2128	(309)	258	(37.4)
As Received C12000 Graphite Yarn	-	2916	(423)	204	(29.6)

Table 8

Final CVD SiC Coating Conditions Chosen for Various Graphite Yarns

Yarn	In-Line Oxidation Temp., K	UTS MPa	UTS (ksi)	Resistance ohms
HMS	873	2145	(311)	2720
T-300	773	-	-	820
Celion 6000	773	2333	(339)	1520
Celion 12000	773	2355	(342)	1400

Reactor temperature: 1398-1423 K
Drawing rates: 30 cm/min
Gas input: 0.110 ℓ/min H_2, 0.110 ℓ/min CH_4, 0.015 ℓ/min CH_3SiHCl_2

Table 9

Individual Fiber Ultimate Tensile Strength and Modulus Test Results for CVD Si_3N_4 Coated HTS Graphite Yarn

Run Number	Temperature K	Time min	Ultimate Tensile Strength MPa	(ksi)	Modulus GPa	(10^6psi)	Apparatus	Comments
Untreated HTS	-	-	2394	(347.4)	222	(32.2)		
156	1723	15	1511	(219.3)	212	(30.8)	Large	Thermal exposure on
153	1723	5	1326	(192.4)	202	(29.3)	Large	
152	1723	10	1540	(223.6)	189	(27.4)	Large	
154	1723	15	878	(127.4)	-	-	Large	
	1673	15	1921	(278.8)	192	(28.4)	Small	Thermal exposure on
SN-8	1673	5	2116	(307.2)	206	(29.9)	Small	
SN-7	1673	10	1394	(202.4)	173	(25.1)	Small	
SN-6	1673	15	1794	(260.4)	205	(29.8)	Small	
SN-12	1593	5	2067	(300.0)	228	(33.0)	Small	
SN-11	1593	10	2015	(292.4)	219	(31.8)	Small	
SN-10	1593	15	2125	(308.5)	219	(31.8)	Small	

Table 10

Individual Fiber Ultimate Tensile Strength and Modulus Test Results on CVD Si_3N_4 Coated HTS Graphite Yarn

Run Number	Temperature K	Time min	Mole Ratio NH_3/SiF_4	Ultimate Tensile Strength MPa	(kpsi)	Modulus GPa	(10^6 psi)
SN-17	1593	10	6.01	1151	(167.0)	169	(24.5)
SN-18	1593	20	6.01	1638	(237.7)	200	(29.0)
SN-19	1593	10	3.72	1082	(157.1)	123	(17.9)
SN-20	1593	20	3.72	1112	(161.3)	185	(26.8)
SN-21	1593	10	1.93	985	(142.9)	212	(30.8)
SN-22	1593	20	1.93	1999	(290.1)	207	(30.1)
SN-23	1673	10	6.01	1336	(193.9)	194	(28.1)
SN-24	1673	20	6.01	907	(131.6)	157	(22.8)

Table 11

Qualitative Arcing Tests on CVD Si_3N_4 Coated HTS Graphite Fiber

Run Number	CVD Time min	Slight Spark	Burn	Catastrophic Arcing	Comments
SN-17	10	90 V	115 V	yes (120 V)	
SN-18	20	105 V	no	no	withstood full voltage
SN-19	10	80 V	95 V	yes (100 V)	
SN-20	20	no	105 V	no	withstood full voltage
SN-21	10	60 V	95-120 V	no	withstood full voltage
SN-22	20	no	90 V	no	withstood full voltage
SN-23	10	no	95 V	yes (120 V)	
SN-24	20	no	105 V	no	withstood full voltage
As-received yarn	-	20 V	25 V	45-50 V	

Table 12

Ultimate Tensile Strength and Modulus Results from Tests on Indivudial CVD Si_3N_4 Coated HMS Graphite Filaments

Run Number	Deposition Temp K	SiF_4 ℓ/min	NH_3 ℓ/min	Mole Ratio NH_3/SiF_4	Ultimate Tensile Strength MPa	ksi	Modulus GPa	(10^6 psi)
S-44	1723	0.0196	0.1657	8.45	1989	(289)	295	(43)
S-43	1623	0.0196	0.1657	8.45	1638	(238)	274	(40)
S-42	1523	0.0196	0.1657	8.45	1950	(283)	288	(42)
S-34	1723	0.0196	0.1179	6.01	1852	(269)	256	(37)
S-31	1623	0.0196	0.1179	6.01	2032	(295)	358	(52)
S-35	1523	0.0196	0.1179	6.01	2223	(323)	311	(45)
S-36	1723	0.0196	0.0727	3.72	1813	(263)	311	(45)
S-37	1623	0.0196	0.0727	3.72	2203	(320)	325	(47)
S-38	1523	0.0196	0.0727	3.72	1882	(273)	318	(46)
S-41	1723	0.0196	0.0379	1.93	1872	(272)	287	(42)
S-40	1623	0.0196	0.0379	1.93	1882	(273)	366	(53)
S-39	1523	0.0196	0.0379	1.93	2252	(327)	378	(55)
As Received HMS Yarn					2284	(311)	319	(46)

Deposition time 20 min

Table 13

Static Experiments CVD Si_3N_4 Coated HMS Yarn

Run Number	Reactor Temp. K	SiF_4 ℓ/min	NH_3 ℓ/min	Mole Ratio NH_3/SiF_4	Time min.
SN 85	1723	0.0196	.1657	8.45	5
SN 88	1723	0.0196	.1657	8.45	10
SN 78	1723	0.0196	.1657	8.45	30
SN 84	1723	0.0196	.1179	6.01	5
SN 87	1723	0.0196	.1179	6.01	10
SN 72	1723	0.0196	.1179	6.01	30
SN 83	1723	0.0196	.0727	3.71	5
SN 86	1723	0.0196	.0727	3.71	10
SN 80	1723	0.0196	.0727	3.71	30

Table 14

Ultimate Tensile Strength and Modulus Results from Tests on Individual CVD Si_3N_4 Coated HMS Graphite Yarn

Run Number	Mole Ratio NH_3/SiF_4	Deposition Time	Ultimate Tensile Strength		Modulus	
		min	MPa	(ksi)	GPa	(10^6psi)
SN 94	3.71	1	2219	(307)	321	(46.7)
SN 93	3.71	3	2458	(357)	323	(46.8)
SN 92	3.71	5	2009	(292)	324	(47.1)
SN 97	6.01	1	1539	(223)	308	(44.7)
SN 96	6.01	3	1839	(267)	275	(39.9)
SN 95	6.01	5	not tested		-	-
SN 100	8.45	1	2428	(352)	286	(41.5)
SN 99	8.45	3	1649	(239)	324	(36.8)
SN 98	8.45	5	2129	(309)	287	(42)
As Received HMS graphite yarn	-	-	2164	(314)	287	(42)

Table 15

Experimental Conditions
CVD Si_3N_4 Coated Celion 6000 Yarn

Run Number	Reactor Temp. K	SiF_4 ℓ/min	NH_3 ℓ/min	Mole Ratio NH_3/SiF_4	Time min
SN 103	1723	.0196	.0727	3.71	5
SN 106	1723	.0196	.0727	3.71	10
SN 105	1723	.0196	.0727	3.71	30
SN 102	1723	.0196	.1179	6.01	5
SN 108	1723	.0196	.1179	6.01	10
SN 107	1723	.0196	.1179	6.01	30
SN 101	1723	.0196	.1657	8.45	5
SN 110	1723	.0196	.1657	8.45	10
SN 109	1723	.0196	.1657	8.45	30

Table 16

Ultimate Tensile Strength and Modulus Results from Tests on Individual CVD Si_3N_4 Coated Celion 6000 Yarn
Deposition Temperature 1723 K

Run Number	Mole Ratio NH_3/SiF_4	Deposition Time min	Ultimate Tensile Strength MPa	(ksi)	Modulus GPa	(10^6psi)
SN 113	3.71	1	1475	(214)	152	(22.0)
SN 114	3.71	3	1889	(274)	186	(27.2)
SN 115	3.71	5	not tested			
SN 116	6.01	1	1868	(271)	186	(27.0)
SN 117	6.01	3	1875	(272)	216	(31.4)
SN 118	6.01	5	2020	(293)	176	(25.5)
SN 119	8.45	1	1779	(258)	170	(24.6)
SN 120	8.45	3	1496	(217)	214	(31.0)
SN 121	8.45	5	not tested			
As Received Celion 6000	-	-	2477	(359)	173	(25.1)

Table 17

CVD BN Coating Runs on HMS Graphite Yarn
BF_3/NH_3 Ratio of 0.229

Run Number	Graphite Yarn	Number of Tows	Deposition Temperature K	Time min
BN 1	HMS	2	1873	30
BN 2	↓	↓	↓	20
BN 3				15
BN 4				10
BN 5				30
BN 6				5
BN 7				180
BN 8			↓	30
BN 9			1848	↓
BN 10			1823	
BN 11			1798	
BN 12			1773	
BN 13	↓	↓	1748	↓

Table 18

CVD BN Coating Runs
Celion 6000 Graphite Yarn
Deposition Temperature 1873 K
BF_3/NH_3 Ratio of 0.229

Run Number	Number of Tows	Time min
BN 14	2	5
BN 15	2	10
BN 16	2	15
BN 17	2	30
BN 18	2	45
BN 19	2	1
BN 20	2	1
BN 21	2	3
BN 22	2	3
BN 23	8	10

Table 19

Ultimate Tensile Strength and Modulus Results from Tests on Individual Filaments from CVD BN Coated Celion 6000 Graphite Yarn

Fiber Condition	Time of Deposition	Ultimate Tensile Strength		Modulus	
		MPa	(ksi)	GPa	(10^6 psi)
CVD BN coated BN-19	1 min	1186	(172)	163	(23.6)
CVD BN coated BN-16	10 min	834	(121)	130	(18.8)

Table 20

Flexural Properties of UTRC 89-Z Epoxy Resin[1]

Flexural Properties[2]

Specimen No.	Strength		Modulus	
	MPa	(ksi)	GPa	(10^6 psi)
1	81.7	(11.8)	3.15	(0.46)
2	109	(15.8)	3.05	(0.44)
3	96.2	(14.0)	3.18	(0.46)
4	95.6	(13.9)	3.52	(0.51)
5	76.5	(11.1)	3.59	(0.52)

[1] Cure cycle: 2 hrs @ 398 K + 2 hrs @ 423 K + 2 hrs @ 448 K
[2] Four point flex, span-to-depth ratio 20/1

Table 21

Short Beam Shear Test Results of Composites with HTS Graphite Yarn

Specimen Number	Fiber Condition	Shear Strength MPa	Shear Strength (ksi)
212-6	untreated	40.3	(5.95)
		36.7	(5.31)
		41.9	(6.07)
		39.6	(5.75)
212-7	CVD SiC	73.8	(10.7)
		79.4	(11.5)
		74.9	(10.9)
		76.0	(11.0)
212-8	CVD SiC In-Line Oxidation	99.4	(14.4)
		103	(14.9)
		101	(14.6)
		101	(14.6)

Table 22

Composite Test Results
Untreated HMS Graphite Yarn

Specimen Number	Resin		Flexural Strength		Modulus		Shear Strength	
			MPa	(ksi)	GPa	(10^6psi)	MPa	(ksi)
T 51	286		1129	(164)	185	(26.8)	66.7	(9.68)
			1142	(166)	168	(24.4)	44.2	(6.42)
			1174	(170)	187	(27.1)	66.9	(9.70)
		Avg	1151	(167)	180	(26.1)	59.3	(8.60
T 52	286		1158	(168)	190	(27.5)	66.5	(9.64)
			1236	(179)	197	(28.5)	68.8	(9.98)
			1229	(178)	193	(27.9)	67.5	(9.79)
		Avg	1206	(175)	193	(28.0)	67.6	(9.80)
T 54	286		1285	(186)	194	(28.1)	80.5	(11.7)
			1063	(154)	199	(28.8)	82.5	(12.0)
			1319	(191)	196	(28.4)	80.0	(11.6)
		Avg	1220	(177)	196	(28.4)	81.3	(11.8)
T 55	286		1271	(184)	205	(29.8)	75.2	(10.9)
			1218	(177)	204	(29.6)	76.1	(11.0)
			1271	(184)	202	(29.2)	75.0	(10.9)
		Avg	1255	(182)	203	(29.5)	75.1	(10.9)
T 56	288		1136	(165)	166	(24.1)	62.0	(9.0)
			1094	(159)	166	(24.1)	74.8	(10.8)
			1153	(167)	164	(23.7)	73.9	(10.7)
		Avg	1131	(164)	165	(24.0)	70.3	(10.2)
T 58	288		1285	(186)	193	(27.9)	74.3	(10.8)
			1383	(201)	193	(28.0)	76.1	(11.0)
			1201	(174)	187	(27.1)	79.0	(11.5)
		Avg	1289	(187)	191	(27.7)	76.5	(11.1)
T 59	288		1394	(202)	191	27.7	81.9	(11.9)
			1313	(190)	197	28.6	81.4	(11.8)
			1365	(198)	193	28.0	79.8	(11.6)
		Avg	1358	(197)	194	(28.1)	81.3	(11.8)
Hercules Values HMS/250°F epoxy			1165	(169)	182	(26.4)	68.9	(10.0)

Table 23

Composite Test Results
Untreated HMS Graphite Yarn in
UTRC 89-Z Resin

Specimen Number		Flexural Strength		Modulus		Shear Strength	
		MPa	(ksi)	GPa	(10^6 psi)	MPa	(ksi)
CCVD-6		747	(108)	165	(24.0)	45.6	(6.61)
		807	(117)	173	(25.2)	44.7	(6.48)
		713	(103)	172	(24.9)	44.5	(6.45)
	Avg	751	(109)	170	(24.7)	44.9	(6.51)
CCVD-7		478	(69.4)	177	(25.6)	36.7	(5.32)
		677	(98.1)	178	(25.8)	44.6	(6.46)
		772	(112)	171	(24.8)	39.2	(5.69)
	Avg	641	(93)	175	(25.4)	40.1	(5.82)
T 97		783	(114)	204	(29.6)	42.2	(6.12)
		631	(91.5)	192	(27.9)	40.6	(5.88)
		1201	(174)	20.9	(30.4)	41.7	(6.04)
						43.0	(6.24)
	Avg	875	(127)	202	(29.3)	41.8	(6.07)

Table 24

Composite Test Results
CVD SiC Coated and Oxidized HMS Graphite Yarn

Specimen Number	Resin		Flexural Strength		Modulus		Shear Strength	
			MPa	(ksi)	GPa	(10^6 psi)	MPa	(ksi)
CCVD-9	UTRC		749	(109)	158	(22.9)	52.9	(7.67)
	89-Z		1001	(145)	159	(23.1)	51.6	(7.48)
			725	(105)	155	(22.5)	47.0	(6.82)
		Avg	827	(120)	157	(22.8)	50.5	(7.32)
CCVD-10	UTRC		872	(126)	195	(28.2)	80.1	(11.6)
	89-Z		864	(125)	185	(26.8)	80.7	(11.7)
			991	(144)	182	(26.4)	65.1	(9.45)
		Avg	910	(132)	187	(27.1)	75.1	(10.9)

Table 25

Composite Test Results
Untreated Celion 6000 Yarn

Specimen Number	Resin		Flexural Strength MPa	(ksi)	Modulus GPa	(10^6 psi)	Shear Strength MPa	(ksi)
T 62A	288		1981	(287)	133	(19.3)	92.5	(13.8)
			1888	(274)	129	(18.8)	88.3	(12.8)
			1970	(286)	134	(19.4)	92.7	(13.4)
		Avg	1944	(282)	132	(19.2)	91.7	(13.3)
T 62B	288		1918	(278)	131	(19.0)	94.0	(13.6)
			1913	(278)	135	(19.6)	94.2	(13.7)
			1864	(271)	128	(18.6)	93.8	(13.6)
		Avg	1903	(276)	132	(19.1)	93.8	(13.6)
T 69	288		1708	(248)	134	(19.5)	98.6	(14.3)
			1779	(258)	130	(18.7)	100.6	(14.6)
			1627	(236)	134	(19.4)	100.6	(14.6)
		Avg	1703	(247)	132	(19.2)	100.0	(14.5)
T 63	UTRC 89-Z		1417	(205)	148	(21.5)	32.5	(4.72)
			1470	(213)	150	(21.7)	34.2	(4.97)
			1705	(247)	149	(21.6)	39.2	(5.69)
		Avg	1530	(222)	149	(21.6)	35.4	(5.13)
T 64	UTRC 89-Z		2118	(307)	149	(21.6)	42.2	(6.12)
			1917	(278)	151	(21.9)	48.5	(7.03)
			2167	(314)	149	(21.6)	44.6	(6.47)
		Avg	2068	(300)	150	(21.7)	45.1	(6.54)
T 80	UTRC 89-Z		1440	(209)	N.A.		47.1	(6.83)
			1290	(187)			52.8	(7.66)
			1222	(177)			60.2	(8.72)
		Avg	1317	(191)			53.4	(7.74)

Table 26

Composite Test Results
CVD SiC Coated and Oxidized
Celion 6000 Graphite Yarn

Specimen Number	Resin		Flexural Strength MPa	(ksi)	Modulus GPa	(10^6psi)	Shear Strength MPa	(ksi)
T-67A	UTRC		752	(109)	135	(19.6)	59.9	(8.69)
	89-Z		1193	(173)	138	(20.1)	50.3	(7.29)
			731	(106)	124	(18.0)	58.7	(8.52)
		Avg	889	(129)	132	(19.2)	56.2	(8.15)
T-67B	UTRC		786	(114)	139	(20.2)	41.7	(6.05)
	89-Z		745	(108)	136	(19.7)	43.2	(6.26)
			958	(139)	125	(18.2)	43.4	(6.30)
		Avg	827	(120)	132	(19.2)	42.4	(6.15)
T-70	UTRC		696	(101)	134	(19.4)	102.7	(11.9)
	89-Z		814	(118)	139	(20.2)	104.1	(15.1)
			958	(139)	143	(20.7)	110.0	(16.0)
		Avg	820	(119)	139	(20.1)	105.5	(15.3)
T-71	UTRC		731	(106)	137	(19.8)	60.5	(8.77)
	89-Z		924	(134)	130	(78.9)	55.5	(8.05)
			931	(135)	138	(20.0)	56.0	(8.13)
		Avg	862	(125)	135	(19.6)	56.7	(8.23)
T-72	UTRC		758	(110)	121	(17.5)	46.7	(6.78)
	89-Z		696	(101)	125	(18.1)	45.9	(6.66)
			848	(123)	125	(18.1)	54.0	(7.83)
		Avg	765	(111)	124	(17.9)	48.9	(7.09)

