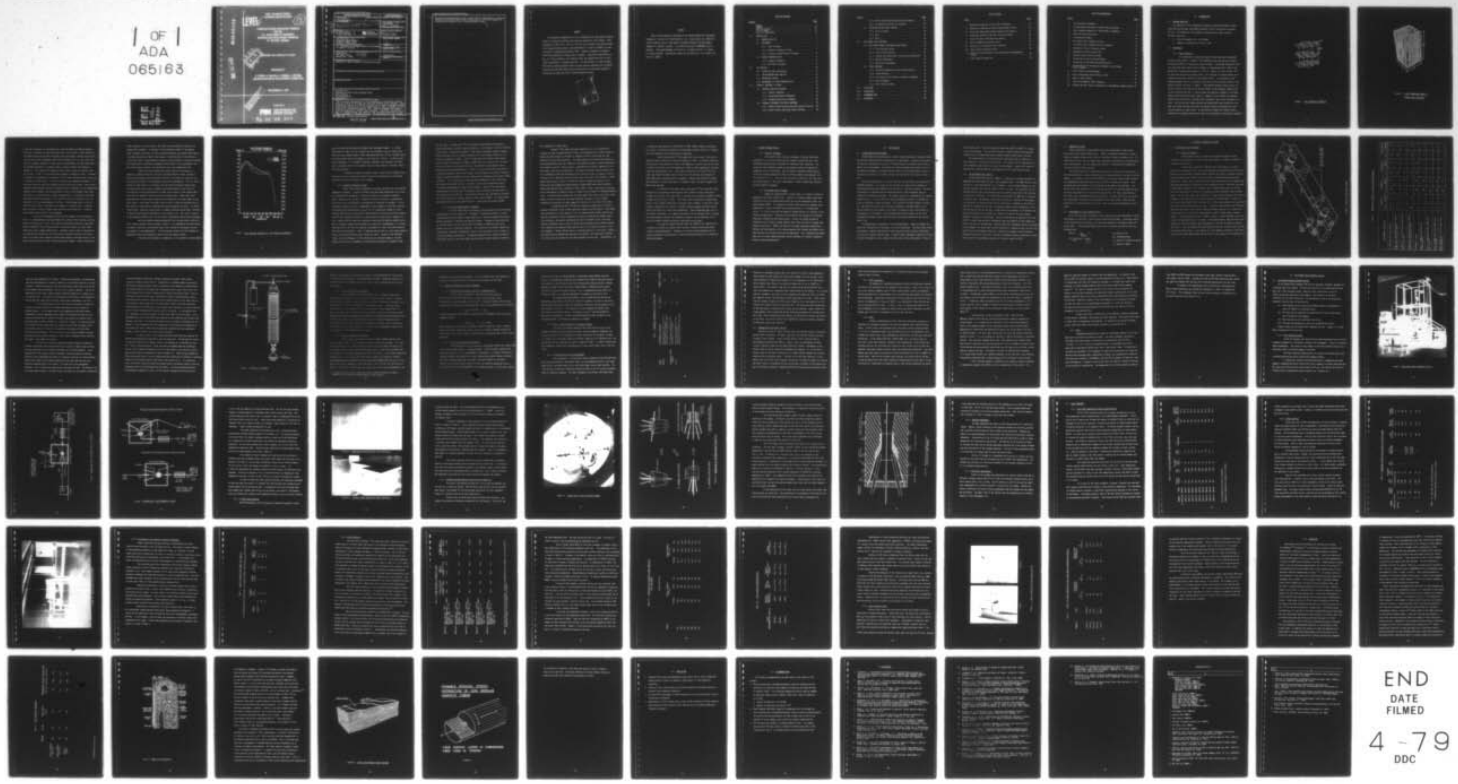
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FINAL TECHNICAL REPORT "IMPROVED GRAPHITE FIBER"

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A MANUFACTURING TECHNOLOGY PROGRAM
FOR THE
U.S. ARMY MOBILITY EQUIPMENT
RESEARCH AND DEVELOPMENT COMMAND
FT. BELVOIR, VIRGINIA

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MAR 1 1979
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CONTRACT NO. DAAK70-77-C-0155

PREPARED BY:

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ADVANCED MATERIALS DEVELOPMENT LABORATORY

SEPTEMBER 12, 1978

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The successful demonstration of the strengthening of high modulus graphite fibers by coating and alloying with boron was achieved on this program. Fiber strengths as high as 473 x 10^3 psi at 63 million psi modulus have been obtained An arc-plasma heating process, with temperatures in excess of 3000°C, has been utilized for strengthening graphite fiber. Chemical treatments on graphite fibers were employed to increase their strengths. Successful intercalation of Br_2, ICl, $FeCl_3$ and $MoCl_5$ into graphite fibers was demonstrated with no significant improvement in strengths observed. The application of a small diameter

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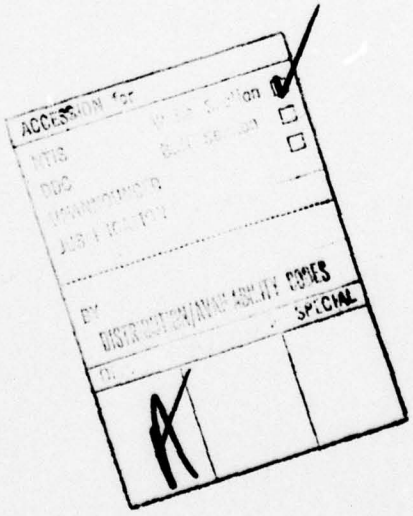
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PAN fiber to produce graphite fibers of much superior properties was initiated. Design plans have been drawn up for construction of a pilot plant capable of processing one pound per hour of improved graphite fibers.

SUMMARY

The successful demonstration of the strengthening of high modulus graphite fibers by coating and alloying with boron was achieved on this program. Fiber strengths as high as 473 x 10^3 psi at 63 million psi modulus have been obtained. An arc-plasma heating process, with temperatures in excess of 3000°C, has been utilized for strengthening graphite fiber. Chemical treatments on graphite fibers were employed to increase their strengths. Successful intercalation of Br_2, ICl, $FeCl_3$ and $MoCl_5$ into graphite fibers was demonstrated with no significant improvement in strengths observed. The application of a small diameter PAN fiber to produce graphite fibers of much superior properties was initiated. Design plans have been drawn up for construction of a pilot plant capable of processing one pound per hour of improved graphite fibers.



PREFACE

Work on this program was performed by the Advanced Materials Development Laboratory, a division of Fiber Materials, Inc., under Contract No. DAAK70-77-C-0155 issued by the U.S. Army Mobility Equipment Research and Development Command, Ft. Belvoir, Virginia. The technical monitor at MERADCOM was Mr. S. Goldfein. The program manager at FMI was Dr. R. Pepper with Mr. D.C. Nelson as project engineer. Engineering support was provided by Mr. D.C. Jarmon, and Miss J.R. Hotham.

Table of Contents

Section		Page
	Summary	i
	Preface	ii
	Table of Contents	iii
	List of Tables	v
	List of Illustrations	vi
1.0	INTRODUCTION	1
	1.1 PROGRAM OBJECTIVE	1
	1.2 BACKGROUND	1
	1.2.1 Fiber Structure	1
	1.2.2 Chemical Treatment of Fiber	7
	1.2.3 In-Process Graphitization Treatment	8
	1.3 CURRENT PROGRAM EFFORTS	11
	1.3.1 Chemical Treatment	11
	1.3.2 Arc-Plasma Treatment	11
2.0	TEST METHODS	12
	2.1 PLASMA EMISSION SPECTROSCOPY	12
	2.2 ION MICROPROBE MASS ANALYSIS	13
	2.3 MECHANICAL TESTING	14
	2.4 MEASUREMENT OF FIBER CHARACTERISTICS	14
3.0	CHEMICAL TREATMENT OF FIBERS	15
	3.1 INTERCALATION WITH HALOGENS	15
	3.1.1 Bromine Treatments	15
	3.1.2 Iodine Monochloride Treatments	21
	3.1.3 Chromium Oxychloride Treatments.	21
	3.2 CHEMICAL TREATMENTS WITH METAL COMPOUNDS	22
	3.2.1 Nickel Surface Coating Using $NiCl_2$ Reduction By H_2	22
	3.2.2 Nickel Surface Coating By Nickel Resinate	22

Section			Page
		3.2.3 Nickel Surface Coating Using Nickel Carbonyl. . . .	23
		3.2.4 Iron Deposition Using Iron Carbonyl	24
	3.3	INTERCALATION WITH METAL HALIDES	25
		3.3.1 $NiCl_2$ and $NiBr_2$	26
		3.3.2 $FeCl_3$	26
		3.3.3 $MoCl_5$	28
4.0	ARC-PLASMA FIBER TREATMENT		30
	4.1	ARC-PLASMA FURNACE EQUIPMENT DESIGN PROCESS	30
		4.1.1 Fiber Handling System	30
		4.1.2 Tri-Arc-Plasma Heating	34
		4.1.3 Cathode and Anode Design, Positioning and Materials	36
		4.1.4 Reaction Atmosphere	41
		4.1.5 Electrical Requirements	41
	4.2	FIBER TREATMENT	42
		4.2.1 Ultrahigh Temperature Stretch Graphitization . . .	42
		4.2.2 Carbon Coatings	44
		4.2.3 Utilization of Arc-Plasma In Chemical Treatments .	47
		4.2.4 Boron Treatment	49
		4.2.5 Fiber Precursor Study	54
5.0	DISCUSSION		58
6.0	CONCLUSIONS		66
7.0	RECOMMENDATIONS		67
8.0	REFERENCES		68

List of Tables

Table		Page
I	Mechanical Properties For Br_2 Fiber Treatments	17
II	Mechanical Properties of Nickel Coated Graphite Fiber	24
III	Ultra High Temperature Stretch Graphitization Results	43
IV	Pyrocarbon Coating of HM Fiber In the Arc-Plasma	45
V	Nickel Plating on HM Fibers Test Results	48
VI	Boron Treatment of Graphite Fibers	50
VII	Variation In As Received Fiber Properties	52
VIII	Fiber Surface Evaporation Data	53
IX	Effect of Fiber Precursor on Arc-Plasma Boron Strengthening Process	56
X	Fiber Property Comparison	60

List of Illustrations

Figure		Page
1	The Structure of Graphite	2
2	A Three Dimensional Model of Carbon Fiber Structures	3
3	Heat Treatment Response of T-300 Gr/A201 Al Composite	6
4	Fiber Hot Stretching System	16
5	Intercalation Chamber	20
6	Arc-Plasma Fiber Treatment Facility	31
7	Arc-Plasma Fiber Treatment Facility Schematic	32
8	Comparison of Fiber Transport Systems	33
9	Compensating Tension Control Unit	35
10	Variable Speed Traversing Winder	35
11	Inside View of the Arc-Plasma Chamber	37
12	Progression of the Anode Design Optimization	38
13	Optimum Design of the Anode and Cathodes For Arc-Plasma Fiber Treatment	40
14	Glassy Carbon Coating Equipment	46
15	Boron Strengthened Fiber Surfaces by SEM	55
16	Model of Fiber Defects	61
17	Typical High Modulus Fiber Structure	63
18	Probable Residual Stress Distribution in High Modulus Graphite Fibers	64

1.0 INTRODUCTION

1.1 PROGRAM OBJECTIVE

The objective of this program was to develop a production method for manufacturing high strength, high modulus graphite fiber at the rate of one pound per hour. The method was to be capable of providing such fibers with the following properties:

a. Tensile strength, min., psi 750,000.

b. Modulus of elasticity, psi 60-70 x 10^6.