Table 27

Composite Test Results
T-300 Graphite Yarn

Specimen Number	Fiber Treatment	Resin		Flexural Strength MPa	Flexural Strength (ksi)	Modulus GPa	Modulus (10^6psi)	Shear Strength MPa	Shear Strength (ksi)
T 73	none	UTRC 89-Z		1303	(187)	132	(19.1)	41.2	(5.98)
				1338	(194)	130	(18.9)	29.4	(4.26)
				1351	(196)	132	(19.2)	29.3	(7.15)
			Avg	1324	(192)	132	(19.1)	40.0	(5.18)
T 77	none	UTRC 89-Z		1606	(233)	139	(20.1)	49.3	(7.15)
				1462	(212)	139	(20.2)	48.1	(6.98)
				1393	(202)	146	(21.1)	52.9	(7.67)
			Avg	1489	(216)	142	(20.5)	50.1	(7.27)
T 78	none	UTRC 89-Z		1376	(200)	143	(19.3)	93	(13.5)
				1913	(278)	144	(20.8)	98	(14.2)
				1672	(242)	138	(20.1)	62	(9.03)
			Avg	1654	(240)	142	(20.0)	84	(12.2)
T 84	CVD SiC/O_2	UTRC 89-Z		813	(118)	119	(17.3)	97.9	(14.2)
				603	(87.5)	113	(16.4)	81.3	(11.8)
				758	(110)	121	(17.6)	95.1	(13.8)
			Avg	724	(105)	118	(17.1)	91.7	(13.3)
T 85	CVD SiC/O_2	UTRC 89-Z		718	(104)	124	(18.0)	63.5	(9.20)
				541	(78.5)	115	(16.7)	66.2	(9.60)
				605	(87.8)	120	(17.4)	65.6	(9.52)
								66.4	(9.64)
			Avg	621	(90.1)	120	(17.4)	65.4	(9.49)

Table 28

Composite Test Results
Celion 12000 Graphite Yarn

Specimen Number	Fiber Treatment	Resin		Flexural Strength MPa	(ksi)	Modulus GPa	(10^6psi)	Shear Strength MPa	(ksi)
T 91*	none	PR-288		N.A.*		N.A.*		106	(15.4)
								111	(16.1)
								112	(16.2)
								111	(16.1)
			Avg					110	(16.0)
T 95*	none	UTRC 89-Z		N.A.*		N.A.*		107	(15.5)
								98.6	(14.3)
								107	(15.5)
								98.5	(14.3)
			Avg					103	(14.9)
T 93	CVD SiC/O_2	PR-288		1317	(191)	115	(16.7)	105	(15.2)
				1425	(207)	116	(16.9)	104	(15.0)
				1122	(163)	117	(17.0)	107	(15.6)
			Avg	1288	(187)	116	(16.9)	105	(15.3)
T 94	CVD SiC/O_2	UTRC 89-Z		1065	(154)	136	(19.8)	75.1	(10.9)
				1065	(154)	133	(19.2)	74.3	(10.8)
				1297	(188)	136	(19.2)	69.4	(10.1)
			Avg	1142	(165)	134	(19.6)	73.1	(10.6)

*Specimens failed in compression

Table 29

Summation of Small Composite Test Results
with UTRC 89-Z Resin

Graphite Fiber	Untreated Graphite Yarn						CVD SiC/O_2 Graphite Yarn					
	Flex. Str.		Modulus		Shear Str.		Flex. Str.		Modulus		Shear Str.	
	MPa	(ksi)	GPa	(10^6psi)	MPa	(ksi)	MPa	(ksi)	GPa	(10^6psi)	MPa	(ksi)
HTS	-	-	-	-	39.6	(5.75)	-	-	-	-	101	(14.6)
HMS	756	(110)	182	(26.5)	42.3	(6.1)	867	(126)	172	(25.0)	62.8	(9.1)
Celion 6000	1638	(238)	150	(21.7)	44.8	(6.5)	833	(121)	132	(19.2)	62.1	(9.0)
T-300	1533	(222)	137	(19.9)	56.6	(8.2)	673	(97.6)	119	(17.3)	78.6	(11.4)
Celion 12000	*	*	*	*	103	(14.9)	1142	(165)	134	(19.6)	73.1	(10.6)

*Test specimens failed in compression

Table 30

Composites Delivered to NASA

Graphite Yarn	CVD SiC/O_2	Number of Panels	Size cm	Unidirectional Plies
HTS	no	3	7.6 x 7.6	16
HTS	SiC only	3	7.6 x 7.6	16
HTS	yes	3	7.6 x 7.6	16
HMS	no	3	7.6 x 7.6	16
HMS	yes	3	7.6 x 7.6	16
T-300	no	3	7.6 x 7.6	16
T-300	yes	3	7.6 x 7.6	16
Celion 6000	yes	3	7.6 x 7.6	16
Celion 12000	no	3	7.6 x 7.6	16
Celion 12000	yes	3	7.6 x 7.6	16

Table 31

CVD Si_3N_4 Coated HMS Graphite Yarn
in PR-288 Resin Matrix

Composite Number	Thickness			Flexural Strength		Modulus	
	cm	(in)		MPa	(ksi)	GPa	(10^6 psi)
T-88	.036	(.014)		713	(103)	77.1	(11.2)
				486	(70.4)	62.5	(9.1)
				775	(112)	137	(19.7)
			Avg	656	(95.1)	92.4	(13.4)
T-89	.056	(.022)		444	(64.3)	83.0	(12.0)
				484	(70.2)	86.2	(12.5)
				767	(111)	144	(21.0)
			Avg	564	(81.8)	105	(15.2)
T-90	.096	(.038)		670	(97.2)	119	(17.3)
				627	(90.9)	108	(15.7)
				604	(87.7)	109	(15.8)
			Avg	634	(91.9)	112	(16.3)

Table 32

Organo-Silicone Materials Selected for Evaluation

Methyltriethoxysilane (MTS)	$CH_3\text{-}Si(OC_2H_5)_3$
Vinyltriacetoxysilane (VTS)	$CH_2{=}CH\text{-}Si\text{-}(O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3)_3$
Silicone Resin GE (SR 355)	$-\overset{CH_3}{\overset{\|}{Si}}\text{-}O\text{-}\overset{CH_3}{\overset{\|}{Si}}\text{-}O-$ (with CH_3 below each Si)
Ethyl silicate prepolymer (ES) R&R Silicate Binder #18	$\left(-\overset{OC_2H_5}{\overset{\|}{Si}}\text{-}O-\right)_n$ (with OC_2H_5 below Si)

Table 33

Conclusions from Static Tests

	Oxidation Results	Resistance Results	SEM Observations	Tensile Results
MTS	Poor	Good	Good	-
VTS	Poor	Good	Poor	Good
SR 355	Good	Good	Fair	Good
ES	Good	Good	Good	Good

Table 34

Properties of Ethyl Silicate Coated
Celion 6000 Graphite Yarn

	Coating Conditions[1,2]			Yarn Properties			
Run No.	Wt % Ethyl Silicate Coating Solution	Steam Temp K	Pyrolysis Temp K	Electrical Resistance ohms[3]	Wt % Coating	Yarn Fracture Load[4,5] (lbs)	(N)
	"As-received"	-	-	4.0	none	143	636
SC-11	2.5	393	1093-1173	18	-	-	-
-12	2.5	none		15	-	-	-
-13	3.5	393		29	-	-	-
-14	5.0	393		27	-	-	-
-15	3.5	393		36	-	-	-
-16	5.0	393		180	-	-	-
-17	8.0	393		60	-	-	-
-18	10.0	393		40	-		-
-19	5.0	393		75	24.7	126	560
-20	5.0	393		95	35.5	105	467
SC-51	2.5	none	473	500	-	-	-
-48	2.5	393	473	2950	25.8	138	614
-50	2.5	none	673	180	19.3	140	623
-49	2.5	393	573	480	22.3	138	614
-54	3.5	none	473	190	20.4	123	547
-55	3.5	393	473	60	34.5	135	601
-53	3.5	none	573	120	21.0	135	601
-52	3.5	393	573	340	22.5	119	529

[1] pyrolysis done in N_2
[2] drawing rate 0.91 m/min
[3] 2.5 cm distance between electrodes
[4] 2.5 cm gage length
[5] average of six specimens

Table 35

Properties of Glass Resin 100 Coated Celion 6000 Graphite Yarn

	Coating Conditions[1,2]			Yarn Properties			
Run No.	Wt % Glass Resin 100 Coating Solution	Steam Temp K	Pyrolysis Temp K	Electrical Resistance ohms[3]	Wt % Coating	Yarn Fracture Loads[4,5] (lbs)	(N)
	"As-Received"	-	-	4.0	none	143	636
SC-41	3.8	none	673	800	25.9	140	623
SC-37	3.8	398	673	2900	20.4	133	592
SC-40	3.8	none	773	1100	24.4	139	618
SC-38	3.8	398	773	1700	22.7	144	641
SC-39	3.8	398	873	800	22.0	140	623
SC-36	3.8	398	573	1100	17.3	143	636
SC-35	3.8	398	573	230	-	-	-
SC-21	3.8	none	573	22	16.2	128	574
SC-22	3.8	398	573	1500	46.9	130	578
SC-23	3.8	none	473	30	23.9	121	538
SC-24	3.8	398	473	500	12.4	132	587

[1] pyrolysis done in N_2
[2] drawing rate 0.91 m/min
[3] 2.5 cm distance between electrodes
[4] 2.5 cm gage length
[5] average of six specimens

Table 36

Properties of Glass Resin 650 Coated Celion 6000 Graphite Yarn

	Coating Conditions[1,2]			Yarn Properties			
Run No.	Wt % Glass Resin 650 Coating Solution	Steam Temp K	Pyrolysis Temp K	Electrical Resistance ohms[3]	Wt % Coating	Yarn Fracture Load[4,5] (lbs)	(N)
-	"as-received"	-	-	4.0	-	143	636
SC-42	2.5	none	1173	100	17.7	135	601
SC-44	2.5	398	473	1250	30.2	140	623
SC-43	2.5	none	573	720	22.1	140	623
SC-46	2.5	398	773	370	22.5	147	654
SC-47	2.5	398	1173	6500	19.9	63.1	281

[1]pyrolysis done in N_2 atmosphere
[2]drawing rate 0.91 m/min
[3]2.5 cm distance between electrodes
[4]2.5 cm gage length
[5]average of six specimens

Table 37

Pyrolyzed tri-n-butyl Borate Coated Celion 6000 Graphite Fibers Produced by the Modified Continuous Coating Apparatus

Run No.	Conc. tri-n-butyl Borate wt %	Drawing Rate m/min	Steam Temp K	Pyrolysis Temp in N_2 K	Electrical Resistance[1] ohms
SC-25	2.5	0.91	398	973	6.8
SC-26	2.5	0.91	398	473	5.7
SC-27	2.5	0.91	398	873	6.7
SC-28	2.5	0.91	398	573	5.9
SC-29	2.5	0.91	398	473	5.6
SC-30	2.5	0.91	398	973	3.9
SC-31	5.0	0.91	398	973	6.8
SC-32	10	0.91	398	973	5.4
SC-33	20	0.91	398	973	5.1
SC-34	20	0.15	398	973	7.5

[1] The resistance of a specimen 7.6 cm long, with a 2.54 cm section free between the copper block electrodes

Table 38

Mechanical Properties of Composites Containing Silica-Like Coated Celion 6000 Graphite Fibers in Epoxy Matrix

Composite No.	Coating Material	Shear Strength[1]		Flexural Properties[2] Strength		Modulus	
		MPa	(ksi)	MPa	(ksi)	GPa	(10^6 psi)
CSC-39	Glass Resin 100	40.3	(5.85)	261	(37.9)	65.3	(9.47)
		38.3	(5.55)	305	(44.3)	66.7	(9.68)
		41.3	(5.99)	355	(51.4)	77.7	(11.3)
CSC-43	Glass Resin 650	35.7	(5.18)	262	(38.1)	88.6	(12.9)
		35.7	(5.18)	288	(41.8)	80.3	(11.6)
		35.1	(5.09)	279	(40.5)	84.6	(12.3)
CSC-48	Ethyl Silicate	35.7	(5.18)	372	(54.0)	70.7	(10.2)
		33.3	(4.83)	374	(54.3)	73.6	(10.7)
		45.4	(6.59)	374	(54.3)	74.6	(10.8)

[1] S/D = 4/1

[2] Four point flexure test at a span-to-depth ratio of 20/1

Table 39

Optimum Conditions for Organo-Silicone Coating of Celion 6000 Graphite Fibers

Run No.	Coating Material	Wt % Coating Solution	Steam Temp K	Pyrolysis Temp, K	Electrical Resistance ohms	Yarn Fracture Loads lbs	N
	"as received"	none	-	-	4.0	143	636
SC-48	Ethyl Silicate	2.5	398	573	2950	138	614
SC-38	Glass Resin 100	3.8	398	573	1700	144	641
SC-43	Glass Resin 650	2.5	none	573	720	140	623

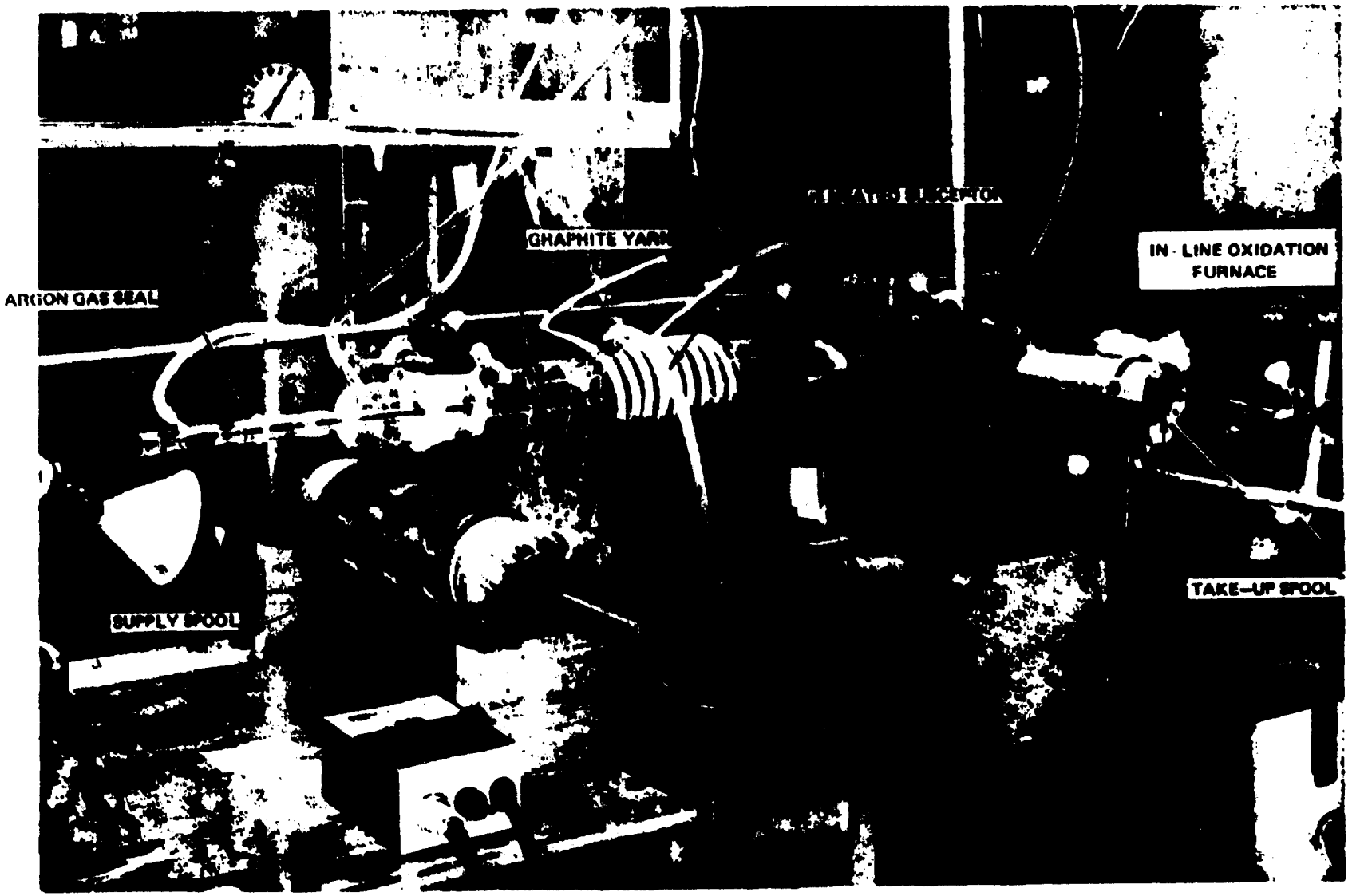


Fig. 1 Continuous Deposition CVD SiC Apparatus

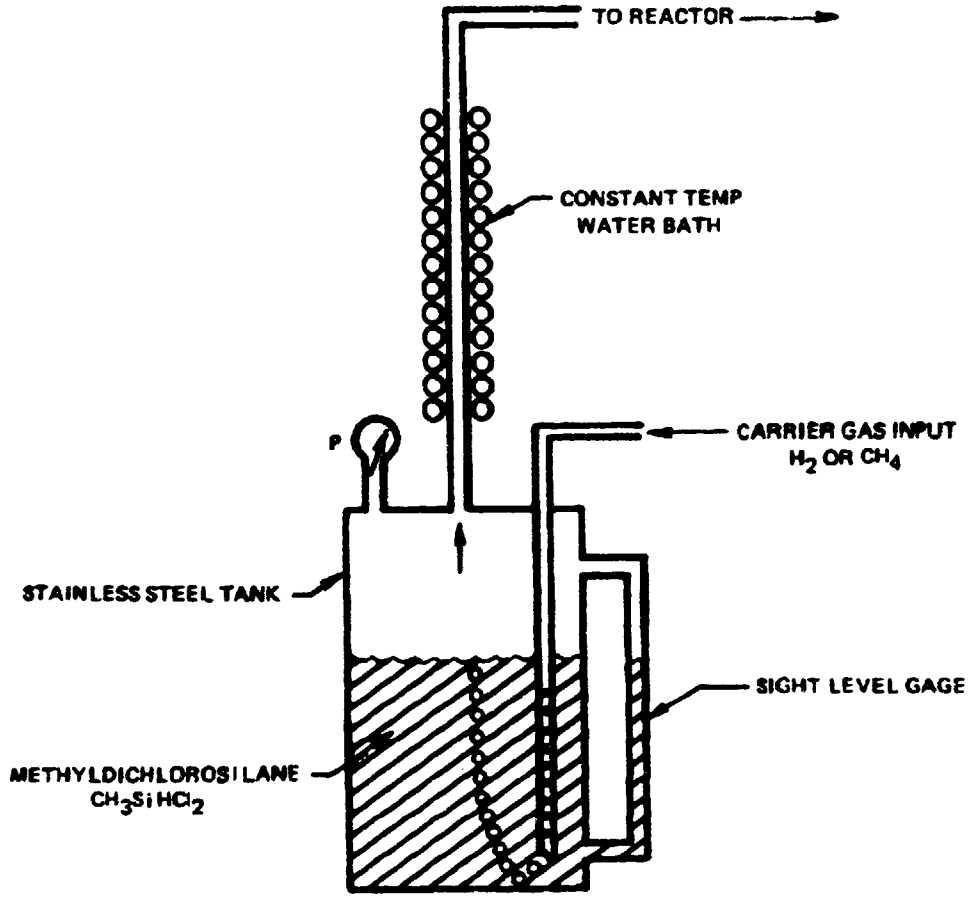


Fig. 2 Silane Evaporator

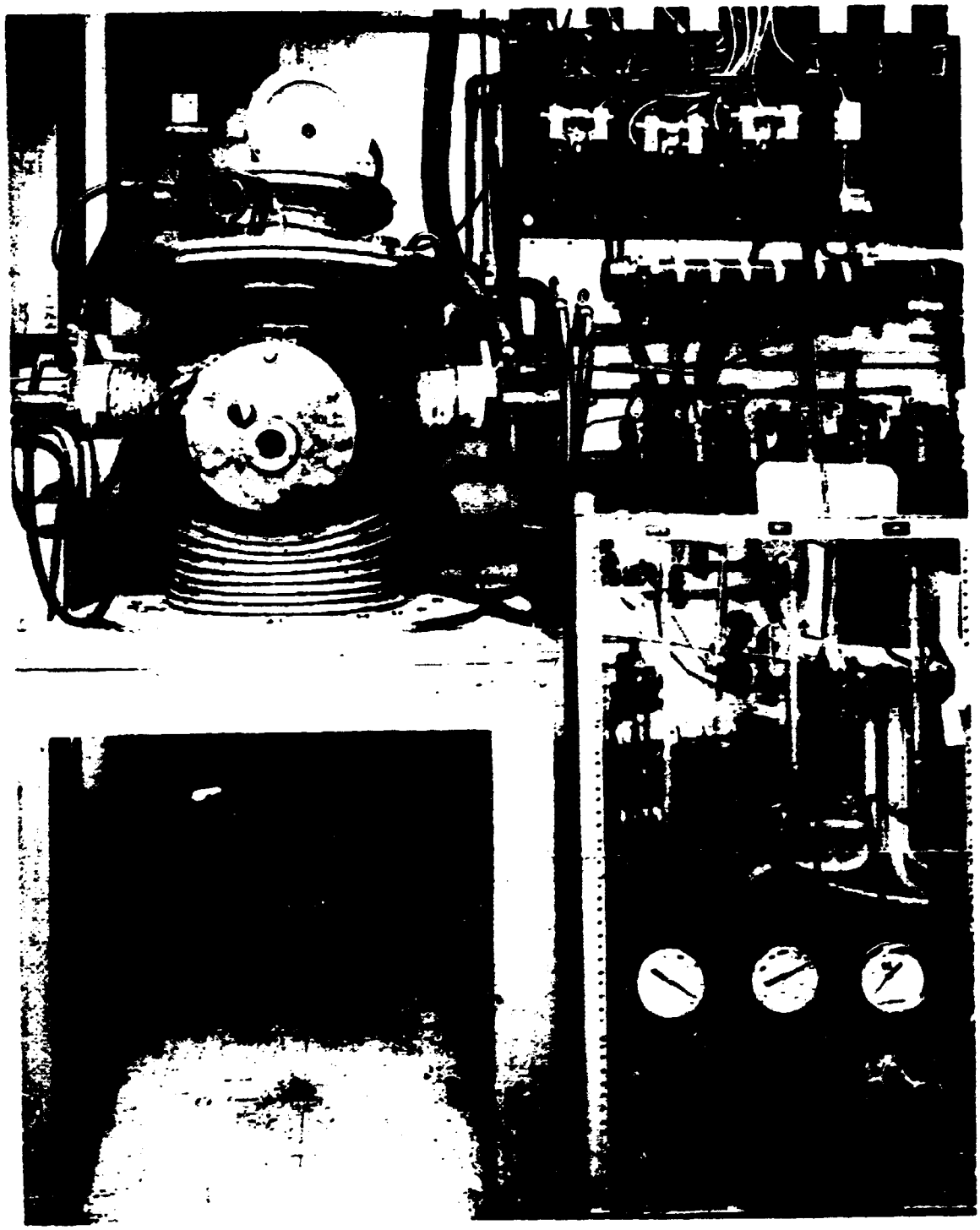


Fig. 3 Graphite Resistance Furnace Used for CVD Si_3N_4

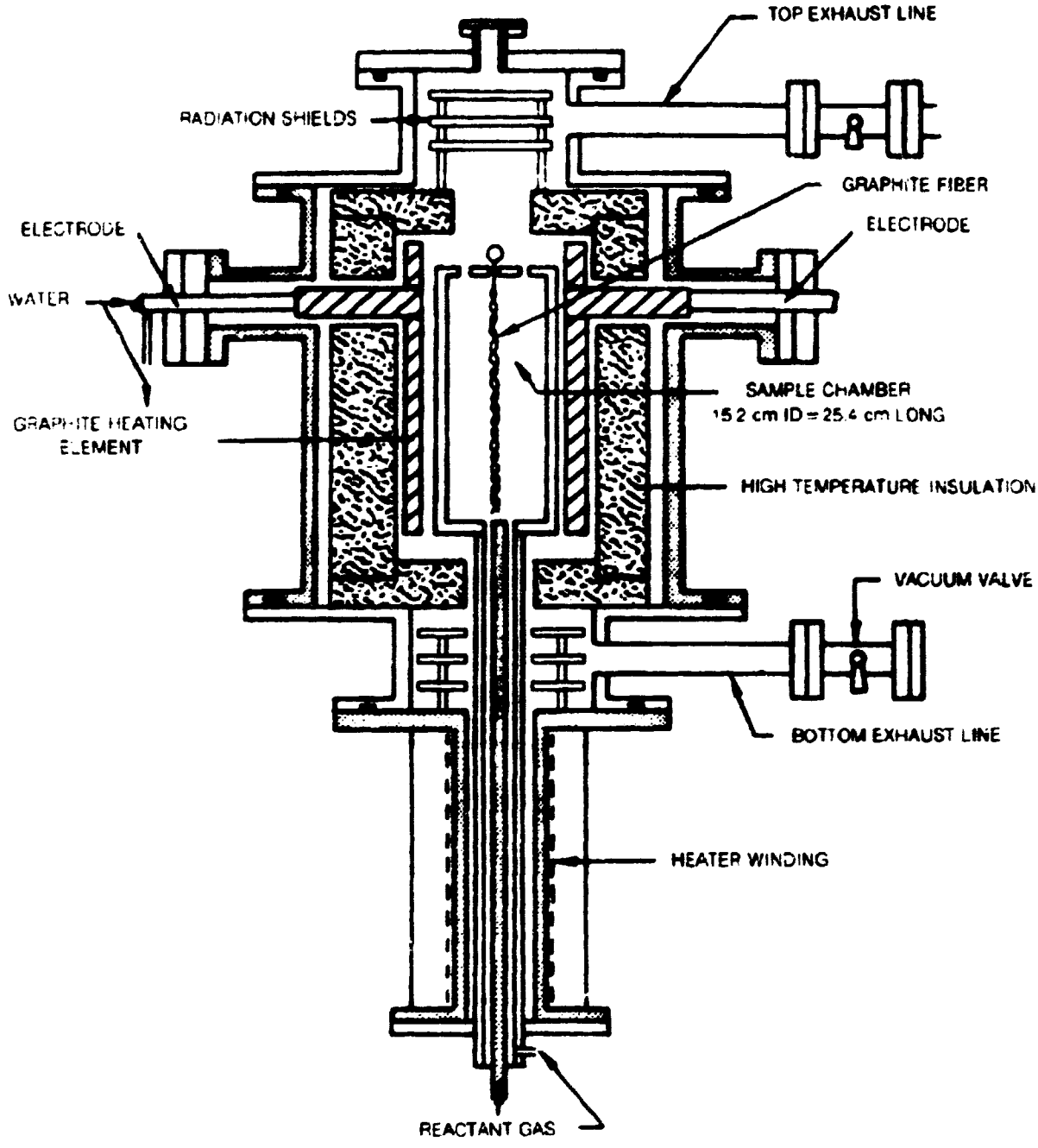


Fig. 4 Schematic of Deposition Furnace

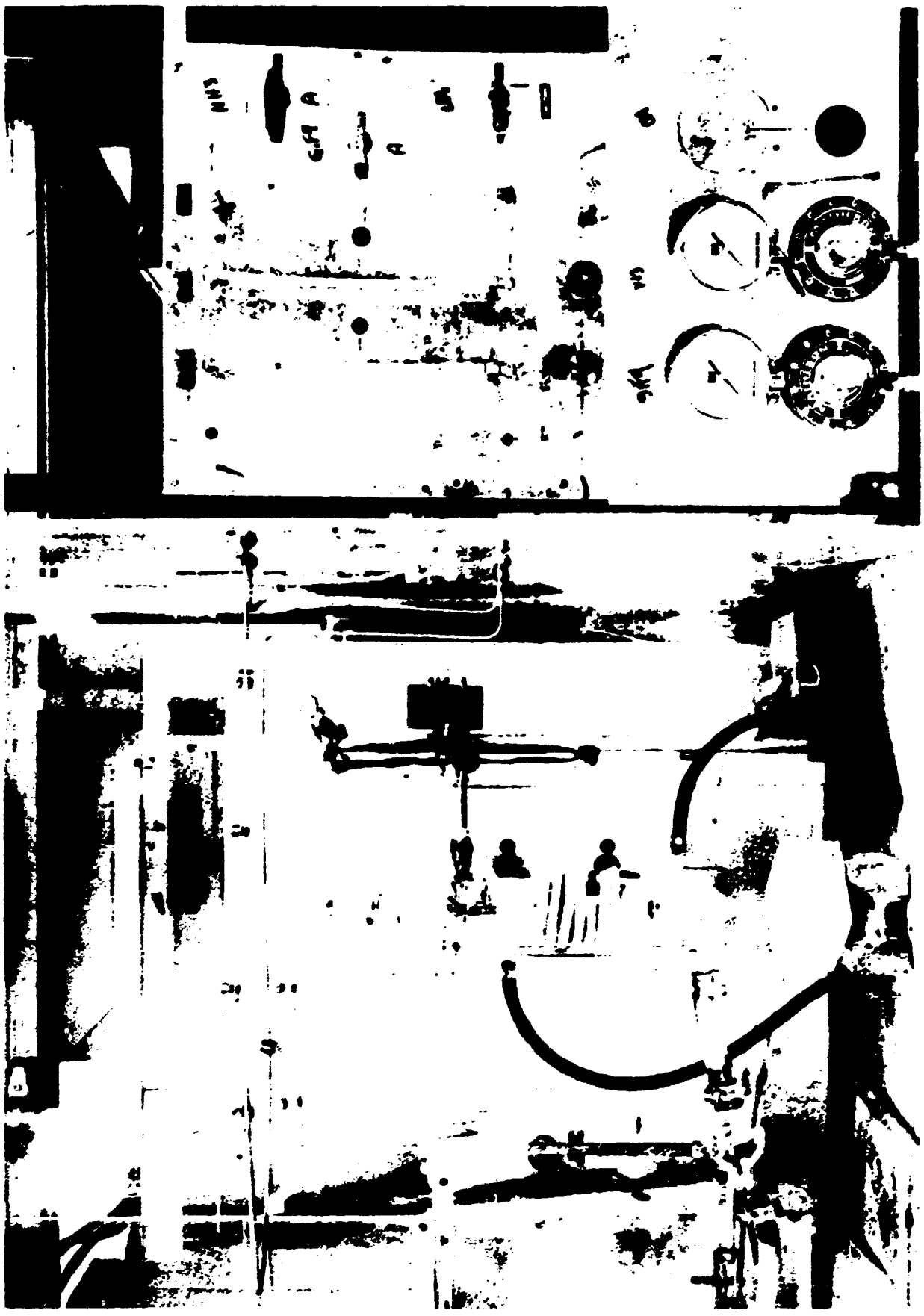


Fig. 6 Induction Unit CVD Si_3N_4 Apparatus

79-263-8 80-4-119-2

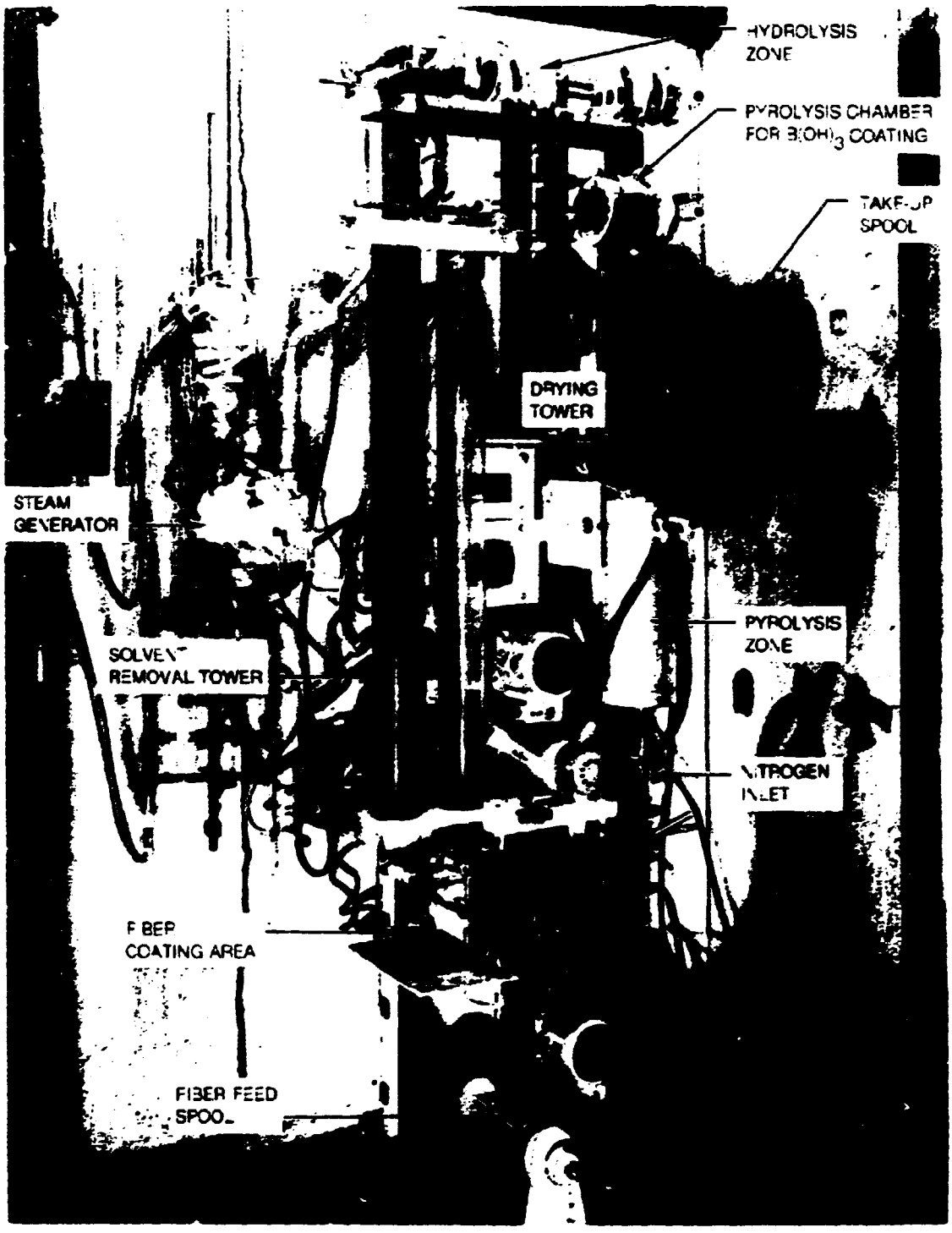


Fig. 6 Modified Continuous Fiber Coating Apparatus

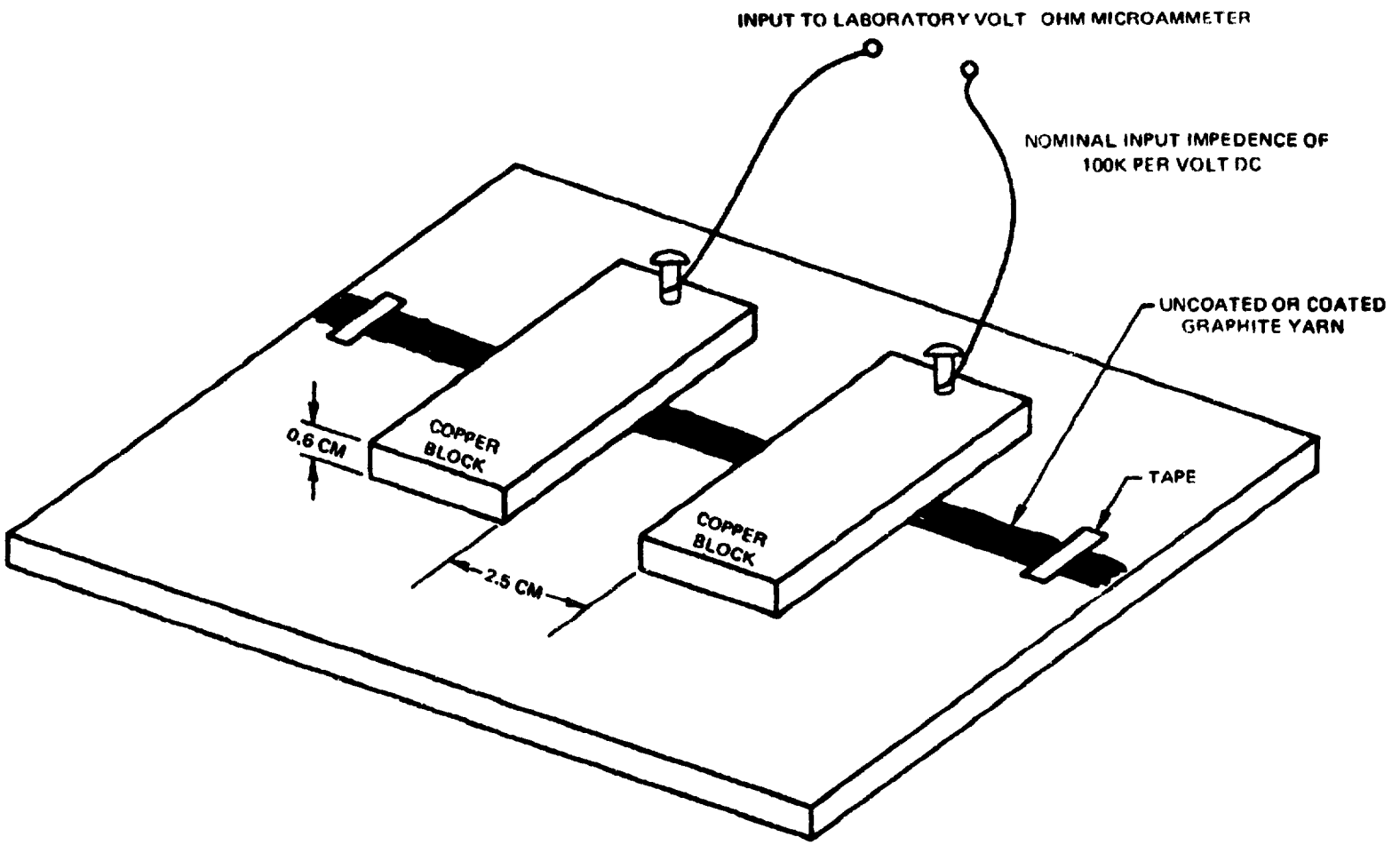


Fig. 7 Copper Block Resistance Measurement Technique

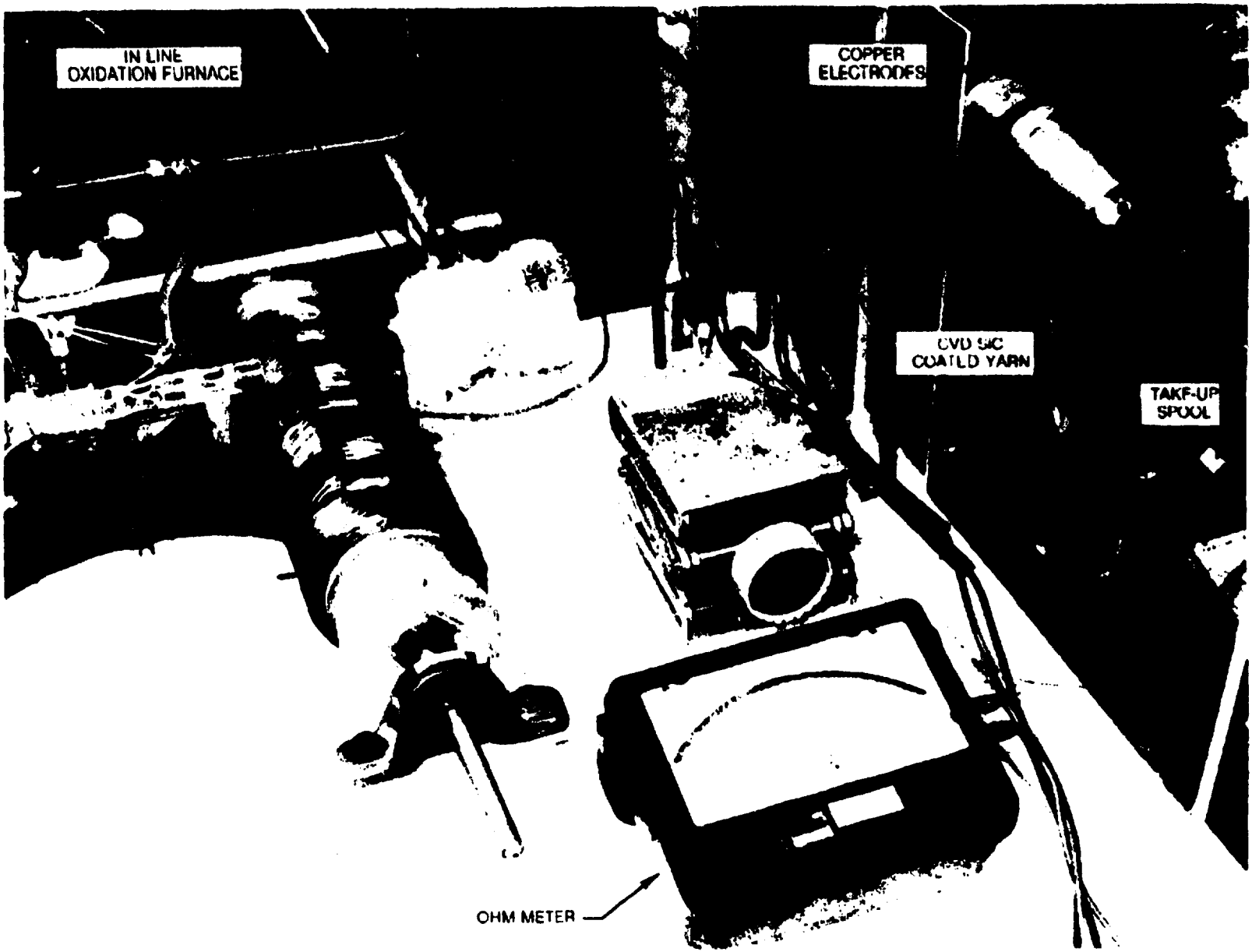