1.2 BACKGROUND

1.2.1 Fiber Structure

The structures of carbon and graphite fibers have been extensively studied by many workers. Goldfein [1] has summarized past work and has reviewed the possible effects of structure on fiber strength. The maximum theoretical modulus obtainable from single crystal graphite is approximately 140 x 10^6 psi and theoretical strength approximately 14 x 10^6 psi. Moduli in excess of 100 x 10^6 psi have been achieved in graphite fibers, but strengths only approximately 3% of theoretical have been realized in high modulus fibers. The strength of small diameter graphite fibers is limited by flaws and by the anisotropic nature of the graphite crystal structure [2], Figure 1. High modulus graphite fibers have an internal structure that consists of twisted ribbons of the hexagonal layered plane crystal structure with the 'C' plane aligned (or partially aligned) in the longitudinal direction of the fiber, Figure 2. Numbers of such ribbons are combined together into microfibrils, and many such microfibrils make up the structure of a fiber. Not only are the ribbons twisted and folded within the microfibrils, but they also extend from one microfibril to another forming overlapping and interlinking networks of layer planes. Discontinuities between the ribbons within a microfibril and between microfibrils result in the presence of microscopic elongated

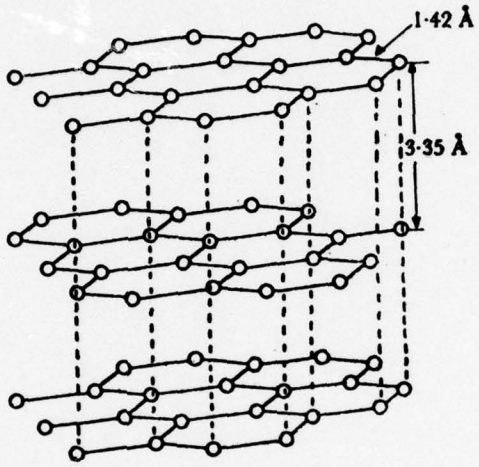


FIGURE 1. THE STRUCTURE OF GRAPHITE

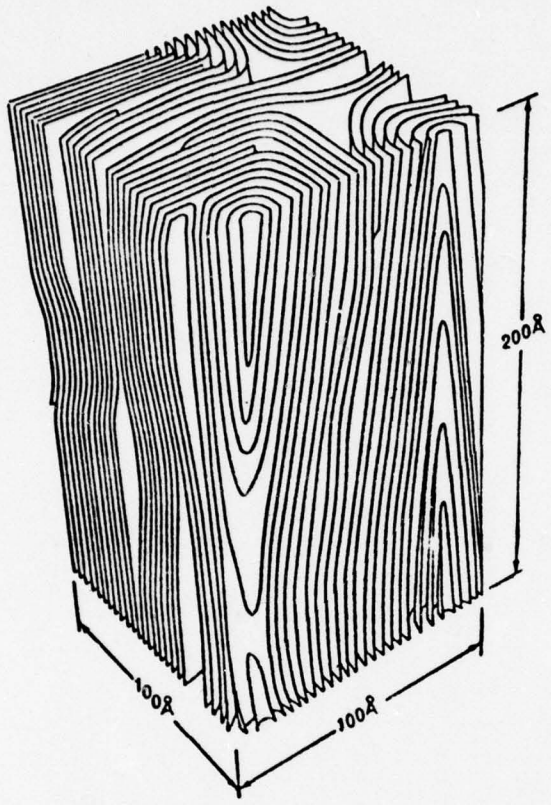


FIGURE 2 A THREE DIMENSIONAL MODEL OF CARBON FIBER STRUCTURES

voids and a structure of considerably less than the density of natural graphite 2.24 g/cc. Typical fiber densities range from 1.5 to 2.0 g/cc. Thus, because of the tangled nature of the fiber structures, many microscopic internal flaws (stress raisers) exist which undoubtedly lower fiber strengths, and it is not surprising that the strengths observed in fibers have been considerably less than theoretical. The strength and modulus of graphite fibers increases rapidly with decrease in diameter [3]. This supports the suggestion that internal flaws, not surface flaws, are the main cause of the low observed strengths in commercial fibers. Decrease in diameter is accompanied by a decrease in fiber volume (therefore fewer flaws) and an increase in surface area. A very likely possibility suggested by Goldfein [1] is failure at the cross-over points between twisted ribbon layer planes. More perfect alignment of the graphite structure achieved by fiber stretching at high temperatures improves fiber strengths, but the anisotropic nature of the hexagonal layer plane structure is a limiting factor in highly aligned fibers. For example, whilst the theoretical modulus of graphite is 140×10^6 psi in the 'A' direction, in the 'C' direction it is only approximately 6×10^6 psi. High strength exists in the 'A' direction, but in the 'C' direction, the strength is virtually zero. A possible mode of failure in highly aligned fibers could be shear within the 'C' plane of the structure which results in low strengths.

Work on the improvement of the tensile strengths of pitch precursor fibers [2] is concentrating on the achievement of a uniform, fine structure over the whole cross-section of a fiber. Past work on PAN and pitch fibers has shown that better alignment of fiber structure occurs in the outer layers, and thus, these outer layers have a higher modulus value. Therefore, when a fiber is subjected to a uniform tensile strain over its cross-section, the major portion of the load is borne by the outer layers because of their higher modulus, which may result in premature tensile failure at flaws in these outer layer regions. Better uniformity of

fiber structure, and thus modulus, over fiber cross-sections will result in improved fiber strengths. In the case of pitch precursor fibers [2], the highest fiber strengths (up to 600 x 10^3 psi) have been observed with single fibers having a uniform structure over their cross-section. Processing work in the pitch precursor fiber area is concentrating on control of the microfibril size and uniformity. The fibers tend to subdivide on emergence from the holes in the spinnerette, and this effect tends to control the microfibril size in the graphitized fiber.

Relatively large internal and surface flaws are also present in commercial graphite fibers and also have a profound effect on fiber strength [4]. These flaws originate from particulate inclusions in the precursor materials and dust particles present in the atmosphere during fiber manufacture. The main effect of most of these flaws is to introduce into the fiber misoriented regions where the basal planes are inclined at greater than average angles to the fiber axis. This results in large concentrations of shear strain energy in these regions when the fibers are loaded in tension to typical breaking loads. These large local concentrations of shear strain energy can be relieved only by cracks normal to the basal planes. Such cracks initiated in the vicinity of flaws are believed to be a main source of fiber failure, provided that crack propagation can occur. In graphitized fibers, enhanced crystallization is commonly observed around flaws, resulting in large crystallites with dimensions of up to about 0.3 μm. This size is similar to the expected Griffith crack size for typical high modulus tensile fiber strengths.

Work with graphite-aluminum composites[5] has indicated that notching of fiber surfaces degrades fiber strengths, Figure 3. This degradation has been traced to chemical reaction of the graphite fibers with aluminum to form Al_4C_3 on excessive exposure to high temperatures. Even microscopic surface pits are indicated to dramatically lower the strengths of both low and high modulus fibers.

To achieve high strengths in composites, it is essential to have graphite

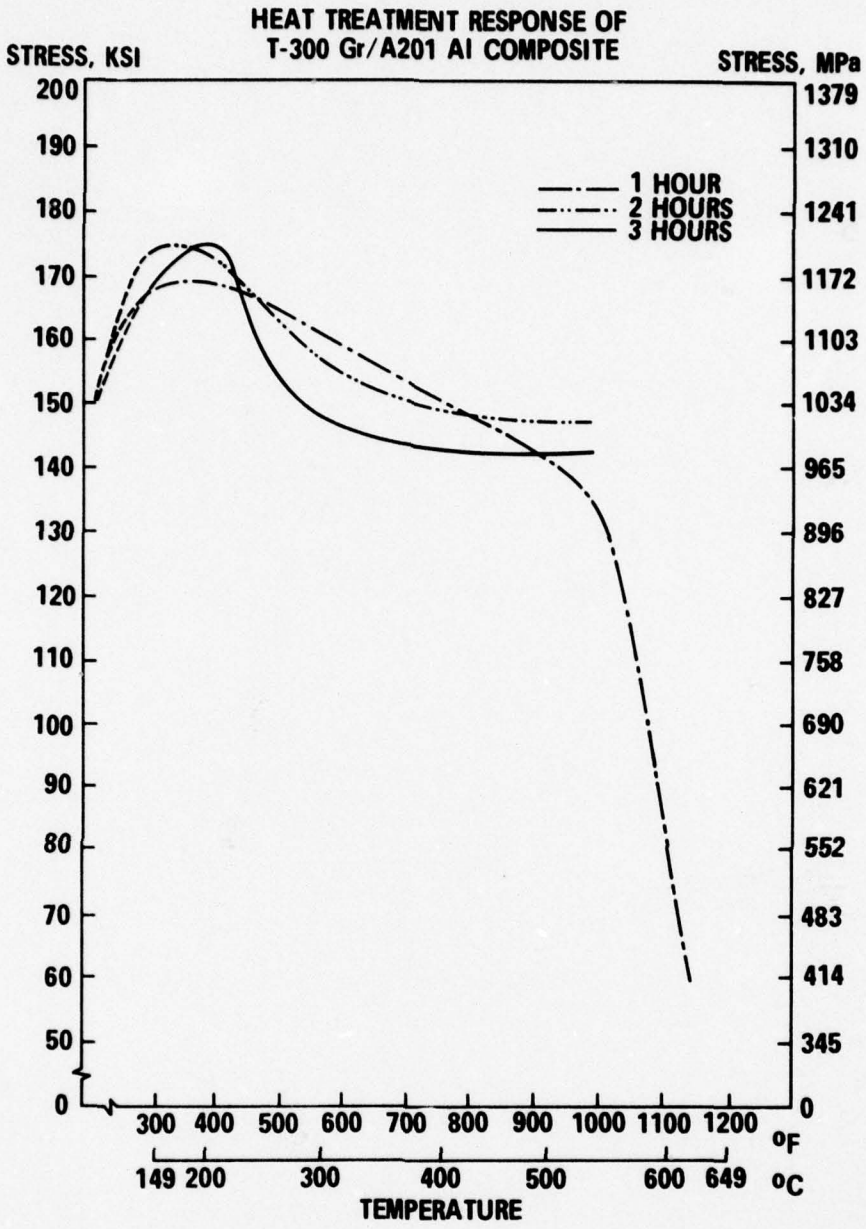


FIGURE 3. HEAT TREATMENT RESPONSE OF T-300 GR/A201 Al COMPOSITE

yarns and tows with high bundle strengths over long gauge lengths. In a given fiber bundle of 300 x 10^3 psi strength, one can frequently find, by single fiber testing at short gauge lengths, fibers approaching the 750 x 10^3 psi strength level, while many fibers have low strengths of less than 200 x 10^3 psi. To achieve high bundle strengths, it is extremely important, therefore, that processes are developed in production which yield graphite yarns and tows where all individual fibers have high strengths.