Fig. 8 Continuous Electrical Resistance Measurement Set-Up

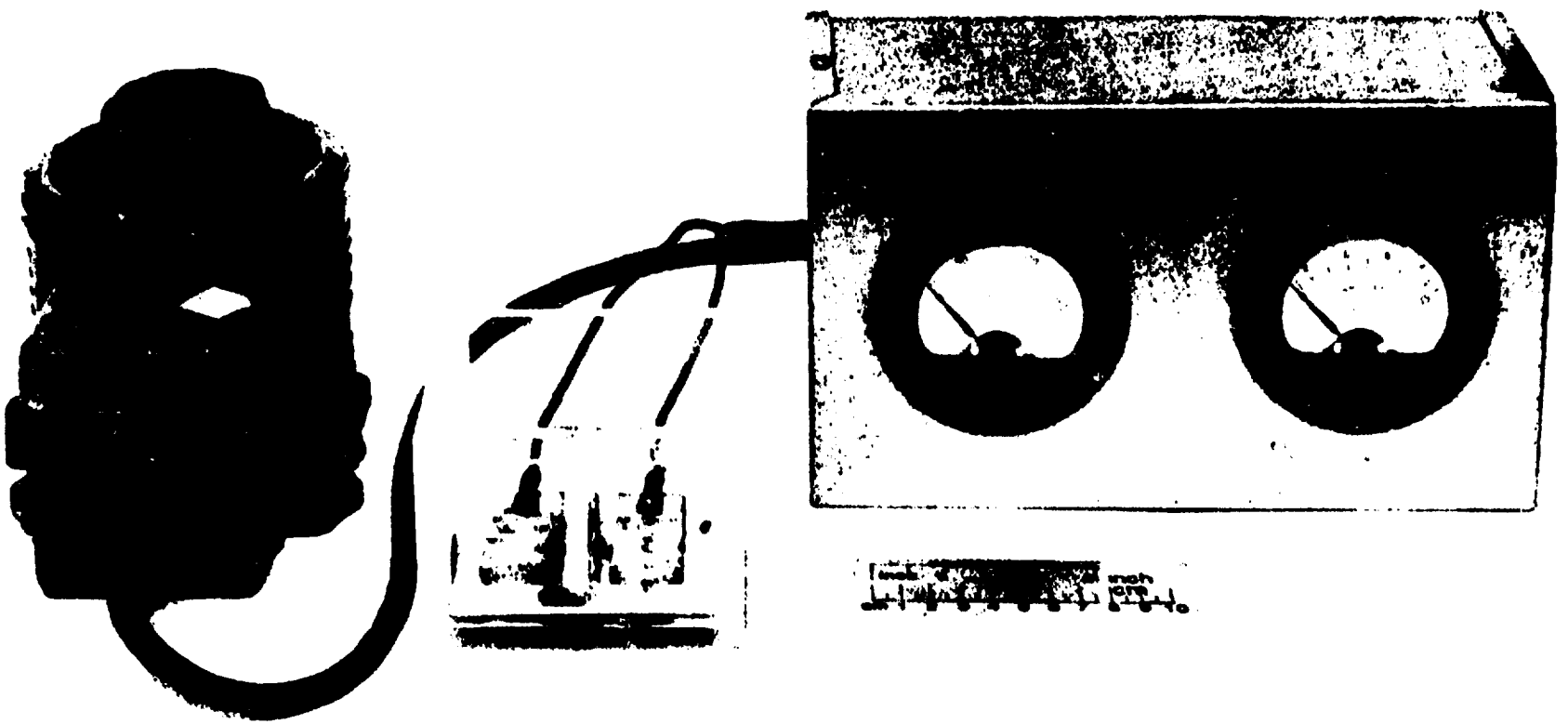


Fig. 9 Experimental Set-Up for Arcing Test

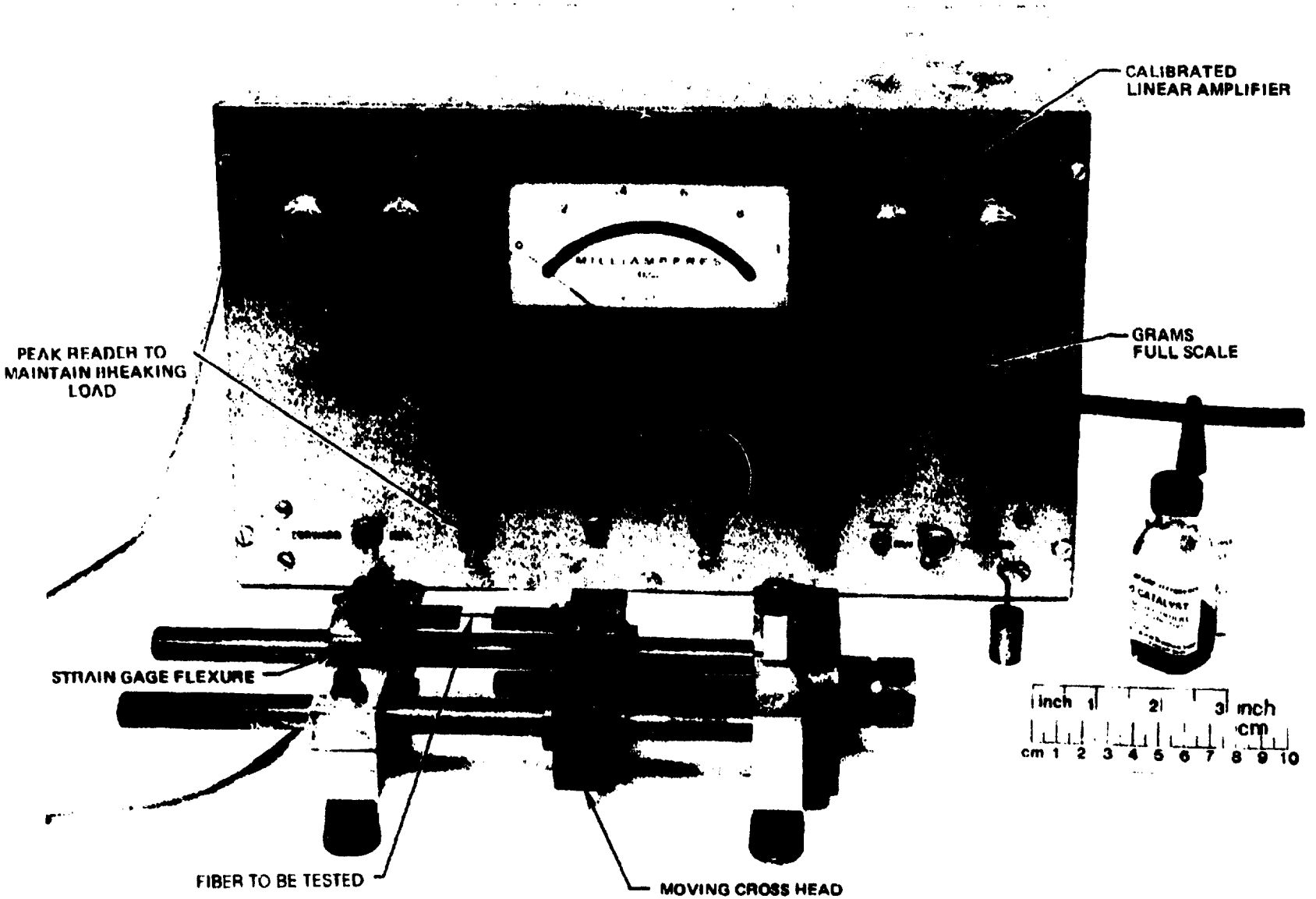
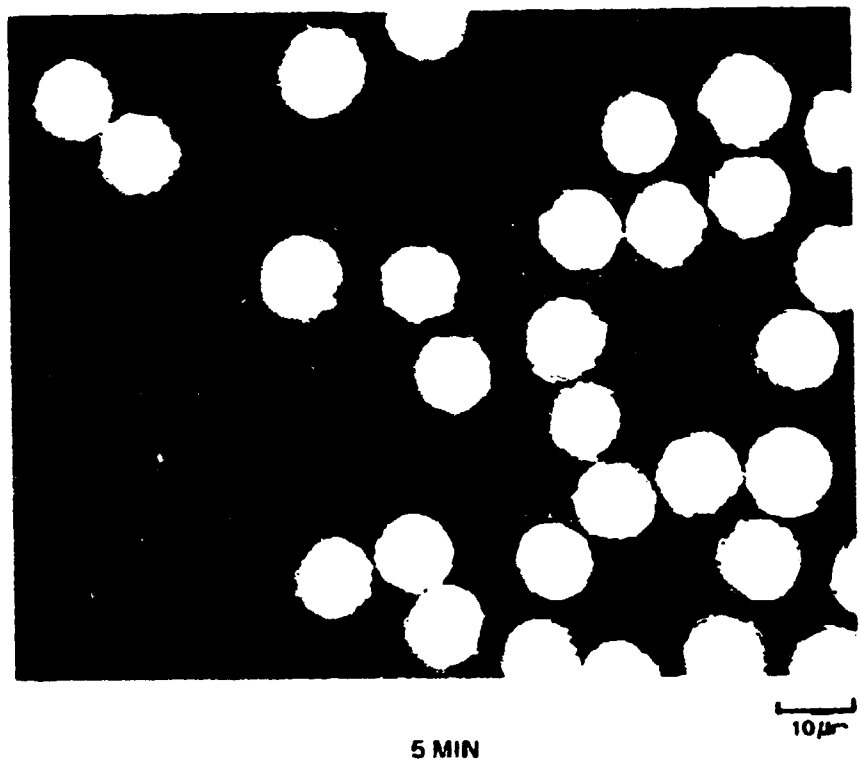


Fig. 10 Single Filament Tensile Tester

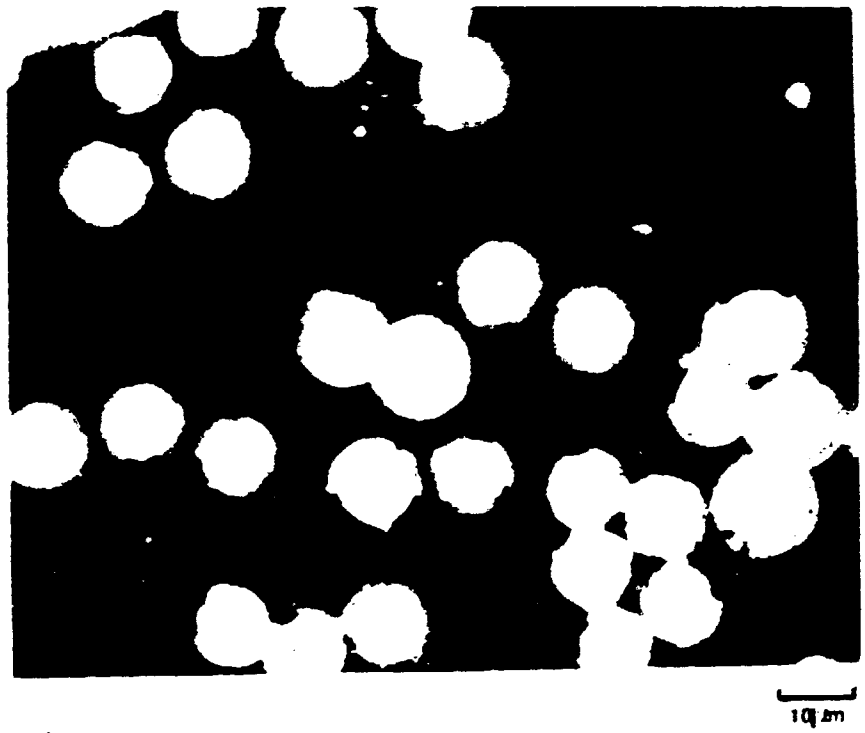
79-05-48-1

GRAPHITE YARN	IN LINE OXIDATION TEMPERATURE																	
	NONE						773 K						873 K					
	DWG. RATE cm/min						DWG. RATE cm/min						DWG. RATE cm/min					
	7.5	15	30	60	90	122	7.5	15	30	60	90	122	7.5	15	30	60	90	122
CELION 6000		✔	✔	✔	✔	✔		✔	✔	✔	✔	✔			✔	✔	✔	✔
T-300			✔	✔	✔	✔			✔	✔	✔	✔			✔	✔	✔	✔
HMS		✔	✔	✔	✔	✔		✔	✔	✔	✔	✔		✔	✔	✔	✔	✔
CELION 12000			✔						✔						✔			

Fig. 11 Experimental Conditions for CVD SiC Coating Runs to Obtain Electrical Resistance Data



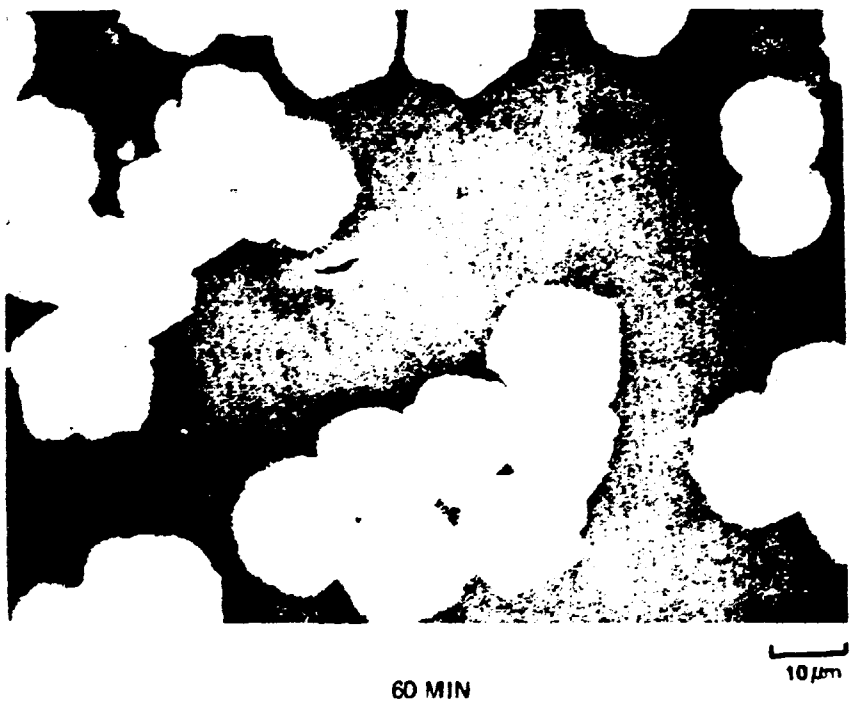
5 MIN



30 MIN

Fig. 12 CVD Silicon Nitride Coated HTS Graphite Fiber

45 MIN



60 MIN

Fig. 13 CVD Silicon Nitride Coated HTS Graphite Fiber

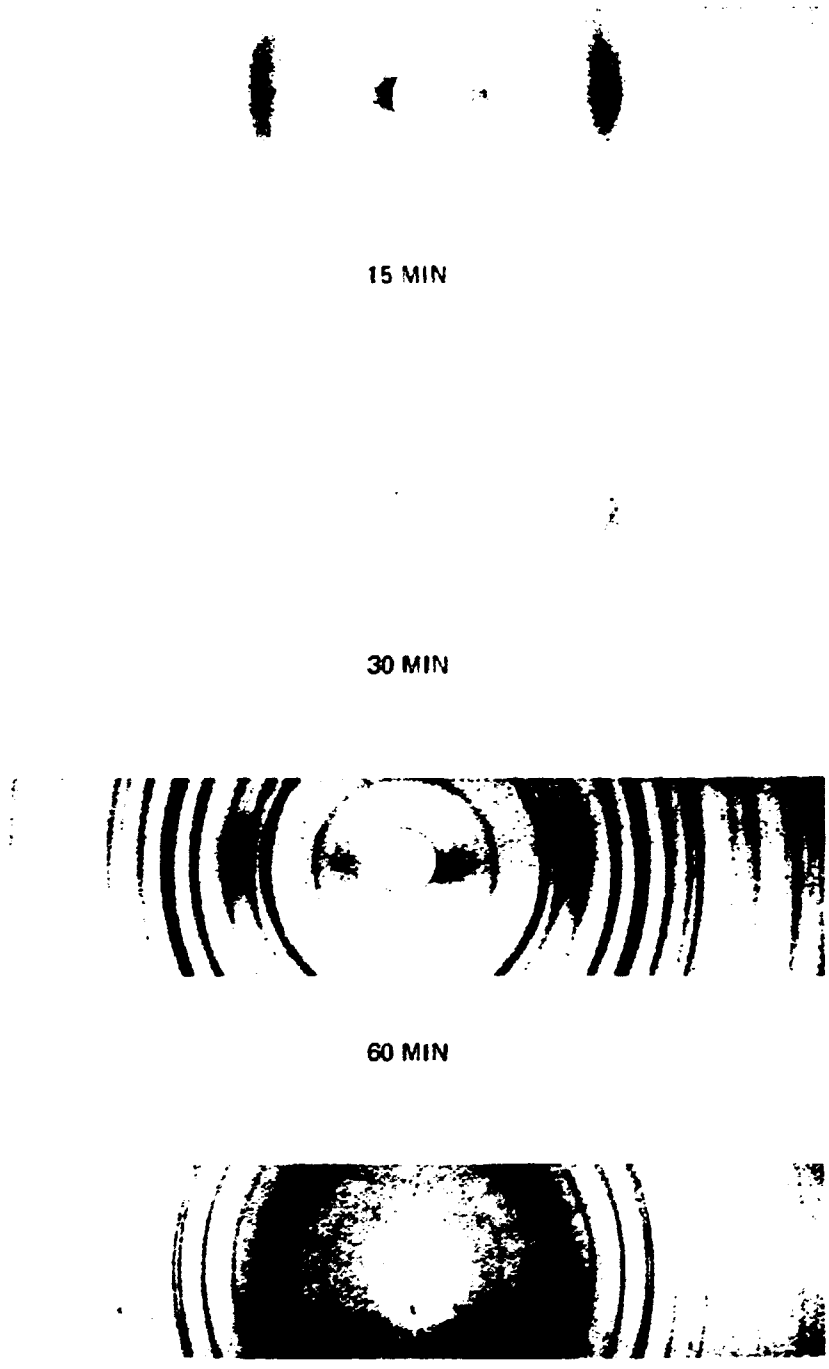


Fig. 14 X-Ray Diffraction Patterns of Silicon Nitride Coated HTS Graphite Fiber

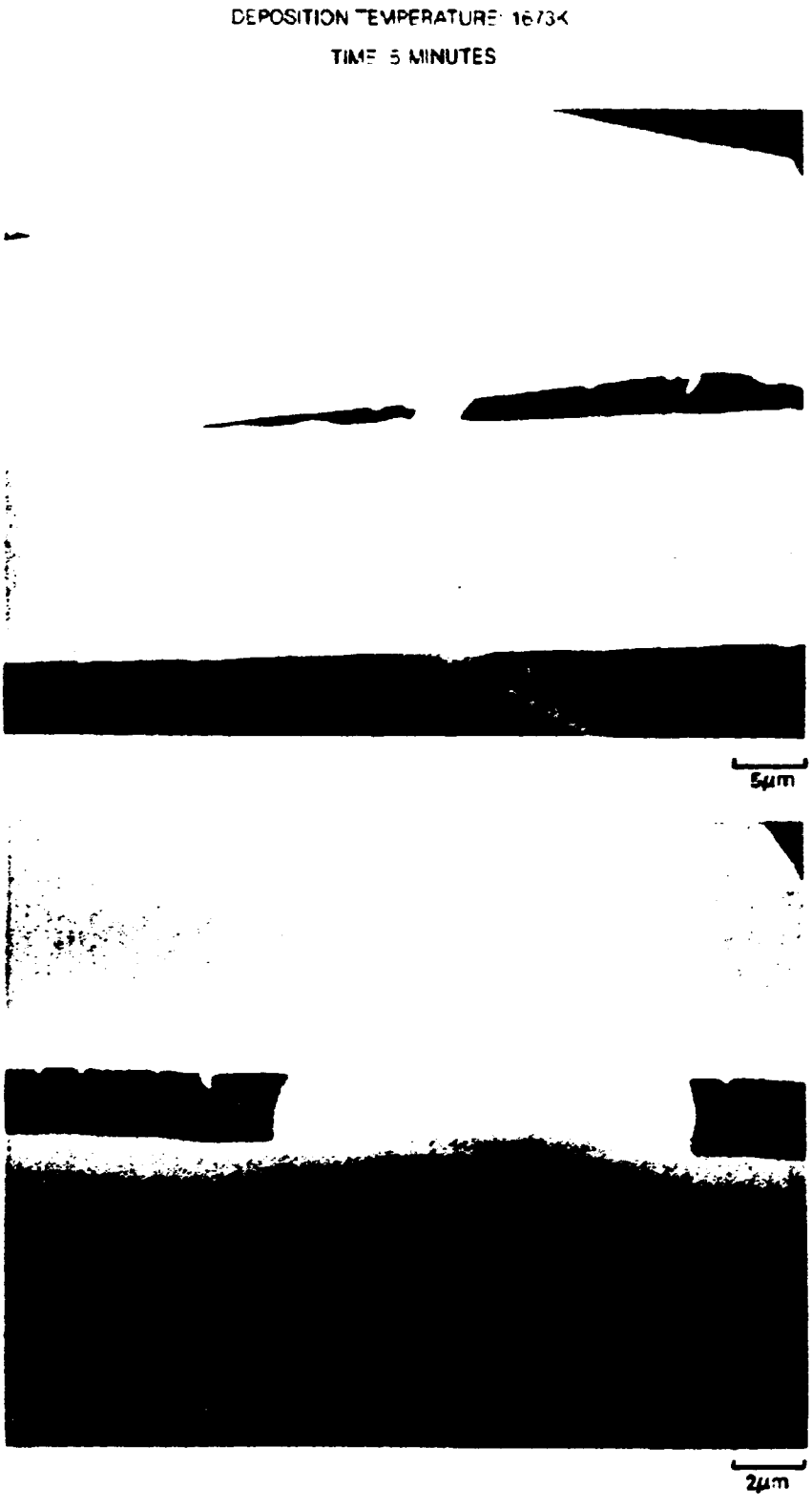


Fig. 15 SEM of Silicon Nitride Coated HTS Graphite Yarn

DEPOSITION TEMPERATURE: 1673K