In practical commercial graphite fibers, mixed failures probably occur, and factors such as internal and surface flaws and the weaknesses of the layered graphite structure all probably limit strengths.

1.2.2 Chemical Treatment of Fiber

Ebert [6] has recently conducted an extensive review of the intercalation compounds of graphite. Successful attempts have been made through the use of chemical intercalation treatments to improve the modulus and strength of graphite. Vogel [7] observed a 69% increase in modulus of Thornel 75 fibers by intercalation with nitric acid, but observed a corresponding 21% reduction in strength. The improvement in modulus was due to enhancement of the alignment of the fiber structure on intercalation and decalation, and the loss of strength was thought to result from the leaching out of particulate foreign material residing on the fiber surfaces. Kalnin [8] also studied the effects of intercalation of strong acids in graphite fibers. Most of Kalnin's work was conducted on medium and low modulus graphite yarns, and no increase in modulus was observed, but significant strengthening (an increase from 360 to 430 x 10^3 psi) was observed on treatment of fibers with high concentration nitric acid solutions. Vogel [7] conducted tensile tests on a few single graphite fibers, and Kalnin carried out many bundle-yarn tests. Because of the different fibers used and differences in test methods used by the above workers, the true effects of nitric acid treatments on the mechanical properties of graphite fibers

are not clear. In other work [9,10], intercalation with bromine was observed to expand the graphite structure causing 'plasticity', and increase in strain-to-failure of the fibers. Unsuccessful attempts [11] were made to impregnate bromine expanded fibers with epoxy resin to improve strengths by filling internal flaws and 'cushioning' the graphite ribbons. Dietz [12] showed that intercalation with bromine could increase the strength of commercial PAN fibers by as much as 70%. No explanation was given of the possible effects of the bromine on the graphite fibers which may have caused strengthening. Stokes [13] has also shown that intercalation of PAN based graphite fibers with nitrogen dioxide produces very similar structural changes to bromine treatments (that of improving the alignment of the layered ribbon structure). It is interesting to note that NO_2 treatments left the fibers with very smooth and uniform surfaces in contrast to the pitting observed by Vogel [7] in nitric acid treatments to lower fiber strengths. Hooley [14] has studied the intercalation of low and high fired graphite fibers with metal chloride vapors in the presence of free chlorine. Low threshold pressures were observed for aluminum and iron chloride with a highly graphitic fiber fired at 2800°C. No intercalation was observed under the same conditions with a fiber which was fired at 1500°C.

1.2.3 In-Process Graphitization Treatment

It is well known that the presence of small amounts of boron accelerate graphitization in bulk graphite [15]. Diefendorf [16] studied the effects of introducing boron during the chemical vapor deposition of pyrolytic graphite and found a marked improvement in hardness and bending strength. A gaseous mixture comprised of 1130 dm^3 CH_4/hr. and 28.3 dm^3 BCl_3/hr. was heated at 2300° and 20 mm Hg to deposit 710 μ/hr. of pyrolytic graphite. X-ray spectra of the product showed that the material conserved a turbostratic structure and contained a very low amount of finely divided B_4C crystallites. The deposited graphite had a bending strength of 336 kg/cm^2, which is two times higher than the value of normal pyrolytic graphite,

and a hardness 2.5 times higher.

Ezekiel [17] has shown that boron additions of 0.1-1.1% dramatically increase the rate of graphitization of fibers, and observed up to a 300% increase in modulus and 50% increase in strength as compared to fibers fired under the same conditions without boron additions. The boron appears to facilitate bond migration during graphitization and the formation of the graphite network at lower temperatures than normally required. Boron acted as a graphitization catalyst regardless of the preliminary steps of yarn preparation. The general techniques used by Ezekiel were to 1) impregnate stabilized polyacrylonitrile precursors with a 5% aqueous solution of H_3BO_3, and 2) impregnate carbonized rayon yarns with boric acid solutions. Boron doped rayon precursor fibers of 376,000 psi tensile strength and modulus of 88 million psi were produced by graphitization at 2600-2700°C under applied tension. These rayon derived fibers produced by boron catalysis have a turbostratic structure with a high degree of graphitic order in comparison with commercial untreated graphite yarns. X-ray diffraction showed that the boron doped fibers have a more axial orientation, are more crystalline, and have interlayer spacings as low as 3.38 Å. Characteristic spacings for other commercial fibers are in the 3.42-3.44 Å range.

Singleton and Pears [18] studied the mechanical properties of pyrolytic graphite containing silicon carbide additions between 8 and 25 percent. They showed that the addition of minor amounts of SiC (14 volume percent) greatly modified the materials properties of the pyrographite by nearly eliminating the thermal expansion anisotropy, and greatly increasing the tensile strength in the C direction. Previous exploratory work at FMI has shown that pyrocarbon-silicon carbide coatings can be deposited on graphite fibers and can give up to 20 percent increase in tensile strength. Thornel 300 was used as a starting precursor in this work. However, the graphitization temperatures used were low (1700°C), and significant diffusion of silicon into the interior of the fibers probably did not occur. Additionally, it

is noted that the reduction or elimination of fiber thermal expansion anistropy will result in significant reduction of troublesome residual stresses in aluminum and other graphite fiber reinforced metal composites.

Jackson and Marjoram [19] have shown that nickel plated high modulus graphite fibers recrystallize rapidly on heating at 1100°C. A dramatic change was observed due to the presence of nickel, which acted as a catalyst causing recrystallization of the fibers and the formation of extensive three dimensional structural order and increased grain size. Other work by Derbyshire and Trimm [20] has also shown that transition metals such as nickel and iron catalyze the formation of three dimensional structural order in graphite. Petersen and Rulison [21] studied the inclusion of various other metals in graphite fibers, but poor strengths and moduli were observed.

In contrast to the above, work by Shorshorov [22] has shown that nickel diffused into a pyrocarbon coated graphite fiber surface increases the tensile strength of the fiber. The nickel layer is reported to be annealed at 1000°C to form a carbon solid solution in nickel. This heavy nickel coating has a plasticizing effect at the filament surface which increases fiber strength. A very inert fiber surface is needed for this process to prevent reaction between the fiber and the nickel layer which will cause fiber degradation. Large information gaps exist in this Russian literature. For example, the modulus of the starting fiber is unknown (very high modulus fibers are more chemically stable), and the thickness of the pyrolytic graphite coating and process conditions are not given.

The range of subject work has shown the potential for improving the strength and stiffness of graphite fiber through in-process and/or post graphitization chemical treatments. Therefore, the current problem addressed by the subject program was the application of these established concepts to a production method development.

1.3 CURRENT PROGRAM EFFORTS

1.3.1 Chemical Treatment

Post-graphitization chemical treatments of carbon fibers were approached in a practical manner and only methods suitable for full scale production processing were considered for improving fiber properties. The success of each treatment process was evaluated by testing the mechanical properties of the yarn bundles. Several chemical treatment methods applied during the subject program were shown to diffuse elements and compounds into the interior of fibers. These include intercalation with Br_2, ICl, NO_2, $FeCl_3$ and plating with Ni. Only minor improvements in fiber strength were observed with the chemical treatments.

1.3.2 Arc-Plasma Fiber Treatment

Commercial graphitization of carbon fibers is currently limited in temperature by furnace capabilities. Typically, resistance heated carbon tube furnaces are used for graphitization where the top end temperature limits are approximately 2800°C. In techniques utilized at FMI during this program, fiber temperatures in excess of 3400°C can be obtained using an arc-plasma heat source. It is well known that the degree of graphitization is a function of the processing temperature. Therefore fiber properties are related to the maximum temperature achieved during graphitization. Usually the higher processing temperatures will produce a higher modulus fiber while the tensile strength goes through a maximum at < 2000°C and drops off at higher processing temperatures. Methods have been adopted in this program whereby both strength and modulus have been improved with increasing processing temperature. FMI's manufacturing method makes use of a boron doped pyrocarbon surface treatment to increase strength at higher processing temperatures.

2.0 TEST METHODS

2.1 PLASMA EMISSION SPECTROSCOPY

Plasma emission spectroscopy was used for chemical analyses of graphite fibers. The work was conducted using a Spectrospan III spectrometer. Samples were prepared for emission spectrometric analysis in a fashion that is consistent with the parameters to be investigated. To determine if various elements were present in or on the graphite filaments, the fibers were dry ashed in a covered porcelain crucible, the ash was dissolved in a suitable solvent and analyzed for the species in question.

Emission spectroscopy is a typical tool used for qualitative and quantitative elemental analyses. It is based on the fact that all elements when thermally or electrically excited emit characteristic radiations in the UV-vis region. Emission spectroscopy is concerned with the characterization of the wavelengths and the intensities of radiation produced. The radiant emission is stimulated by the thermal energy of an arc. The arc source for the spectrochemical analysis is formed with a pair of graphite or metal electrodes. This provides sufficient energy to volatilize the sample and convert the individual components to gaseous atoms or ions. The distribution of the elements in the vapor is related to their distribution or concentration in the sample. The instrument automatically blanks out all other superimposed radiation except that produced by the outer electrons of the excited atom or ion.

The Spectrospan III operates in the following manner. Samples, standard and blank, are introduced into the argon plasma from a nebulizer. The high energy plasma jet produces a complex spectrum and a high resolution Echelle grating spectrometer is utilized to measure spectral data. A special camera attachment interfaces directly with the instrument in such a manner that the output of the spectrometer is focused

onto a camera film. The entire spectral range from 1900 Å to 8000 Å is covered on one film exposure. For qualitative analyses, identification of photographed spectra lines is accomplished using standard element identification overlays.

Two characteristics of plasma emission spectroscopy made it important in these analyses. First was its specificity. The character of the wavelength pattern produced by each element is unique to that element. Second, this method of analysis has a high sensitivity, the detection limits range from ppm to ppb.

2.2 ION MICROPROBE MASS ANALYSIS

Ion Microprobe Mass Analysis (IMMA) was conducted on selected specimens to determine the distribution of boron in the graphite fiber. The IMMA focuses a beam of ions to a spot approximately 2 μm in diameter. This ion beam impinges on a surface and sputters ions from the surface in the 2 μm spot. The sputtered ions are directed through a mass spectrograph, and the chemical composition of the specimen in that spot is analyzed. The information obtained from the IMMA can be displayed in several ways: the detector output can be plotted as a function of mass/charge in a spectrum, the detector output can be displayed on a cathode-ray tube (CRT) as the spot is rastered over an area, the detector output can be displayed as a function of time on a CRT as the spot is swept across the specimen, or the detector output can be monitored on a recorder as a function of time as the spot sputters through a thickness of the specimen. The mass spectrum can be obtained in the spot mode or a raster mode and gives information about the quantity of each element present in the spot or rastered area. The mass map gives information about distribution of the elements in a given area, but the resolution is limited by the 2 μm spot size. The CRT plot of the detector output as a function of distance is also limited in resolution by the 2 μm spot size. The plot of detector output as a function of time can be used for a quantitative analysis of a layer as small as 100 Å.

2.3 MECHANICAL TESTING

Tensile properties of the graphite fibers were determined by fiber bundle tests rather than single filament tests. There is substantial variation in tensile properties between filaments and within an individual filament of graphite yarn. By bundle testing with a ten-inch gage length, properties representative of the graphite yarns were obtained. The test method used complies in substance with ASTMD2343-67 (72) and with Union Carbide WC-2551.

This method consists of impregnating the yarns or fibers with a suitable polymeric binder material, curing, and testing the finished strands in a universal testing machine. The binder used was Hysol R9-2039 resin with 35 phr Hysol H2-3561 hardener. The impregnated strands were cured at 68 $\pm$ 5°C for a minimum of 45 minutes. Load spreading tabs were bonded at 10-inch spacings to the ends of the specimens. The tensile tests were performed on an Instron machine with X-Y recording capability and precision crosshead dials for setting the gage length. All tests, except those on GY70 fiber, were instrumented with an extensometer. The GY70 fiber would not support the extensometer, so modulus was calculated from the chart speed. Tests were performed with a crosshead speed of 0.5 in/min and six tests were performed per fiber sample.

2.4 MEASUREMENT OF FIBER CHARACTERISTICS

Cross-sectional area and density of the graphite yarns were determined by liquid displacement as described in Union Carbide specification WC-2550. A one meter sample of the graphite yarn was weighed in air and then suspended in isopropyl alcohol and weighed again. The following formulas were used to determine the density and cross sectioned area:

$$\text{Density} = \frac{W_D}{(W_D - W_S)} \times \rho_\ell$$

$$\text{Cross Sectional Area} = \frac{(W_D - W_S)}{\rho_\ell \times L}$$

W_D = Weight in Air

W_S = Suspended Weight

ρ_ℓ = Density of suspension medium

L = Length of sample

3.0 CHEMICAL TREATMENT OF FIBERS

3.1 INTERCALATION WITH HALOGENS

3.1.1 Bromine Treatments

Initially processing to increase the strength of graphite fibers centered around treatment of various fibers with bromine. A number of different treatments were applied.

Previous work by Warner [9] indicated that intercalation of bromine plasticizes the graphite fibers and it was theorized that stretching the plasticized fibers during the chemical treatment would optimize this effect of bromine, helping move the graphite basal planes into a more highly aligned orientation along the fiber axis. Several fiber intercalation trials were carried out at room temperature using the vapor phase of liquid Br_2 as the intercalant source. Variations were made in the time of exposure to the saturated vapor, ranging from 48 hours to 14 days, and in the application of tension for stretching during bromination and/or debromination. Of the trials made, two isolated runs showed slight increases in the tensile properties upon mechanical testing of the chemically treated fibers. In the first run, Celion 6000, HMS/PVA 3000, and Pitch VSA-11 fibers were exposed to the saturated Br_2 vapor at room temperature for 50 hours. Following intercalation, the brominated tows were tensioned to their maximum loading (without breaking) on a variable tensioning device, and continuously debrominated at 160°C in argon under a constant tension. The experimental set-up is shown in Figure 4. Fiber residence time in the furnace for debromination was ∿3 minutes. After debromination, when the fibers were tested, the HMS fiber showed slight improvements in UTS with no change in modulus, see Table I. The Celion 6000 and Pitch properties from this run were lower than the as received fiber values. In the second run that showed an increase in fiber properties, Celion 6000, HMS/PVA 3000, and Pitch VSA-11 were exposed to the saturated Br_2

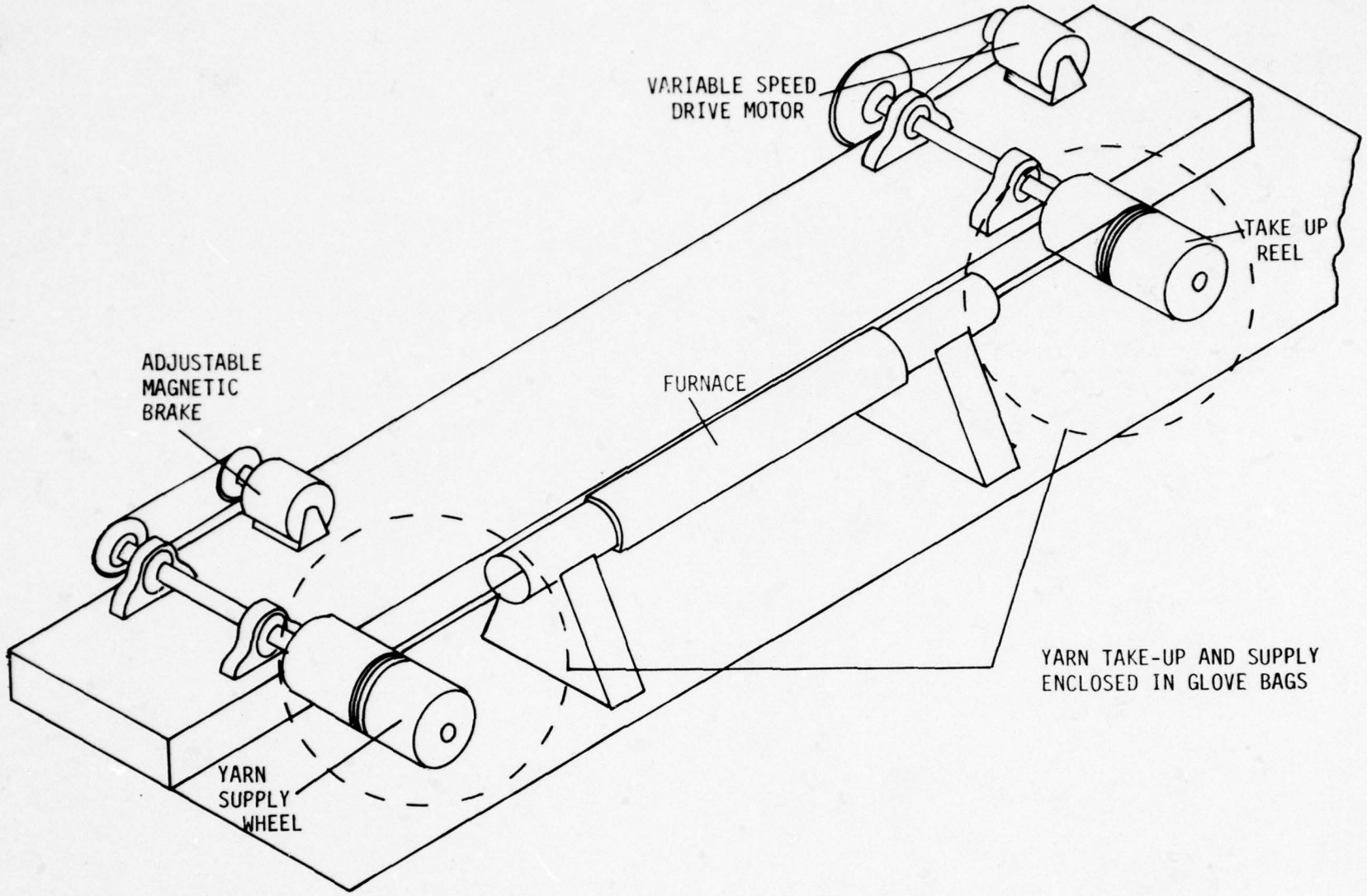


FIGURE 4. FIBER HOT STRETCHING SYSTEM

TABLE I. MECHANICAL PROPERTIES FOR BR_2 FIBER TREATMENTS

EXPERIMENTAL CONDITIONS	HMS/PVA 3K		HM/PVA 3K		CELION 6000		PITCH VSA-11	
	U T S (10^3 psi)	MODULUS (10^6 psi)	U T S (10^3 psi)	MODULUS (10^6 psi)	U T S (10^3 psi)	MODULUS (10^6 psi)	U T S (10^3 psi)	MODULUS (10^6 psi)
As received fiber (FMI tested)	407	51	389	54	411	36	147	72
2 days in a saturated Br_2 vapor; debrominated under tension at 150°C	425	51	---	--	376	35	158	69
4 days at R. T. and slightly reduced pressure in Br_2 vapor	---	---	358	48	377	31	---	--
14 days in a saturated Br_2 vapor; debrominated without tension at 100°C	424	48	---	--	374	33	130	63
Stretched in epoxy	---	--	285	45	378	34	---	--
3 min in 200mm Br_2/Aratm; 500°C without tension	---	--	334	53	---	--	---	--
3 min in 200mm Br_2/Ar atm; 500°C with 3lb. tension	---	--	337	52	---	--	---	--
3 min in 200mm Br_2/Ar atm; 800°C with 3 lb. tension	---	--	349	53	---	--	---	--
Boron coated HM in sat. Br_2 vapor 6 hrs. with 50g tension	---	--	260	55	---	--	---	--

vapor at room temperature for 14 days. Following intercalation, the brominated tows were debrominated in a batch at 100°C for 1 hour without tension or special restraint. After debromination, when the fibers were tested, again only the HMS fiber showed slight improvements in UTS, with no change in modulus. The Celion 6000 and the Pitch fibers showed slightly decreased properties in comparison to as received fiber. The other Br_2 intercalations of HM fiber at room temperature did not show the same promising results toward fiber improvement, see Table I.

In a related group of trials, HM fiber was chemically treated with Br_2 for short time intervals at elevated temperatures with and without an applied tension. It was thought that a high temperature (500-1500°C range) stretching in the Br_2 atmosphere would enhance and increase the rate of intercalation and optimize the effects of bromine intercalation on graphite fibers. Runs were made at 500°C and 800°C in $\sim$ 150 mm Br_2 in argon. The tension applied to the fiber tow was varied from 0 to 3 pounds and the fiber residence time in the reaction zone was 3 minutes. No measurable stretching of the HM fiber occurred during treatment. The fiber did not visibly appear degraded although mechanical testing showed a decrease in fiber tensile strength from as received. See Table I for average test results.