TIME: 10 MINUTES

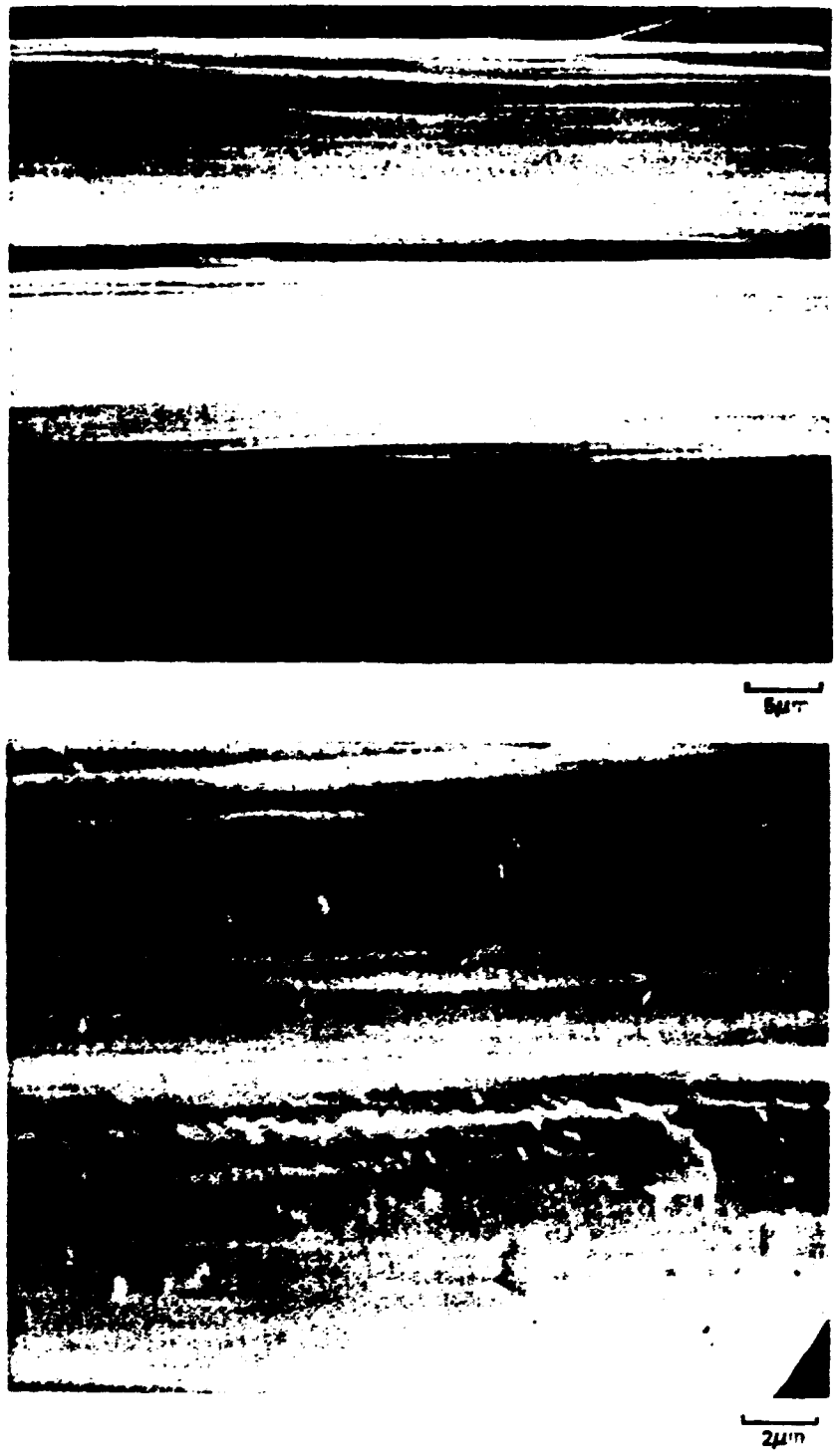


Fig. 16 SEM of Silicon Nitride Coated HTS Graphite Yarn

DEPOSITION TEMPERATURE: 1673K

TIME: 15 MINUTES

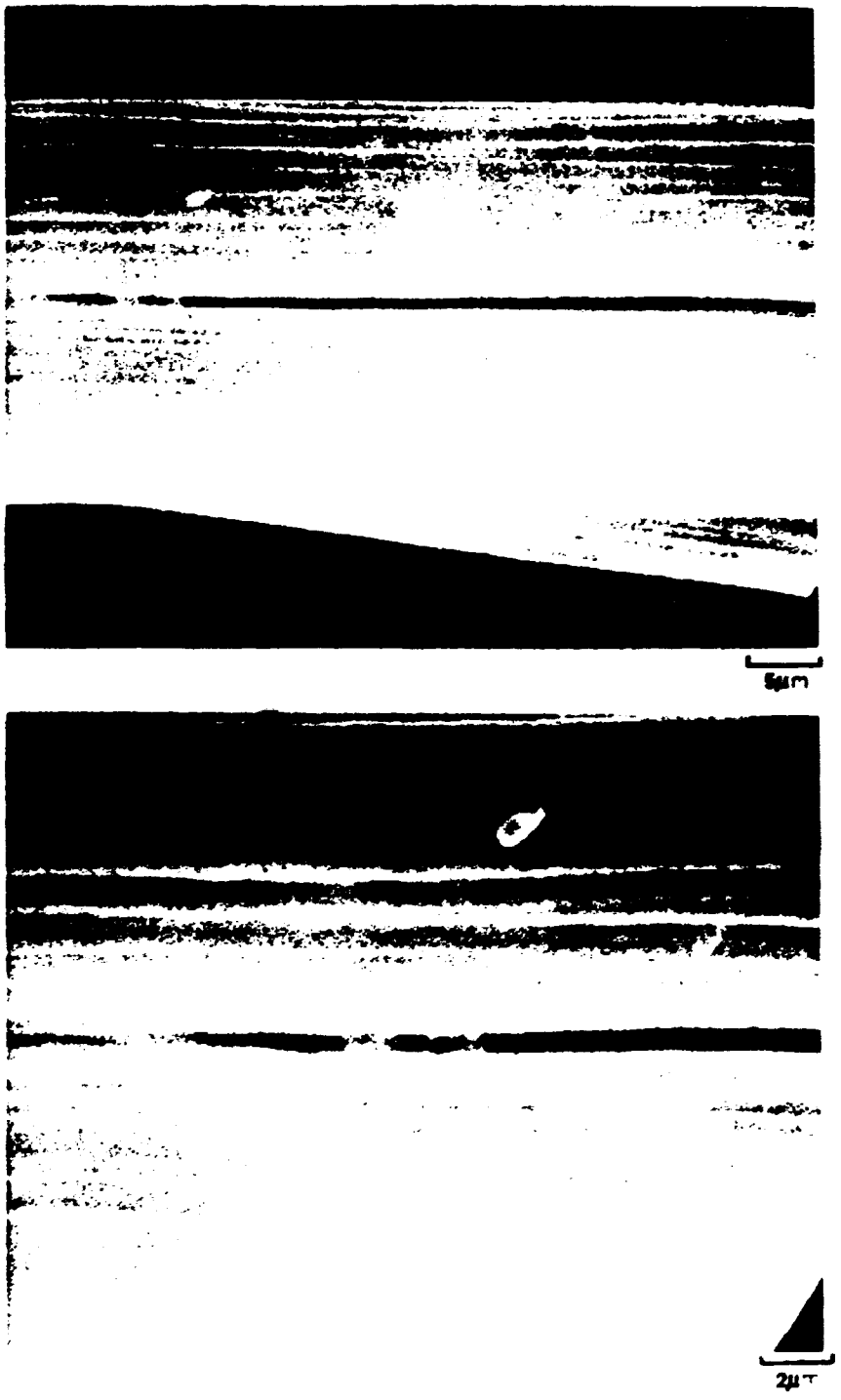


Fig. 17 SEM of Silicon Nitride Coated HTS Graphite Yarn

DEPOSITION TEMPERATURE: 1593K
TIME: 5 MINUTES

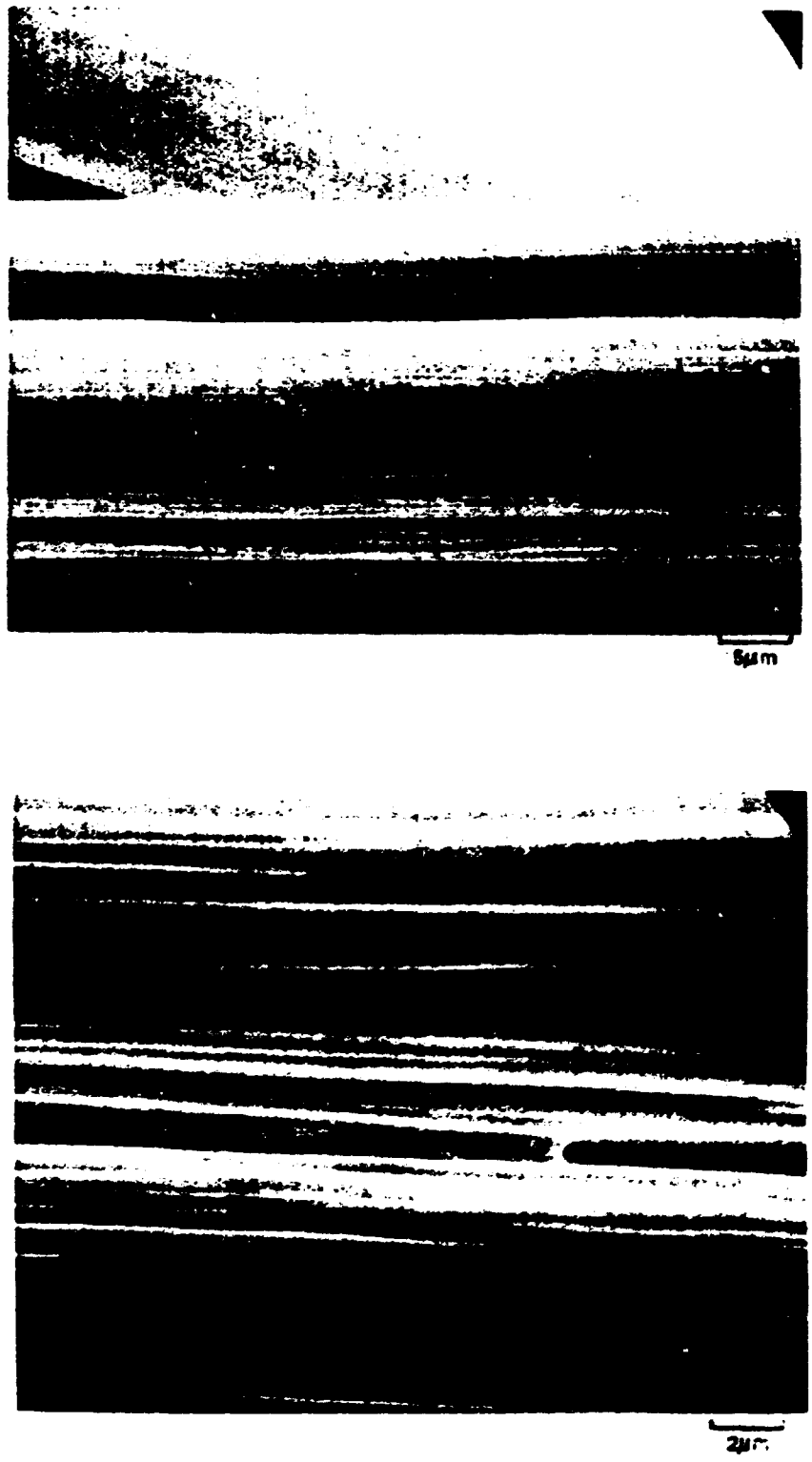


Fig. 18 SEM of Silicon Nitride Coated HTS Graphite Yarn

DEPOSITION TEMPERATURE: 1693K
TIME: 10 MINUTES

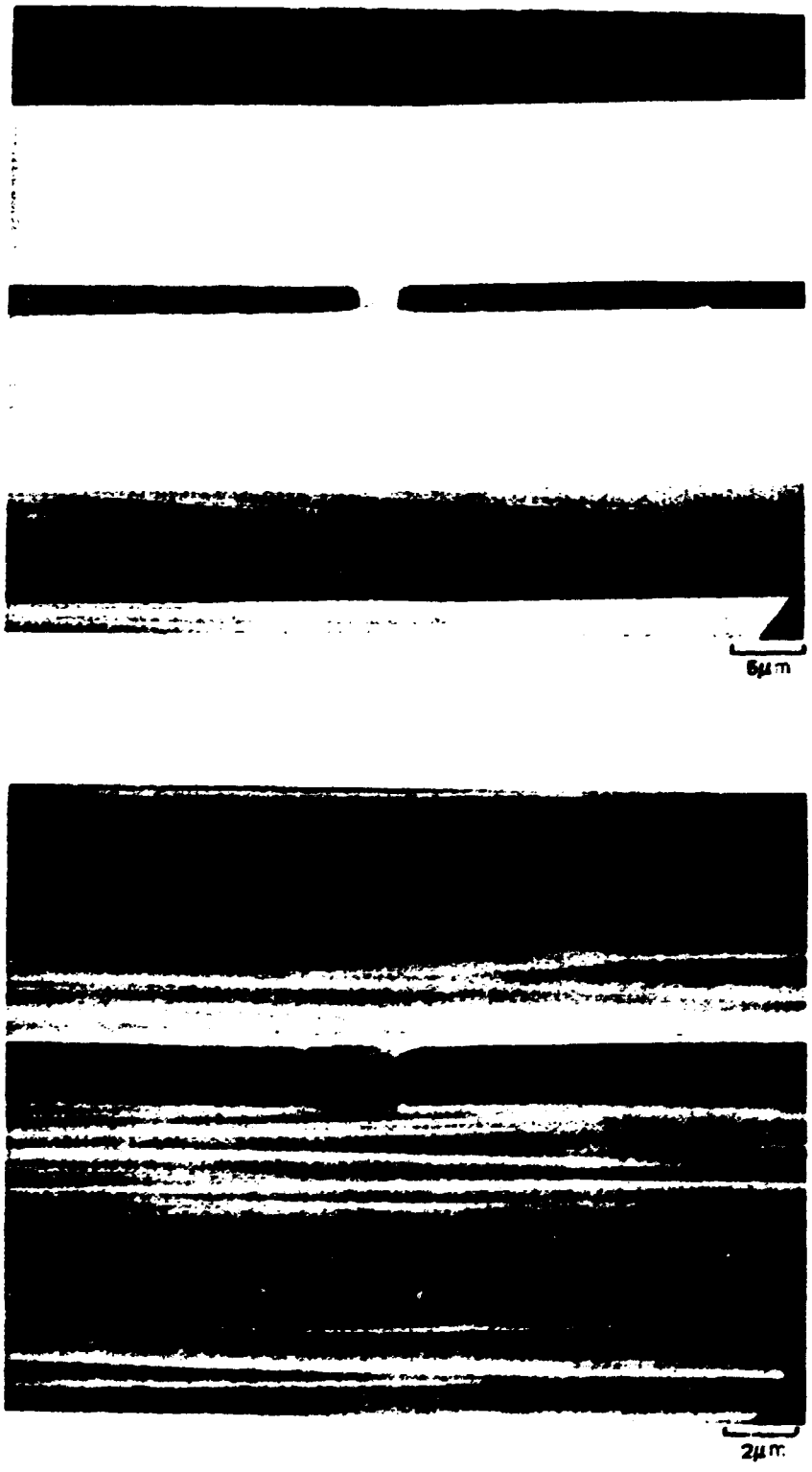


Fig. 19 SEM of Silicon Nitride Coated HTS Graphite Yarn