The ability to actually stretch the graphite fibers by combining bromine intercalation and plasticization with a physical loading along the fiber axis was considered to be limited by the amount of load being applied. It was thought that if the loading could be increased, stretching would be achieved. HM fibers, when impregnated with epoxy for mechanical testing, will have breaking loads in the range of 60-70 pounds whereas the same fiber tows dry were only achieving breaking loads of 4-6 pounds; less than 10% of the impregnated strength. This is because the epoxy matrix translates the load. The polymer fills the interfilament spaces in the fiber bundle and stress is more readily transferred

from one filament to the other, thereby increasing the overall fiber stress, preventing premature fiber failure. Knowing this, a different mode of stretching was devised, enabling greater loads to be applied to the chemically treated fibers. The fibers treated with Br_2 vapor were impregnated with an epoxy (resin Hysol R9-2039, hardener Hysol H2-3561) following their removal from the Br_2 vapor. Some debromination occurred before epoxy impregnation, however, previous workers report that debromination does not change the plasticization effects on the fibers due to the hysteresis effect, where some residual bromine remains even after decalation. After impregnation with the epoxy, fiber samples were tensioned in an Instron machine to 75% of their predetermined breaking load for 30 minutes. For the HM/PVA fiber this 'prestress' load was 50 pounds, for the Celion 6000 it was 103 pounds. An extensometer was used to record the fiber behavior during stretching and following the release of the load. The prestressed samples were then broken to determine UTS and modulus. It was determined that the prestressed fiber maintained an elongation of only 0.005" per inch of fiber and the mechanical properties were not appreciably changed. Refer to Table I for actual tensile averages.

In another trial a Br_2 intercalated HM/PVA 3000 fiber was prepared for further high temperature processing in the arc-plasma unit. The HM fiber was placed in the vapor intercalation chamber, Figure 5, and exposed to a saturated Br_2 vapor for 7 days at room temperature. After the fiber was removed from the intercalant source, it was allowed to decalate in air for a day before it was sealed in plastic bags and set aside for processing in the arc plasma unit. After the Br_2 treated HM fibers were graphitized in the arc plasma they were tested with no increase in strengths observed (for processing details and results see section 4.2.3). In a reciprocal trial, an HM fiber that had already been graphitized and borocarbon coated in the arc-plasma was taken and intercalated with the bromine. The boron processed HM fiber, with mechanical properties of 426×10^3 psi tensile strength and 64.4 million psi

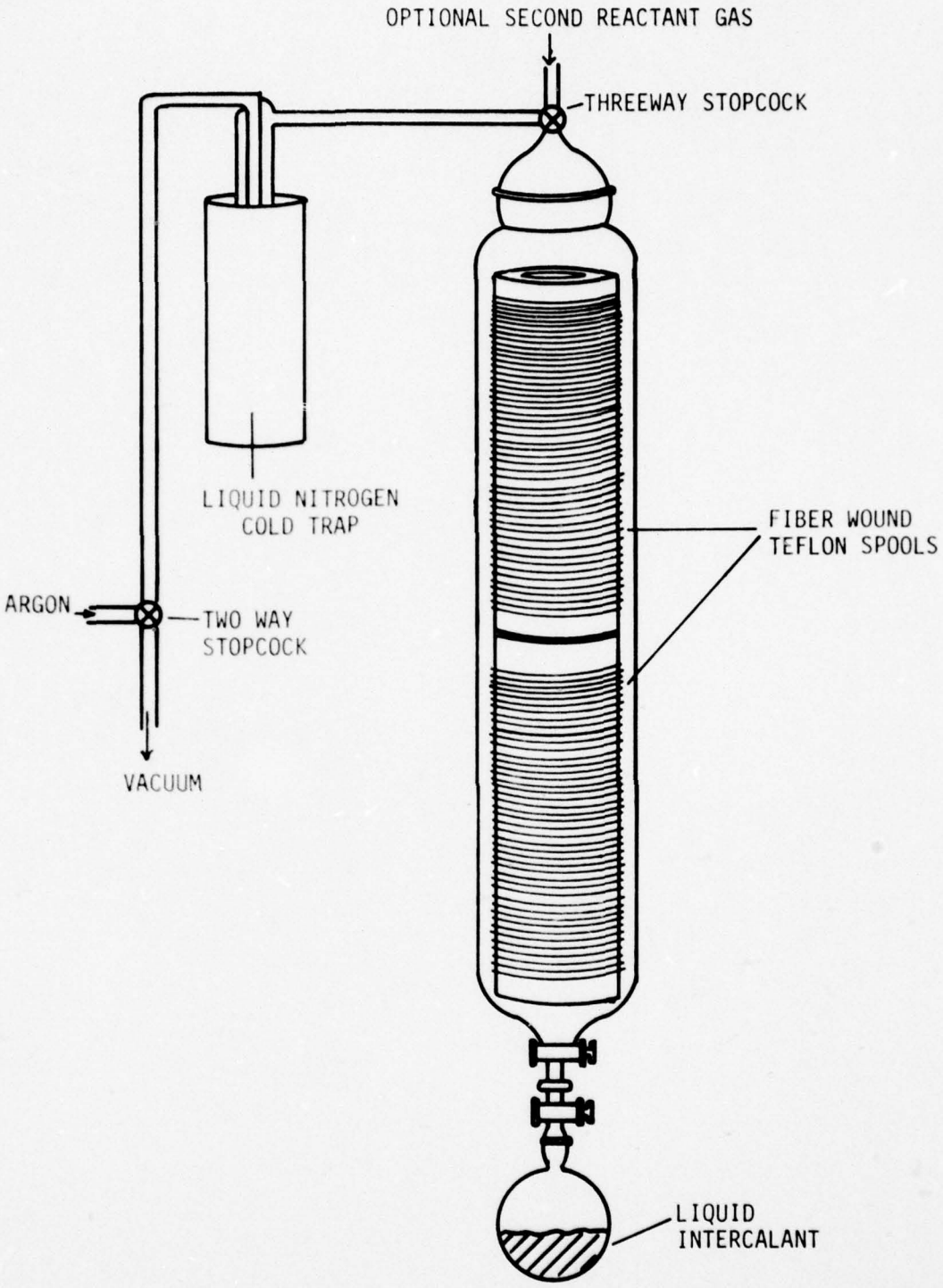


FIGURE 5. INTERCALATION CHAMBER

modulus, was treated in a saturated Br_2 vapor at room temperature for 6 hours with 50 grams of tension applied. Fiber degradation resulted. Mechanical properties of the fiber after Br_2 treatment were 260 x 10^3 psi tensile strength and 54.6 million psi modulus.

3.1.2 Iodine Monochloride Treatments

The interhalogen iodine monochloride, ICl, is known to intercalate graphite and have effects similar to bromine. Warner reported [9] that ICl created the same plasticization in graphite fibers as bromine. Therefore, in several of the bromine trials carried out, parallel ICl treatments were run. HM fibers were intercalated at room temperature* for various lengths of time ranging from 3-14 days. The fibers intercalated with ICl were mounted in epoxy for prestress testing and were also processed through the arc-plasma in conjunction with the bromine trials. In all of the trials it was found that the effect of chemical treatment with ICl was similar or identical to that already reported for bromine. The ICl either had little effect on the fiber properties, as with the epoxy impregnated stretch trial, or it caused a slight degradation of the fiber.

3.1.3 Chromium Oxychloride Treatments

Several trials were made exposing high modulus HM/PVA 3000 and Pitch VSA-11 graphite fibers to the intercalant chromium oxychloride (CrO_2Cl_2). The fibers were intercalated at room temperature for varying lengths of time (4-10 days) using a saturated vapor of CrO_2Cl_2 as the intercalant source. Pitch fiber and HM/PVA were also exposed to a CrO_2Cl_2/Ar atmosphere at 100°C for 4 hours, in an elevated temperature intercalation. In all cases, the fibers were degraded by the chemical treatment. The average mechanical properties for the intercalated HM/PVA 3000 were 307 x 10^3 psi UTS, 52 million psi modulus; for the Pitch VSA-11, 122 x 10^3 psi UTS, 63 million psi modulus. An HM fiber, intercalated with CrO_2Cl_2 for 11 days at room temperature, was

* ICl does not have as high a vapor pressure as bromine and often the experimentation was initiated by slight warming of the liquid ICl.

prepared for arc-plasma graphitization. As in the other trials, the presence of CrO_2Cl_2 or the reduced chromium oxide was most destructive to the fiber.

3.2 CHEMICAL TREATMENTS WITH METAL COMPOUNDS

3.2.1 Nickel Surface Coatings Using $NiCl_2$ Reduction By H_2

Initial chemical treatments utilizing nickel were based on Russian claims that nickel deposited on a carbon coated graphite fiber increased the tensile strength of the fiber [22]. A pyrolytic carbon surface coating was deposited on medium and high modulus PAN fibers via the decomposition of methane.

$$CH_4 \xrightarrow{1200\text{-}1700^{o}C} C + 2H_2$$

A nickel coating was then applied by the reduction of anhydrous nickel chloride by hydrogen at 900°C.

$$NiCl_2 + H_2 \longrightarrow Ni + 2HCl$$

The Ni coating on the fiber was annealed at 1000°C in argon for 1 hour. Measurements of mechanical properties showed a decrease in tensile strength (average UTS of HM fiber - 289 x 10^3 psi with Ni coating, prior to annealing; 220 x 10^3 psi after annealing.)

3.2.2 Nickel Coating by Nickel Resinate

The formation of a nickel coating on the graphite fibers was accomplished using a nickel metal-organic resinate solution. The Ni resinate, obtained from Engelhard Industries, Inc., Electro-Metallic Department, is a highly fluid metallic solution formed by the reaction of a metal compound with special organic compounds. The nickel resinate contained ~ 10% metal, the major fraction of the metal-organic consisting of organics which on firing are thermally decomposed leaving a very thin nickel film (500-2000 Å) on the filament surfaces. In the runs, several

graphite fibers were Ni coated; HM/PVA, a pyrocarbon coated HM/PVA, and GY70 fiber. The resinate was used both full strength and diluted to 25% with toluene. The method consisted of passing the fiber through the resinate solution, thereby wetting the fibers with a thin coat of metal-organic, evaporating the solvent at 100°C, oxidizing the organic portion in air at temperatures above 350°C, and firing the fibers in a reducing atmosphere of hydrogen to form the Ni film.

The coated fibers were ashed in air at 1000°C and the residue was analyzed by plasma atomic emission to verify the presence of nickel on the fiber. The Ni coated fibers were tested for mechanical properties and the average results are presented in Table II. The presence of nickel degraded the HM/PVA fiber, even with the pyrocarbon coating. The Russian claims of improved properties were never substantiated. The Ni coated GY70 properties were identical to the as received fiber, no increase or decrease in strength.

3.2.3 Nickel Surface Coating Using Nickel Carbonyl

The process of coating graphite fibers with nickel using a nickel carbonyl ($Ni(CO)_4$) decomposition was reviewed, but was judged too dangerous and costly a technique to be considered an inhouse method for this program. $Ni(CO)_4$ is a highly toxic carcinogen, making the process expensive on a laboratory basis and facilities were only available to coat 4" lengths of fiber. In light of these facts this method was dropped from consideration as a way to get nickel into or onto the fiber.

3.2.4 Iron Deposition Using Iron Carbonyl

Iron pentacarbonyl ($Fe(CO)_5$) was used to chemically treat HM 3000 fiber and a non-intercalating T-300 control fiber, at room temperature both in the vapor phase (with a saturated vapor) and in the liquid phase using a neat solution. The fiber surface sizings were removed by heating at 350°C in air for ½ hour to prepare them for chemical treatment. For vapor treatments, the HM and T-300 fibers were

TABLE II. MECHANICAL PROPERTIES OF NI COATED FIBER

FIBER	EXPERIMENTAL CONDITIONS	UTS (10^3psi)	MODULUS (10^6psi)
HM/PVA	Resinate/Toluene Soln. (2.5% Ni) 500°C Preheat in Ar/H_2atm Processed in arc plasma @ ~2700°C	313	52
Pyrocarbon coated HM/PVA	Full strength Resinate (10% Ni) Decomposed in H_2 @ 1000°C	110	46
GY 70	Full strength Resinate (10% Ni) Dried in air @ 100°C Decomposed in H_2 @ 400°C and 1000°C	265	63

exposed to a saturated $Fe(CO)_5$ vapor for a period of 4 days at room temperature. After exposure to the $Fe(CO)_5$ the fibers were allowed to sit for an hour in air (the equivalent of reducing the pressure of the intercalant) to "de-intercalate" before samples were placed in crucibles and burned off in air at 1000°C for several hours. The control T-300 left no residue ash while the HM fiber left a rust color powdery ash, evidencing fiber intercalation of the $Fe(CO)_5$. For solution chemical treatments, the fibers (sizing removed) were wound onto teflon cylinders and immersed in neat liquid $Fe(CO)_5$ at room temperature for ½ hour. After removal from the reactant liquid, the fibers were allowed to sit in the open air to "dry"- allowing the surface $Fe(CO)_5$ to volatilize off. The fibers were then burned away in the same manner as above and the residue ash was examined. Again, there was a slight powdery oxide residue from the HM fiber and no evidence of a residue from the T-300. After intercalation with $Fe(CO)_5$, the HM fiber was brittle and friable to the touch. Due to the visible fiber degradation caused by chemical treatment, no mechanical testing was conducted.

3.3 INTERCALATION WITH METAL HALIDES

According to Ebert [6], there are more than sixty halides known to intercalate various forms of graphite. Of these, three were of particular interest and were included in this program: nickel chloride ($NiCl_2$), ferric chloride ($FeCl_3$) and molybdenum pentachloride ($MoCl_5$). Nickel, iron, and molybdenum are known to have a catalytic effect on the graphitization of carbon. Molybdenum in particular forms an unusual intercalate compound with graphite. As a rule there is either a weak van der Waals interaction or a charge transfer between the inserted substance and the graphite layers. With Mo, the filled layer thickness is much smaller than the filled layer thickness calculated in an additive fashion by summing the atomic radius of molybdenum and the van der Waals thickness of the graphite net. Such a discrepancy indicates a chemical bonding of Mo atoms with the graphite net[23]

which could be expected to be beneficial in aligning and stabilizing an improved graphite layer structure.

3.3.1 $NiCl_2$ and $NiBr_2$

The methods for intercalating graphite fibers with $NiCl_2$ were examined and found to be unsuitable for the purposes of this process. $NiCl_2$ is not soluble in any of the solvents commonly used in liquid intercalations, such as nitromethane, carbon tetrachloride or chlorosulfonic acid, and therefore vapor phase intercalation must be employed. Vapor phase intercalation of $NiCl_2$ requires that fiber and reactant be at temperatures in excess of 500°C, in an atmosphere of free chlorine gas, for an extended period of time ($\sim$ 4 days). This is a process that would not be easily adaptable to this program for safety reasons and ease of operation so other methods were utilized to incorporate Ni into or onto the fiber.

3.3.2 $FeCl_3$

Solution intercalation of ferric chloride ($FeCl_3$) was evaluated as a technique for introducing catalytic iron into the graphite layer plane of carbon fibers. Initial trials with anhydrous $FeCl_3$ dissolved to form a dilute solution ($\sim$ 0.1 M) in nitromethane (NM), carbon tetrachloride (CCl_4), chlorosulfonic acid ($ClSO_3H$) and bromine (Br_2), were performed and evaluated to find the most successful intercalant. A high modulus PAN fiber, HM/PVA 3000, and a low modulus PAN control fiber T-300, were chemically treated at room temperature in the dilute intercalating solutions for 30 minutes and rinsed with pure solvent until no color was observed in the wash (bromine treated fibers were washed with dilute HCl). The fiber samples were then placed in porcelain crucibles and burned off in air at 1000°C for several hours. When the ash residues were examined, the results were as follows: 1) both the HM and the T-300 fibers treated in bromine/$FeCl_3$ solution left a slight iron oxide ash, indicating an incomplete wash or that surface adsorption was taking

place (since T-300 is a non-intercalating fiber) 2) there was no appreciable residue, only a slight dust from the HM fibers treated in the $ClSO_3H/FeCl_3$ solution 3) a large amount of iron oxide residue was found from the HM treated in $NM/FeCl_3$ and the HM in $CCl_4/FeCl_3$ (the residue maintaining a fiber-like integrity). The T-300 samples showed no ash. From these preliminary trials it was concluded that $FeCl_3$ in nitromethane and in carbon tetrachloride were both satisfactory intercalating solutions. The $NM/FeCl_3$ system seemed to be the better intercalating solution, and was chosen as the sole method for incorporating iron into the fibers in subsequent trials. In addition, under consideration was the fact that nitromethane is less noxious than CCl_4 and is thought to enhance the intercalation of metal halides by participating in the reaction as an intercalant rather than as an inert solvent matrix [24].

In optimization of the intercalation of HM fibers with the $NM/FeCl_3$ solution, the fiber was cycled through multiple chemical exposures and solvent washes. It is known that on 'decalation' of an intercalated graphite, there is not complete removal of the intercalant species and a residue remains. Repeating the intercalation and decalation increases the residue amount, making it an additive effect. For this study, the HM fiber and the T-300 control fiber were placed in dilute ($\sim$ 0.1 M) solutions of the $FeCl_3$ in NM for 30 minutes at room temperature. This cycle was repeated three times, then samples of the treated fibers were placed in porcelain crucibles and burned off in air at 1000°C for several hours. The HM residue ash observed after burnoff was much the same as the ash from a single chemical exposure and wash. The weight of ash was not significantly increased. It is questionable whether this repeated treatment of the fiber was a more effective intercalation technique than a single exposure with a brief wash in pure solvent.

Ferric chloride present in graphite can be reduced in place by hydrogen at temperatures greater than 600°C to yield a combination of $FeCl_2$ and Fe. The

degree of reduction depends on reaction time and temperature. For example, reduction at 700°C for 80 hours results in an 80% reduction of $FeCl_3$ to Fe. When graphite is intercalated with $FeCl_3$ and reduced by hydrogen, it is known that a metal atom monolayer is formed between graphite layers with van der Waals forces between planes [24]. This type of intimate mixture of null-valent iron and graphite was thought to be the most desireable for catalyzing further graphitization of the high modulus graphite fibers and so $FeCl_3$ intercalated fibers were processed accordingly. The HM fiber, chemically treated in the dilute NM/$FeCl_3$ for 30 minutes and washed with NM, was reduced in an argon/hydrogen atmosphere at ∿ 675°C for 100 hours. The fiber was then processed through the arc-plasma unit (see section 4.2.3 for procedures) for graphitization.

Visually the fibers intercalated with the NM/$FeCl_3$ appeared unaffected by the chemical treatments, both before and after reduction. No fuzzing, brittleness or other signs of degradation were apparent. No mechanical testing was performed on the fiber until after the arc-plasma processing, see section 4.2.3 .

3.3.3 $MoCl_5$

Molybdenum pentachloride is known to intercalate graphite in its vapor phase and in solution with various solvents. The trial treatments carried out with $MoCl_5$ were chosen based on the results of similar work with the $FeCl_3$. A dilute (∿ 0.1 M) solution of anhydrous $MoCl_5$ in nitromethane was used to treat both a high modulus HM/PVA fiber and a T-300 control fiber. All handling of the $MoCl_5$ was performed in an atmosphere of argon with the exclusion of oxygen and moisture which decompose $MoCl_5$ immediately to Mo_2O_5, the characteristic "molyblue". The fibers were treated in the NM/$MoCl_5$ solution for 30 minutes, followed by a wash with nitromethane. A sample of each of the fibers was taken for burnoff evaluation of the success of intercalation. The temperature of the fiber burnoff was lowered

from 1000°C to 675°C because the molybdenum oxide, MoO_3, formed on heating $MoCl_5$ with oxygen, melts at 795°C. The MoO_3 ash from the HM fiber remaining after burnoff was taken as evidence that the $MoCl_5$ was diffusing/intercalating into the fiber.

To produce a Mo intercalated fiber, the HM fiber intercalated with $MoCl_5$ as described above, was reduced with hydrogen at $\sim$ 325°C, at temperature for 5 hours. This molybdenum fiber was then further processed or graphitized in the arc-plasma unit (see section 4.2.3).

4.0 ARC-PLASMA FIBER TREATMENT PROCESS

4.1 ARC-PLASMA FURNACE EQUIPMENT DESIGN

An arc-plasma fiber treatment facility was designed, assembled, debugged and optimized under this program. The facility consists of arc-plasma heating equipment and a fiber handling system. Both units were constructed in parallel efforts during the beginning of the program. The results is an extremely versatile tool for fiber processing. The following are some of the processing parameter characteristics of the facility.

(1) Fiber bundles can be quickly and uniformly heated to temperatures in excess of 3200°C on a continuous basis.

(2) The fiber process speed can be varied from 0 to 100 feet per minute with a minimum of fiber damage.

(3) Fiber tension can be varied from 0 to 20 lbs.

(4) The reaction atmosphere can easily be controlled and varied.

Figure 6 shows the arc-plasma fiber treatment facility. Figure 7 is a schematic illustration of the facility.