DEPOSITION TEMPERATURE: 1593K

TIME: 15 MINUTES

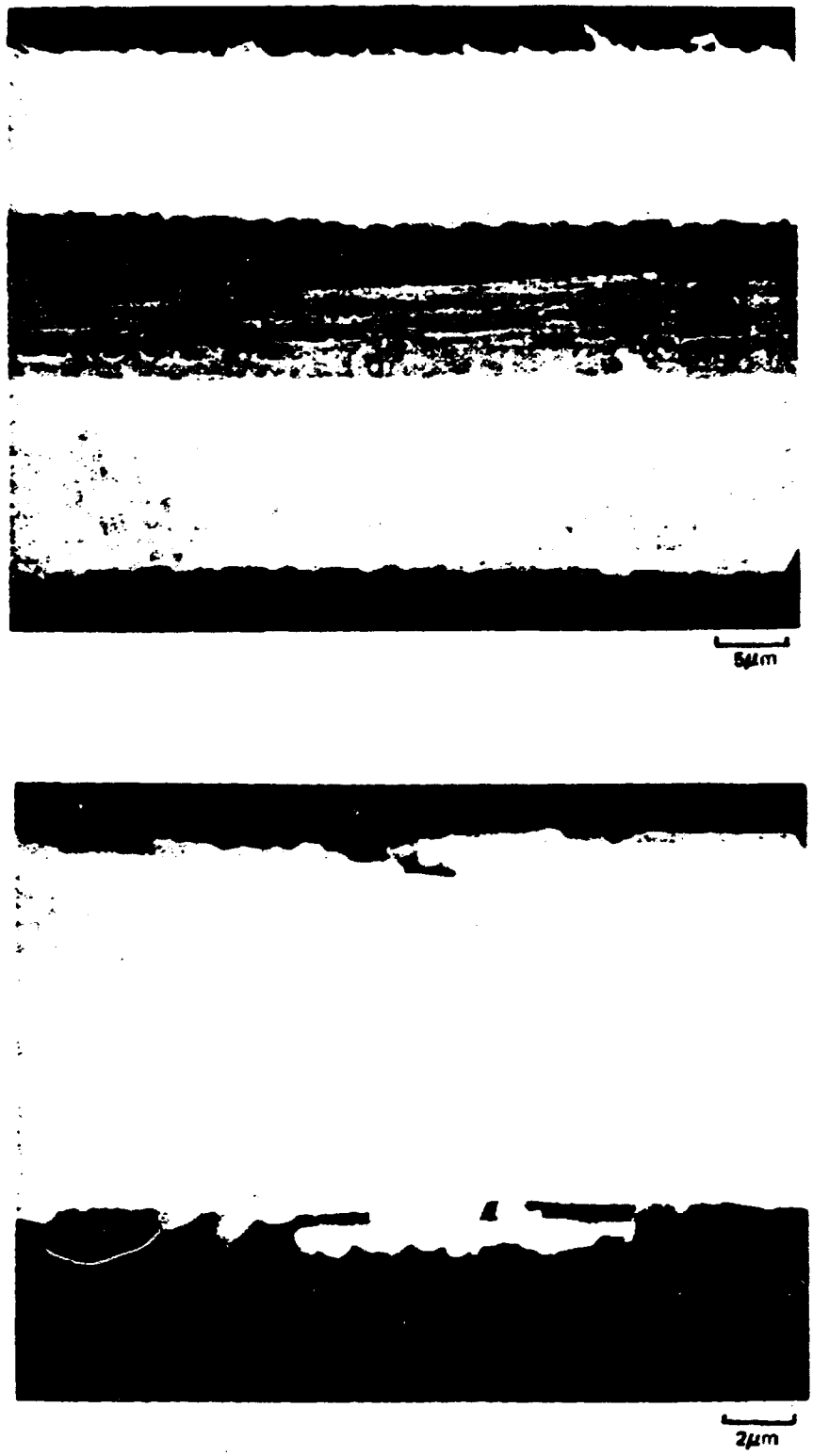


Fig. 20 SEM of Silicon Nitride Coated HTS Graphite Yarn

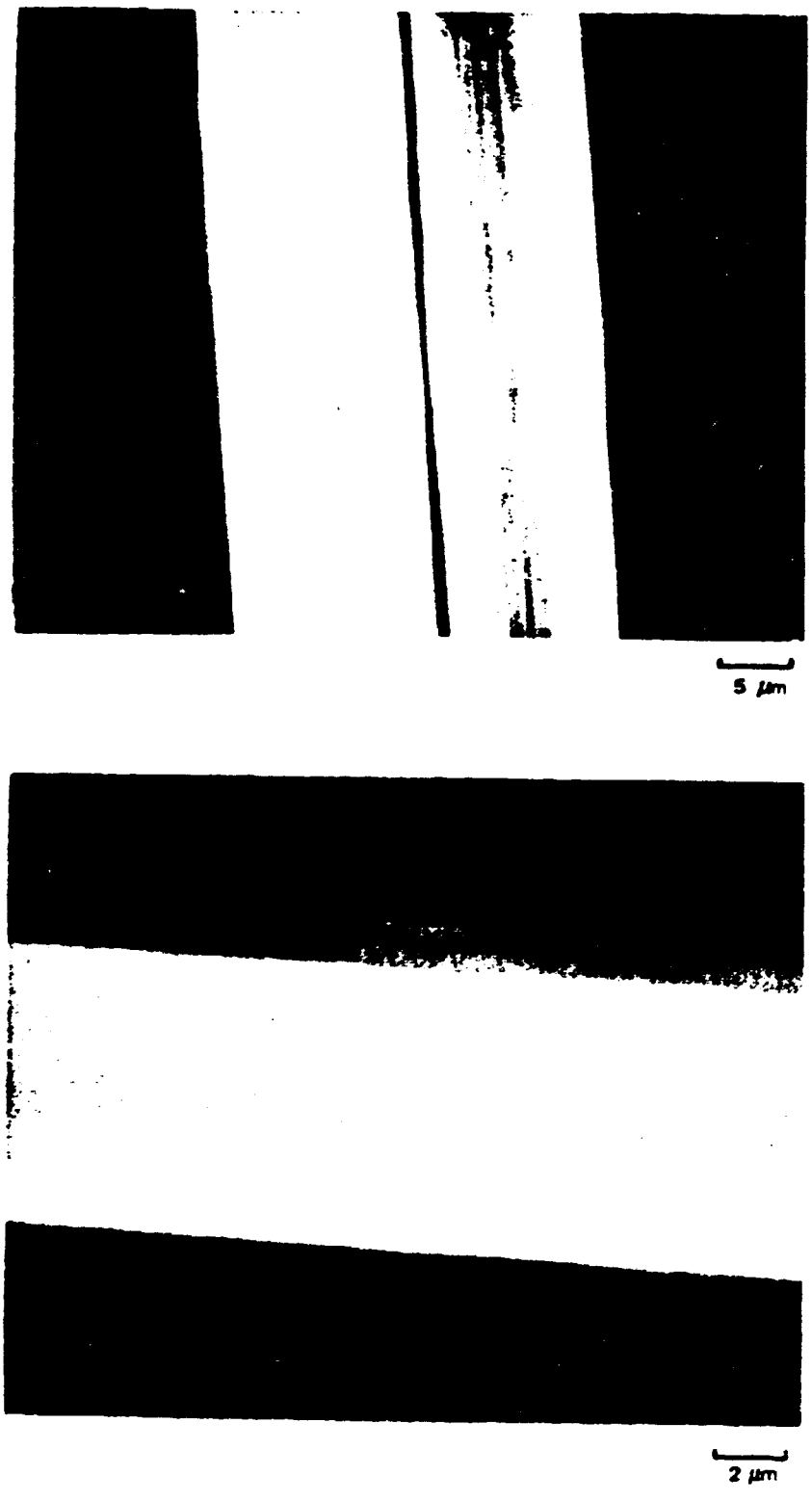


Fig. 21 SEM of "As Received" HTS Graphite Fiber

5 MINUTE DEPOSITION

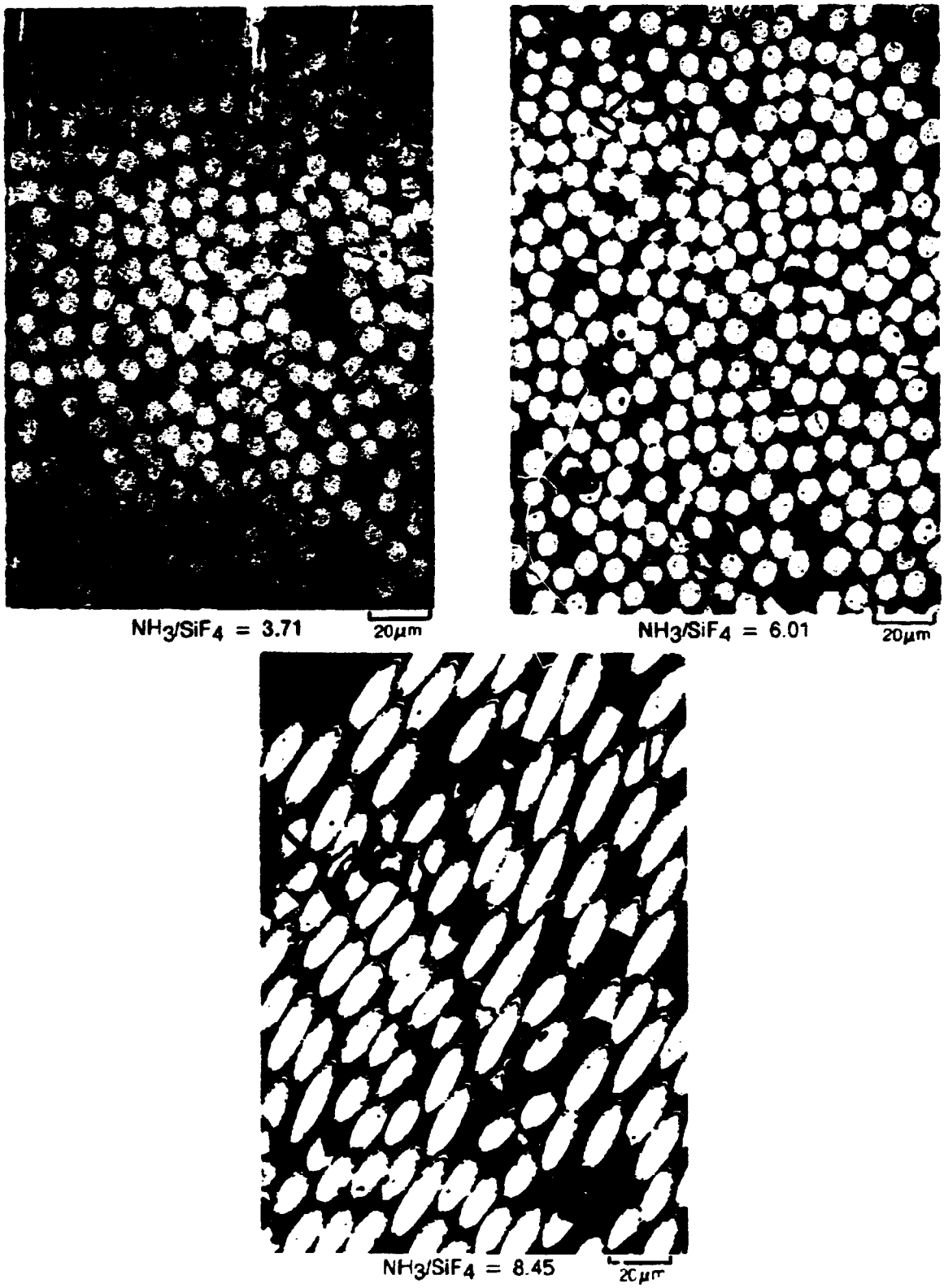


Fig. 22 CVD Si_3N_4 Coated HMS Yarn

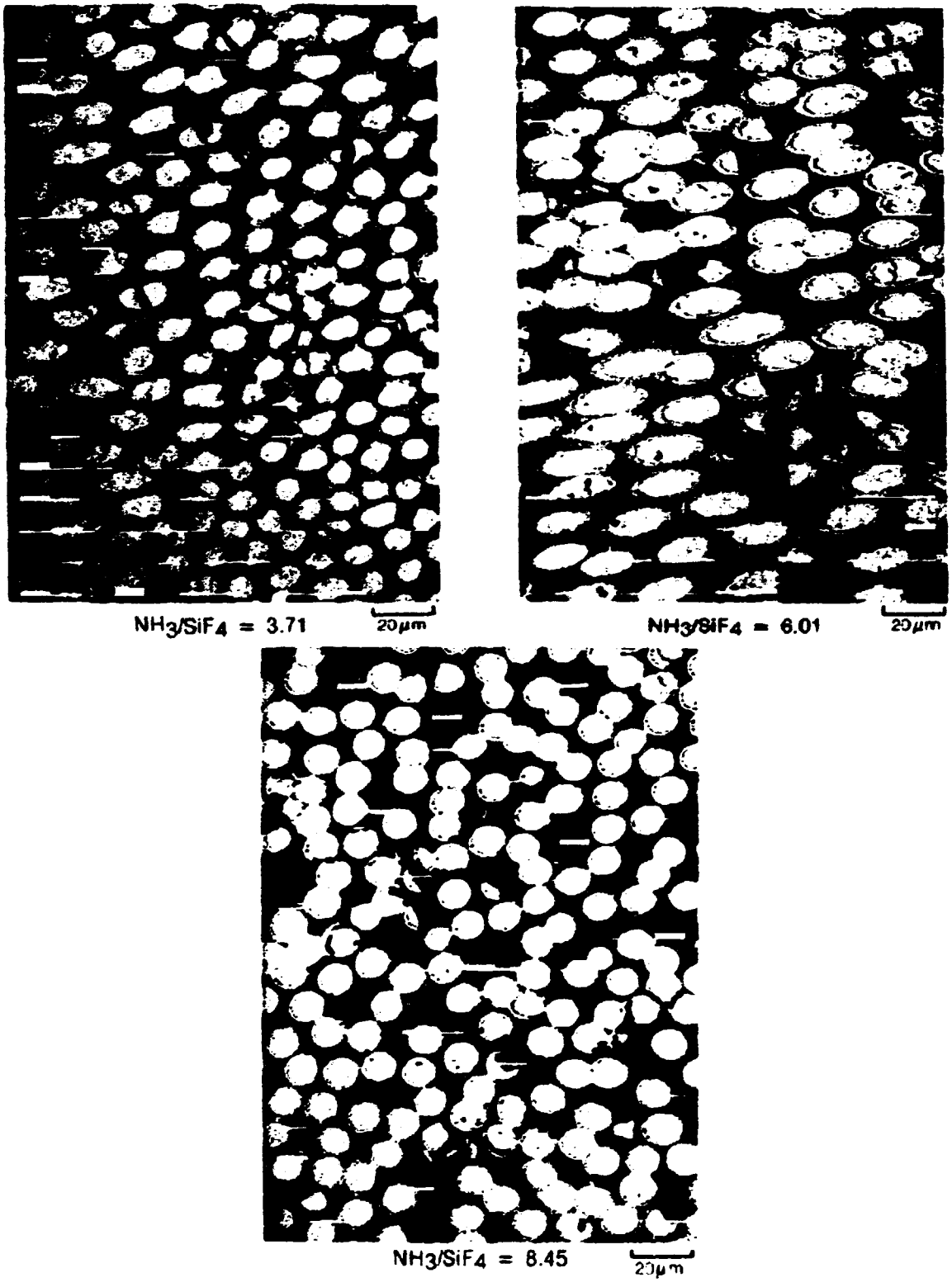


Fig. 23 CVD Si_3N_4 Coated HMS Yarn

30 MINUTE DEPOSITION

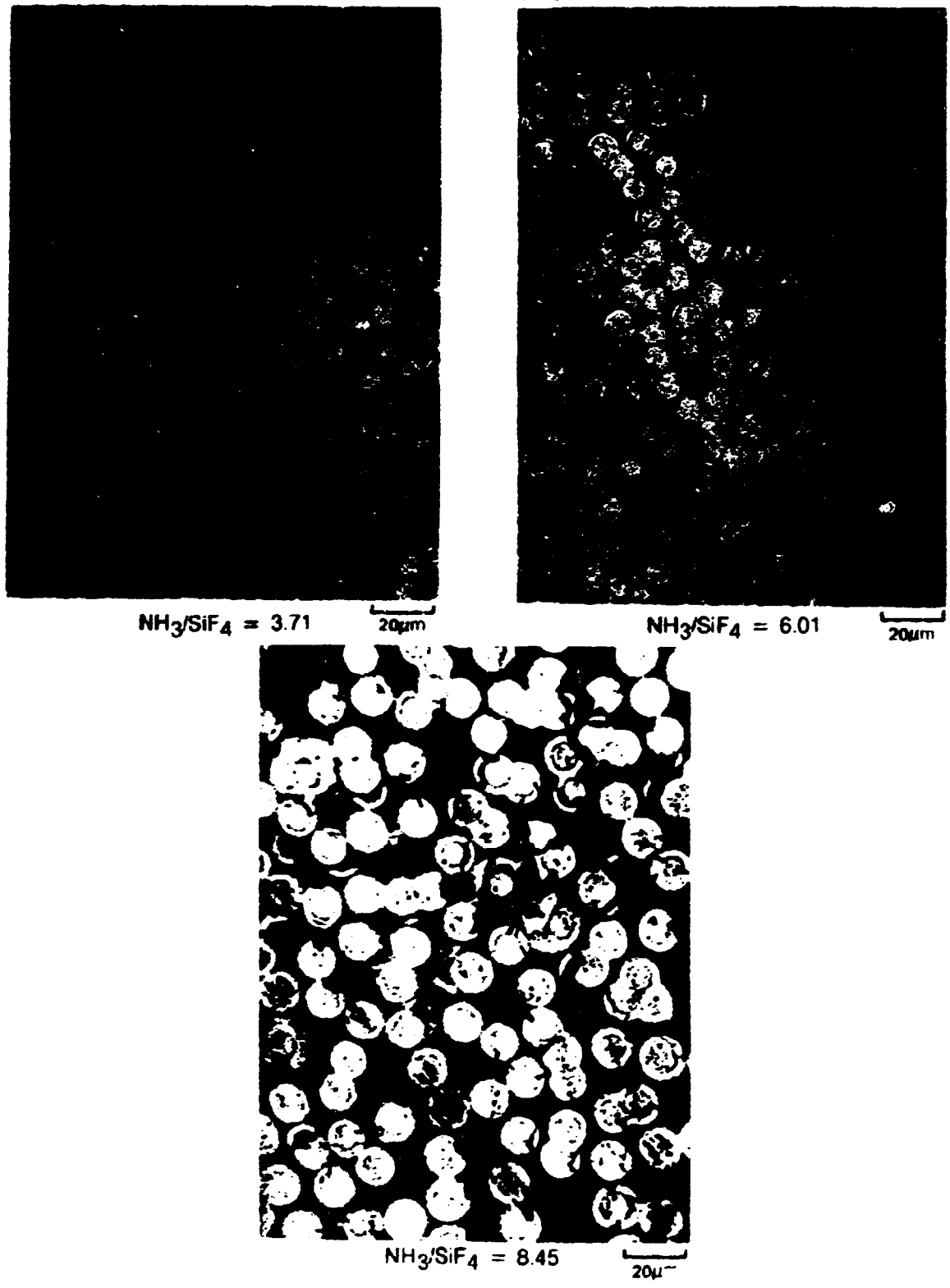
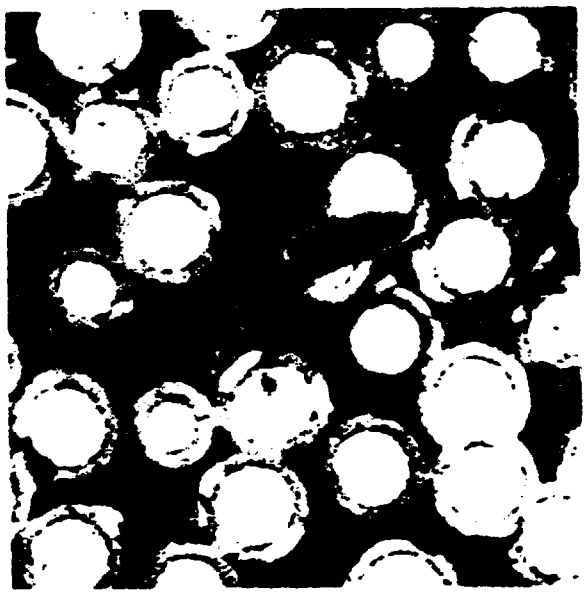