4.1.1 Fiber Handling System

During the program, the fiber handling system progressed from a vertical U-shaped arrangement to a horizontal straight line arrangement. Figure 8 illustrates these arrangements. The reason for the changes in the fiber handling system, was a continuous effort to minimize damage to the fiber.

The fiber handling system consists of a tension controlled feed roller, a winding mechanism, and various guide and alignment pulleys.

In selecting a tension controlled feed roller, a comparison was made between a Compensating Tension Control Unit* and a magnetic slip brake tensioned reel. The load on the fiber could be varied from 0 to 20 lbs. with the CTC unit and 0 to

* Manufactured by Compensating Tension Control, Inc., Orange, N.J.

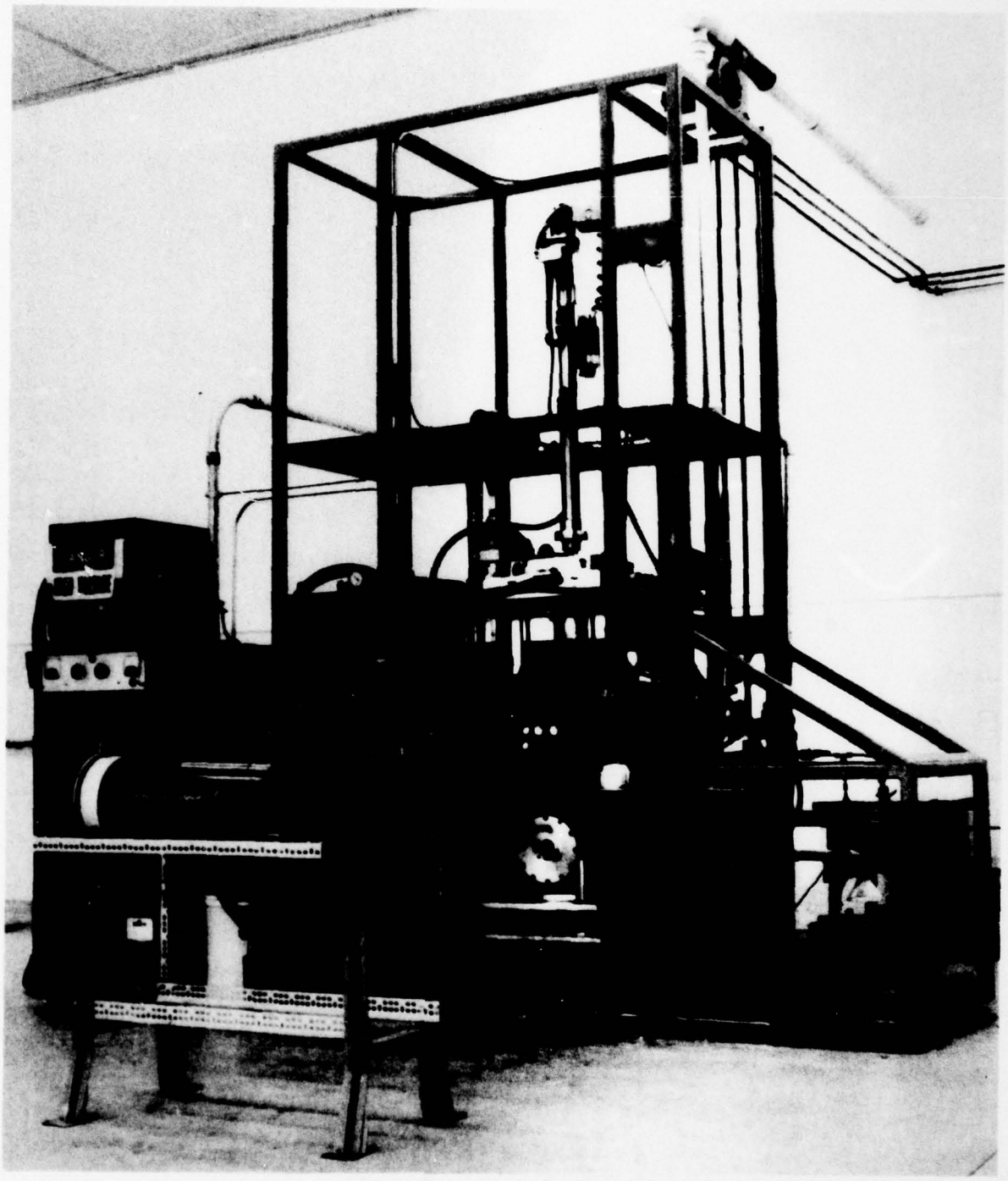


FIGURE 6. ARC-PLASMA FIBER TREATMENT FACILITY

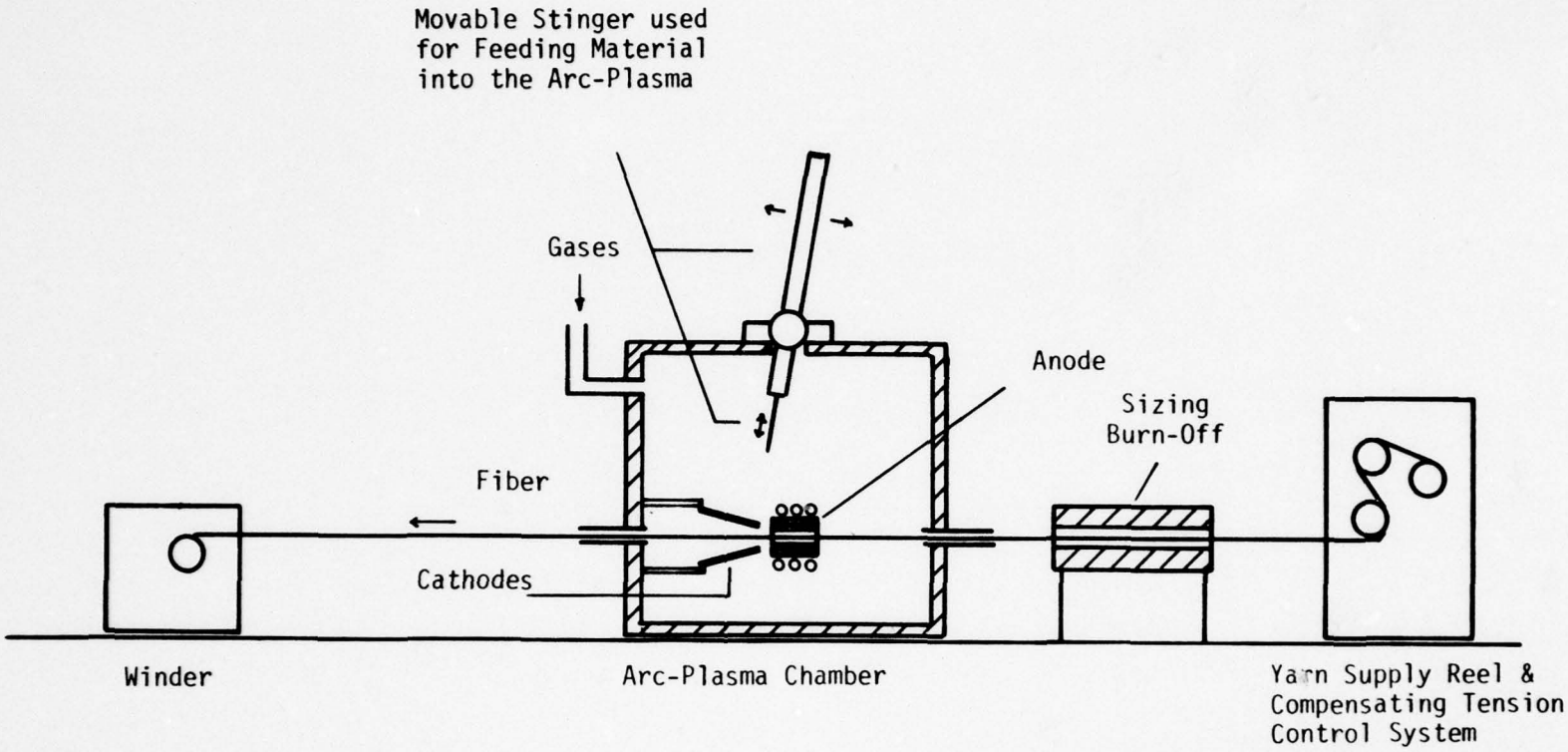
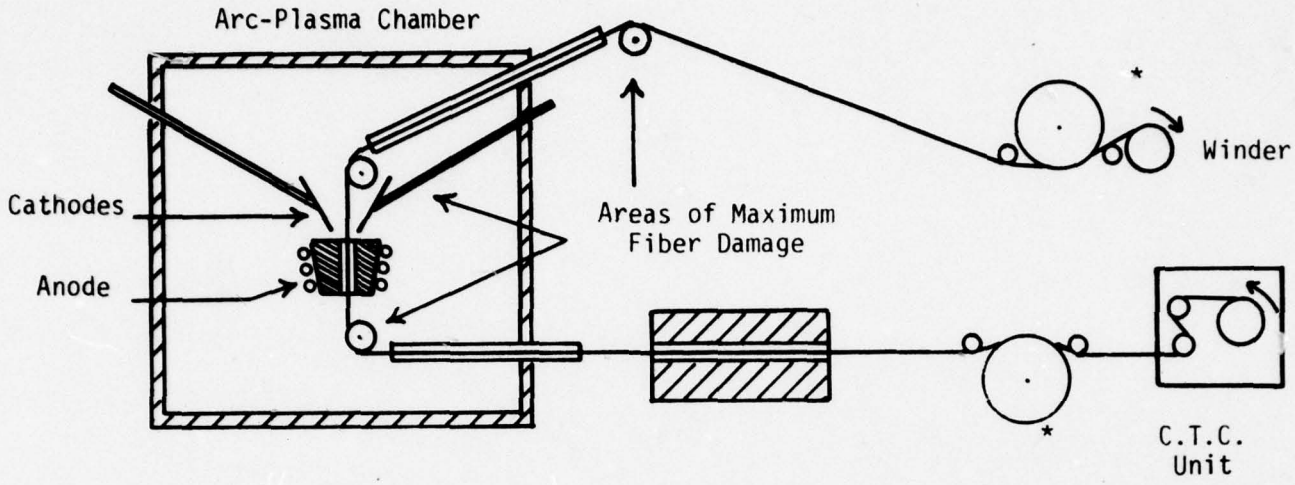


Figure 7. ARC-PLASMA FIBER TREATMENT FACILITY SCHEMATIC

Vertical Fiber Handling System (Original System)



Horizontal Fiber Handling System (Modified System)