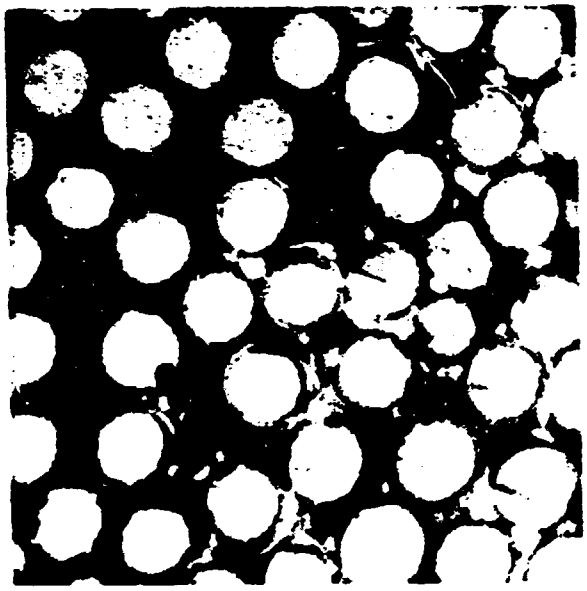
Fig. 24 CVD Si_3N_4 Coated HMS Yarn

HMS GRAPHITE YARN
LOCATION WITHIN COMPOSITE



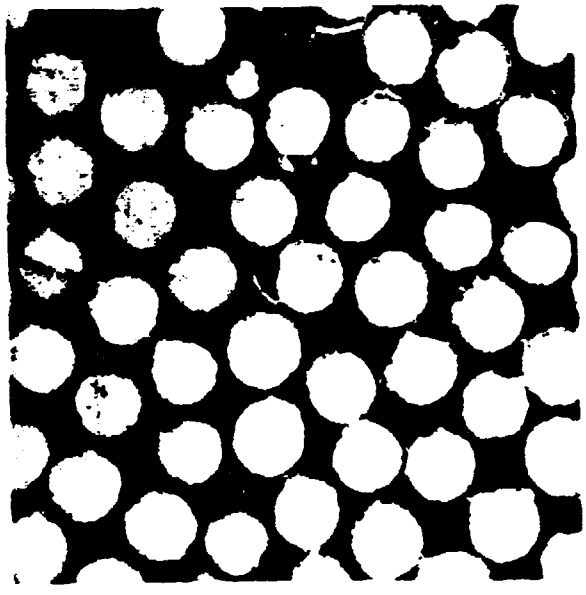
END OF TOW NOT
INCLUDED IN COMPOSITE

8μm



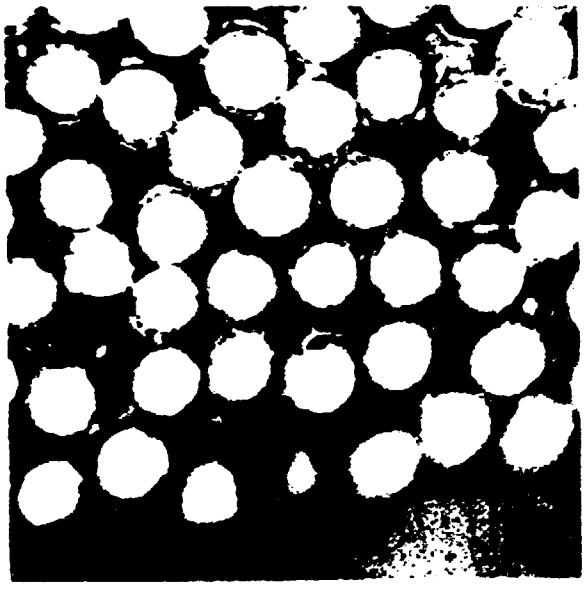
TOP REGION

8μm



MIDDLE REGION

8μm



BOTTOM REGION

8μm

Fig. 25 CVD Si_3N_4 Coatings

80-3-19-1

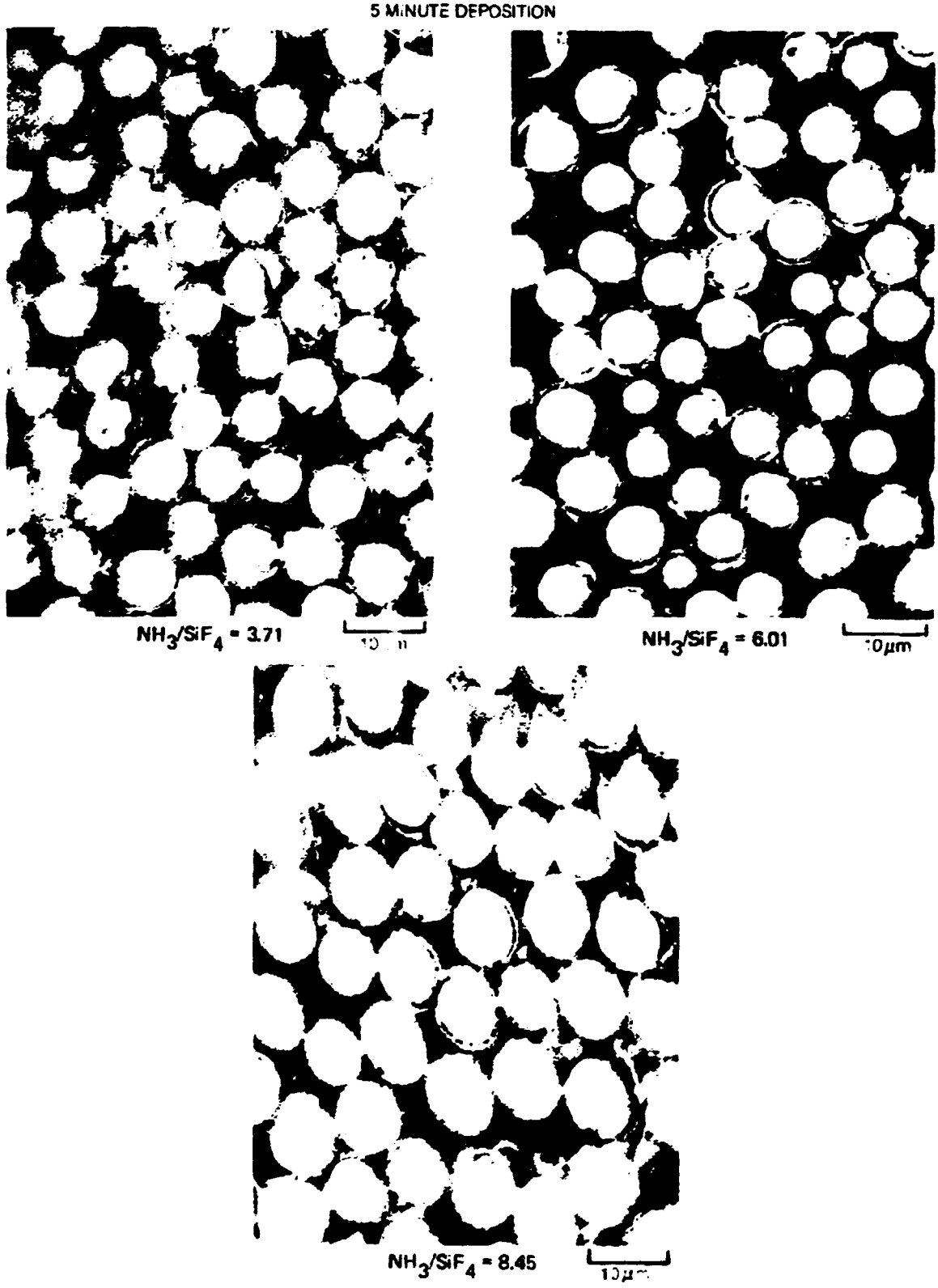


Fig. 26 CVD Si_3N_4 Coated Cellon 6000 Yarn

79-09-150-3

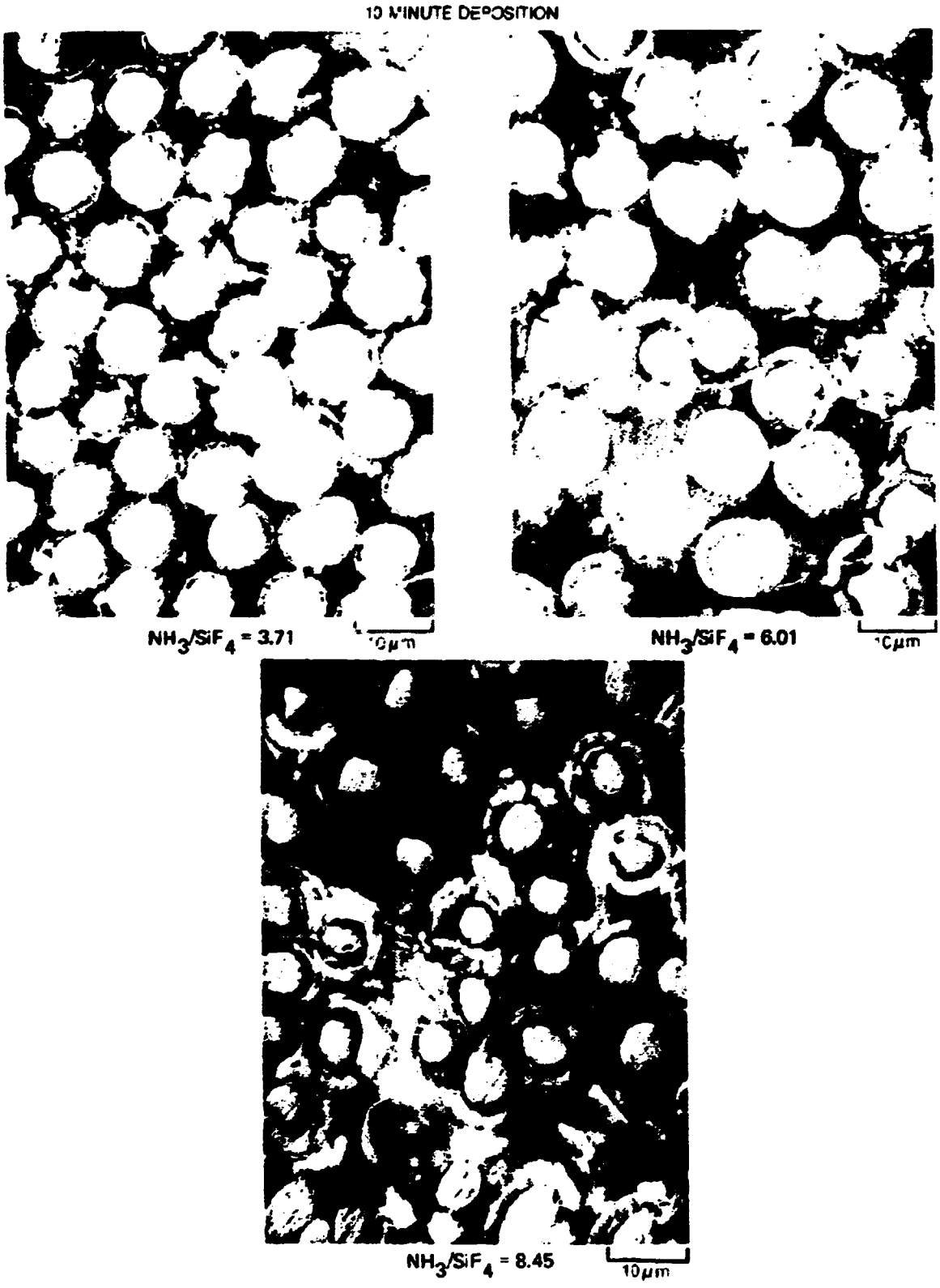


Fig. 27 CVD Si_3N_4 Coated Celion 6000 Yarn

30 MINUTE DEPOSTION

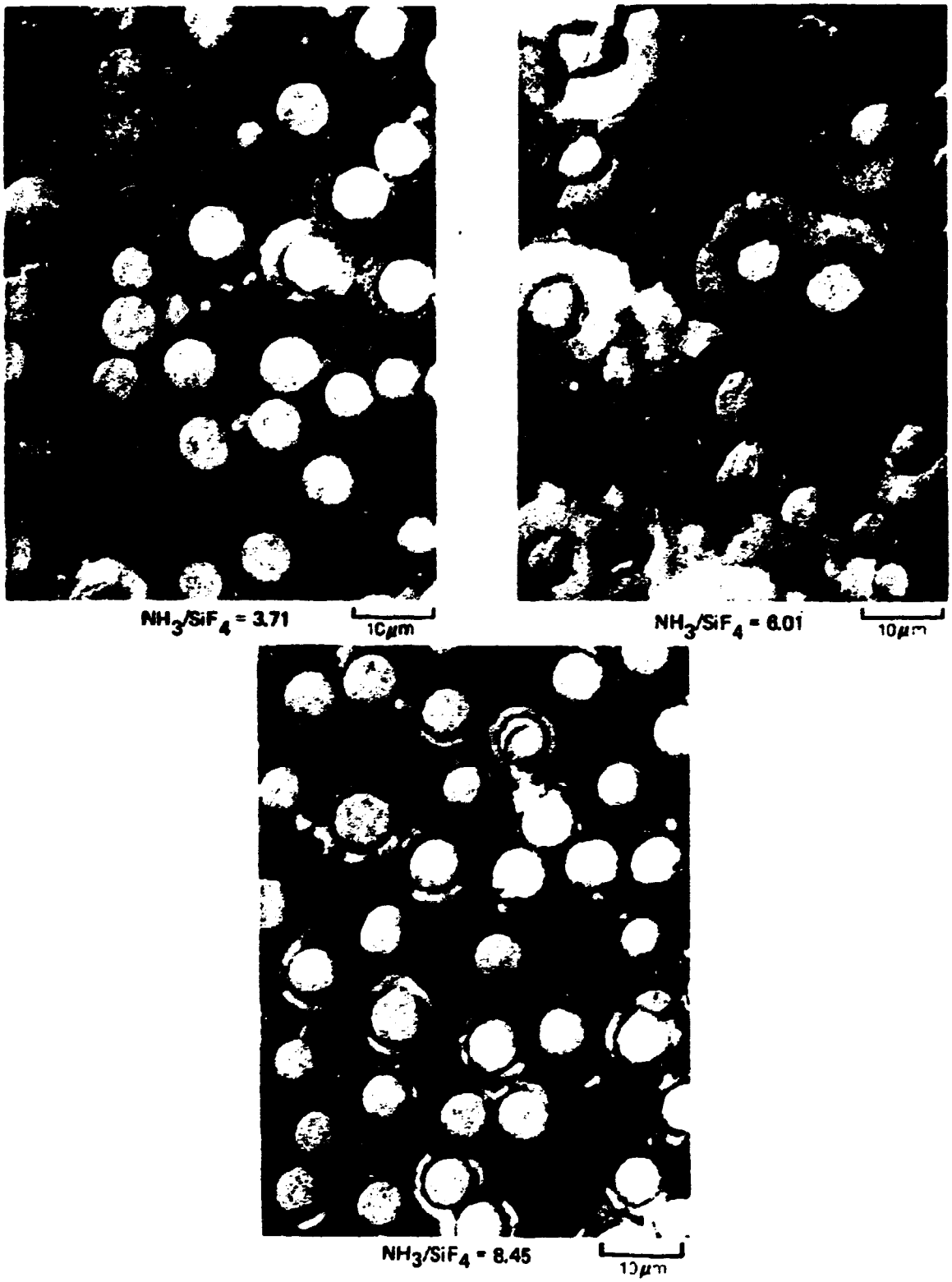
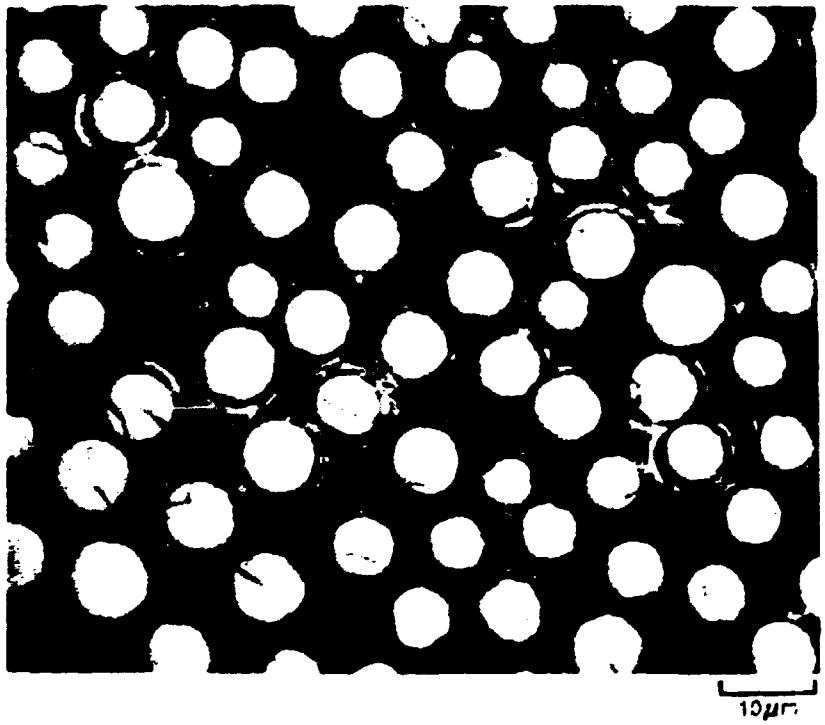


Fig. 28 CVD Si_3N_4 Coated Celion 6000 Yarn

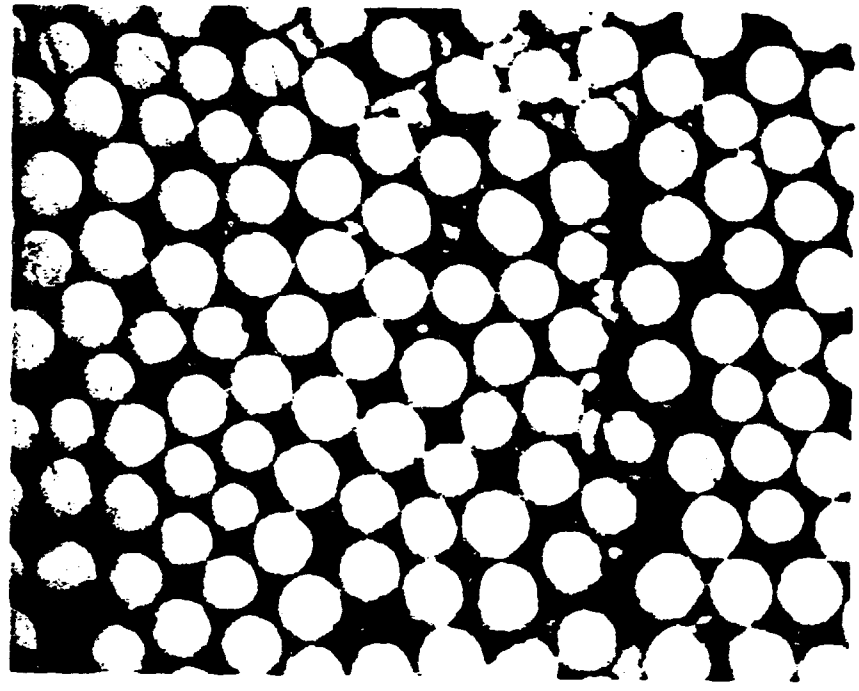


C12000 GRAPHITE YARN

Fig. 29 CVD Si_3N_4 Coatings

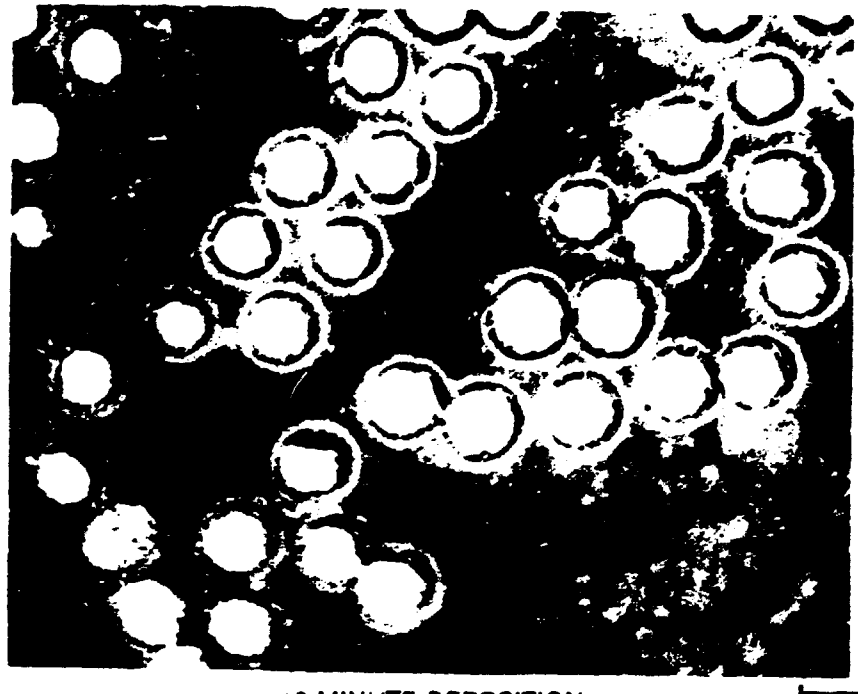
20 MINUTES

CELION 6000 GRAPHITE YARN



1 MINUTE DEPOSITION

8μm

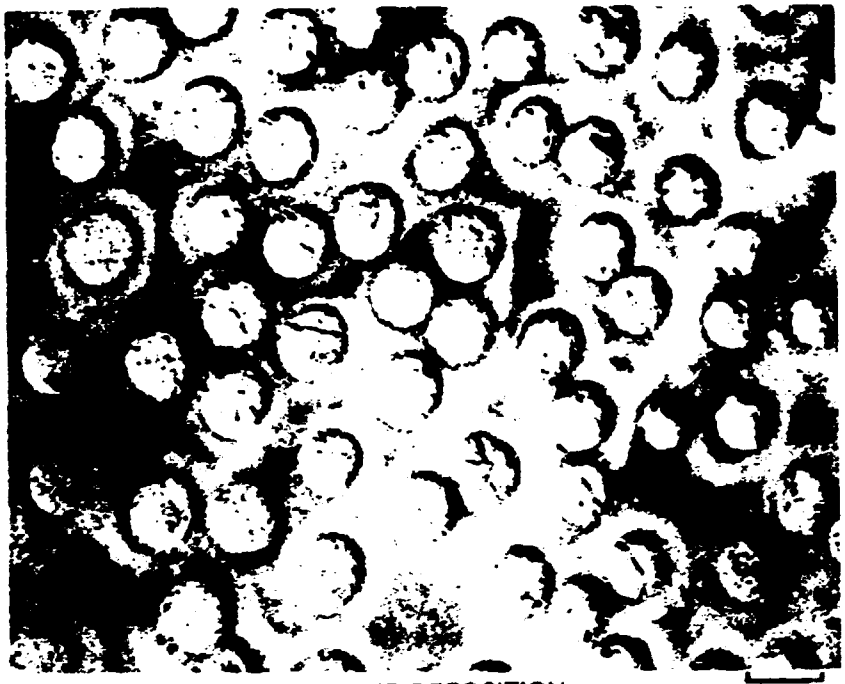


10 MINUTE DEPOSITION

8μm

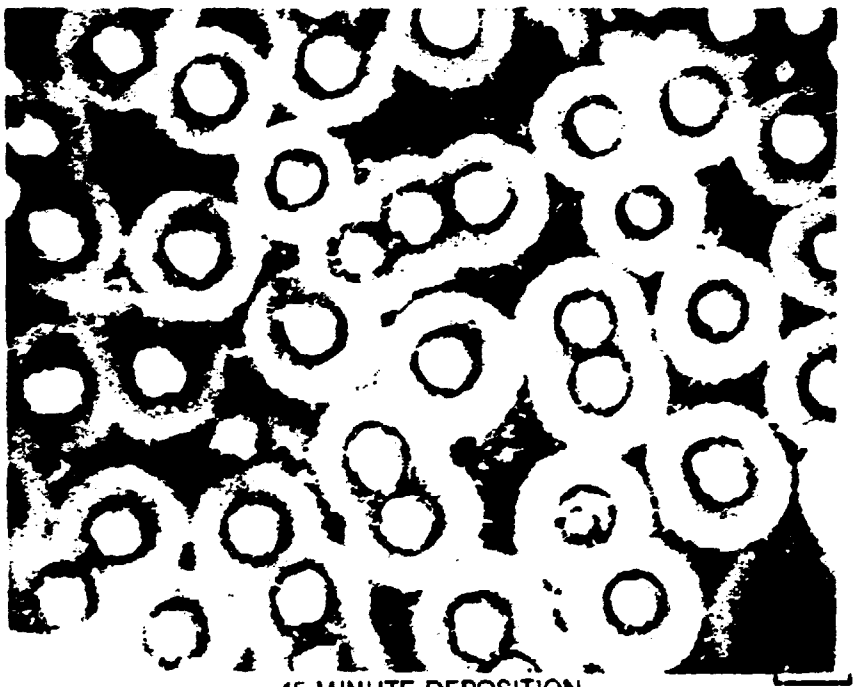
Fig. 30 CVD BN Coatings

CELION 6000 GRAPHITE YARN



30 MINUTE DEPOSITION

8μm



45 MINUTE DEPOSITION

8μm

Fig. 31 CVD BN Coatings

80-3-19-3

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Contract Monitor: Dennis Dicus, NASA Langley Research Center

16. Abstract

It was reported that graphite fibers released from composites during burning or an explosion could cause shorting of electrical and electronic equipment. In this program, silicon carbide, silica, silicon nitride and boron nitride were coated on graphite fibers to increase their electrical resistances. A chemical vapor deposited silicon carbide followed by an oxidation process developed for HTS fiber was used to coat HMS, C-6000, C-12000 and T-300 graphite fiber. Resistances as high as three orders of magnitude higher than uncoated fiber were attained without any significant degradation of the substrate fiber. Silicon nitride and boron nitride coated fibers have resistances greater than 10^6 ohms/cm. An organo-silicone approach to produce coated fibers with high electrical resistance was also used. Celion 6000 graphite fibers were coated with an organo-silicone compound, followed by hydrolysis and pyrolysis of the coating to a silica-like material. Although a low pyrolysis temperature (573 K) resulted in large increase in electrical resistance (2950 ohms), relative to coated fibers pyrolyzed at 1093 K (18 ohms), the shear and flexural strengths of composites made from high electrically resistant fibers were considerably lower than the shear and flexural strengths of composites made from the lower electrically resistant fibers. The lower shear strengths of the composites indicated that the coatings on these fibers were weaker than the coating on the fibers which were pyrolyzed at higher temperature.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Organosilane coating, Chemical vapor deposition, Silica-like coatings, Silicon carbide coating, Composites, Graphite fiber, Silicon nitride coating, Boron nitride coating	Unclassified-Unlimited

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