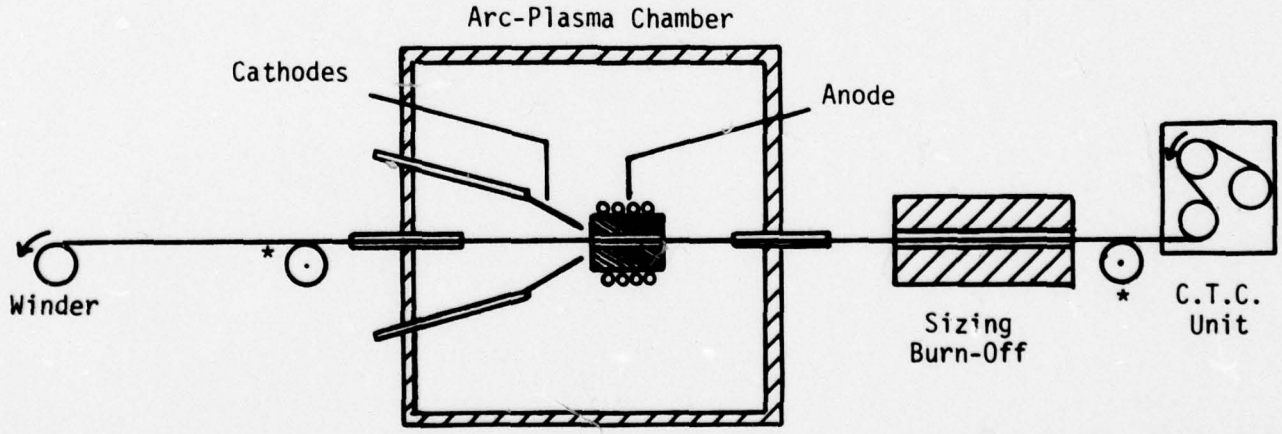


Figure 8. COMPARISON OF FIBER TRANSPORT SYSTEMS

10 lbs. with the magnetic slip brake tensioned reel. The CTC unit was selected because it proved superior in providing a more uniform load on the fiber. Non-uniform spacing of the fiber on the as received spool is compensated for by the two front rollers on the CTC unit. These rollers were modified by increasing the diameter from 2 to 4 inches in order to eliminate a sharp radius for the fiber to negotiate. Figure 9 shows the modified CTC unit.

The winder selected for the program was a No. 5 traversing winder manufactured by Auburn Machine Company of Providence, R.I.. The reeling mechanism can collect fiber on standard cardboard spools at speeds up to 500 feet/minute. It is powered by a variable speed motor and features an adjustable traversing mechanism. The unit was purchased with steel alignment pins on the traversing mechanism to guide the fiber. These pins were replaced with large diameter guide pulleys to prevent damage to the fiber, Figure 10.

The original vertical U-shaped fiber handling system consisted of numerous guide and alignment pulleys and several sharp angles for the fiber to negotiate, see Figure 8. Due to space limitations inside the arc furnace chamber, the two pulleys inside the chamber had diameters of only 2 inches. As a result of negotiating the numerous pulleys and sharp angles, the fiber was being degraded. The tensile strength of the as received HM fiber was degraded at room temperature from 382×10^3 psi to 297×10^3 psi by running it through this system.

In order to solve the fiber handling problems, the system was rearranged so that the fiber was pulled in a straight line from the feed reel through the arc-plasma chamber and to the take-up reel. To accomplish this, the arc-plasma anode and cathodes were changed from vertical to horizontal, see Figure 8. HM graphite fiber run through this system at room temperature showed no loss in tensile strength.

4.1.2 Tri-Arc-Plasma Heating

Reed [25] developed a tri-arc furnace for Czochralski growth of single

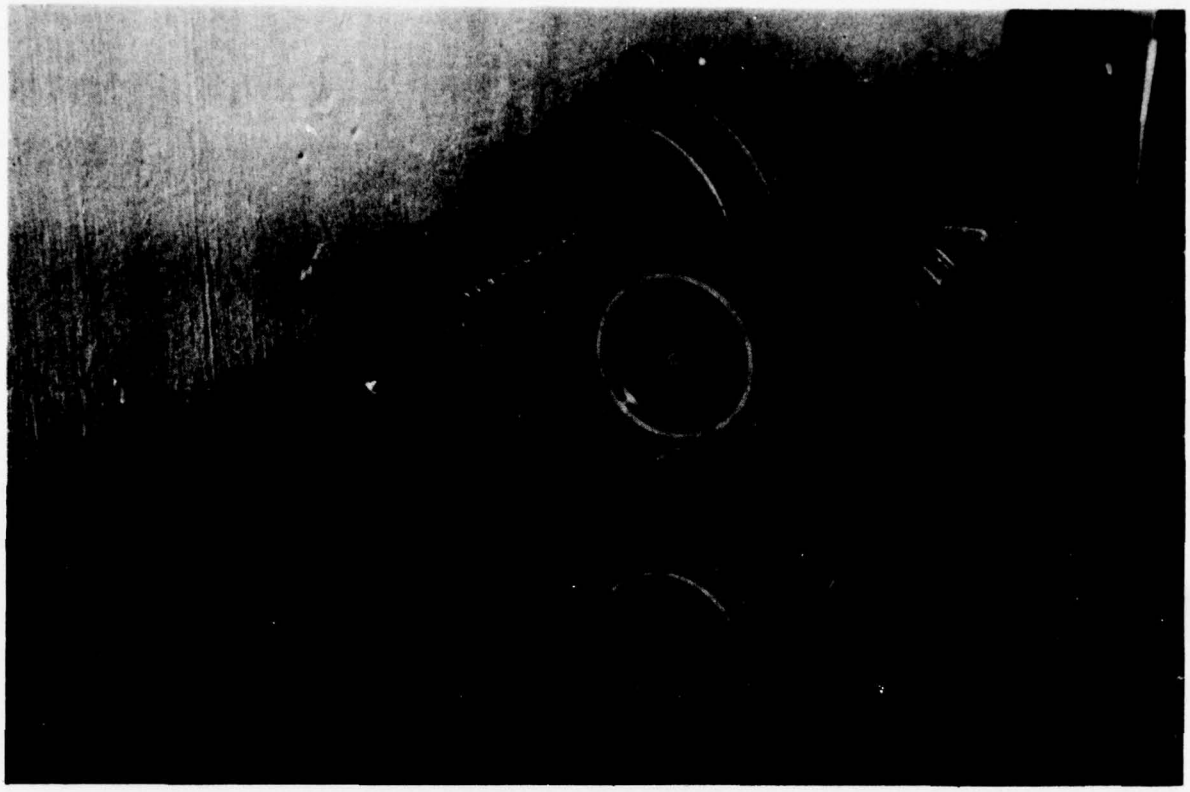


FIGURE 9. COMPENSATING TENSION CONTROL UNIT (MODIFIED)

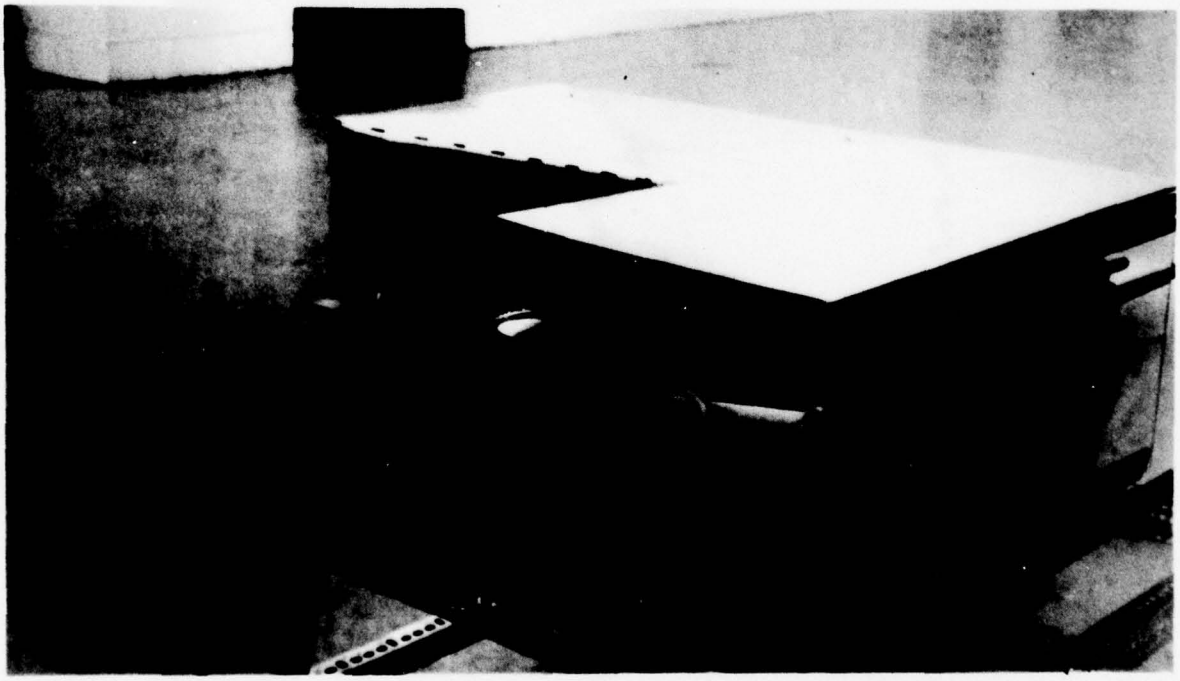


FIGURE 10. VARIABLE SPEED TRAVERSING WINDER (MODIFIED)

crystals during the 1960's. His furnace demonstrated the high temperature and uniform heating capabilities of tri-arc-plasma heating (> 3000°C). Under this program, equipment similar to Reed's tri-arc furnace was designed and assembled for heating fiber.

A typical arrangement of the equipment for tri-arc-plasma heating of fibers is shown in Figure 11. Three separately powered cathodes are uniformly positioned at 120° apart, pointing toward the edge of a centered hole in a cylindrical annular graphite anode. A water cooled copper coil is used to support, cool, and provide electrical contact with the anode. The cathodes are supported by water cooled rods which also provide electrical contact. The components are enclosed in a stainless steel chamber which has numerous ports. The ports are used for gas inlets, electrical feeds, fiber entrance and exit tubes, and viewing. The anode and cathodes are electrically insulated from this chamber. Power is provided by a 2000 ampere D.C. welding generator, to which the three cathodes are connected in parallel.

The initial objective with the arc-plasma furnace was to generate a stable tri-arc-plasma flowing from the cathode down the anode hole. To accomplish this task, the operating variables related to the cathodes, anode, reaction atmosphere and electrical requirements had to be determined. Once a stable arc-plasma was generated, optimization of the system continued throughout the program.

4.1.3 Cathode and Anode Design, Positioning and Materials

The design, positioning and materials of the anode and cathodes are critical for a stable arc-plasma. Many different combinations of these variables were tried in the attempt to find the optimum combination for fiber treatment. Figure 12 illustrates the sum of these combinations.

Various sizes of carbon and tungsten cathodes were evaluated. One quarter inch carbon rod cathodes provided the best performance. The tips of the

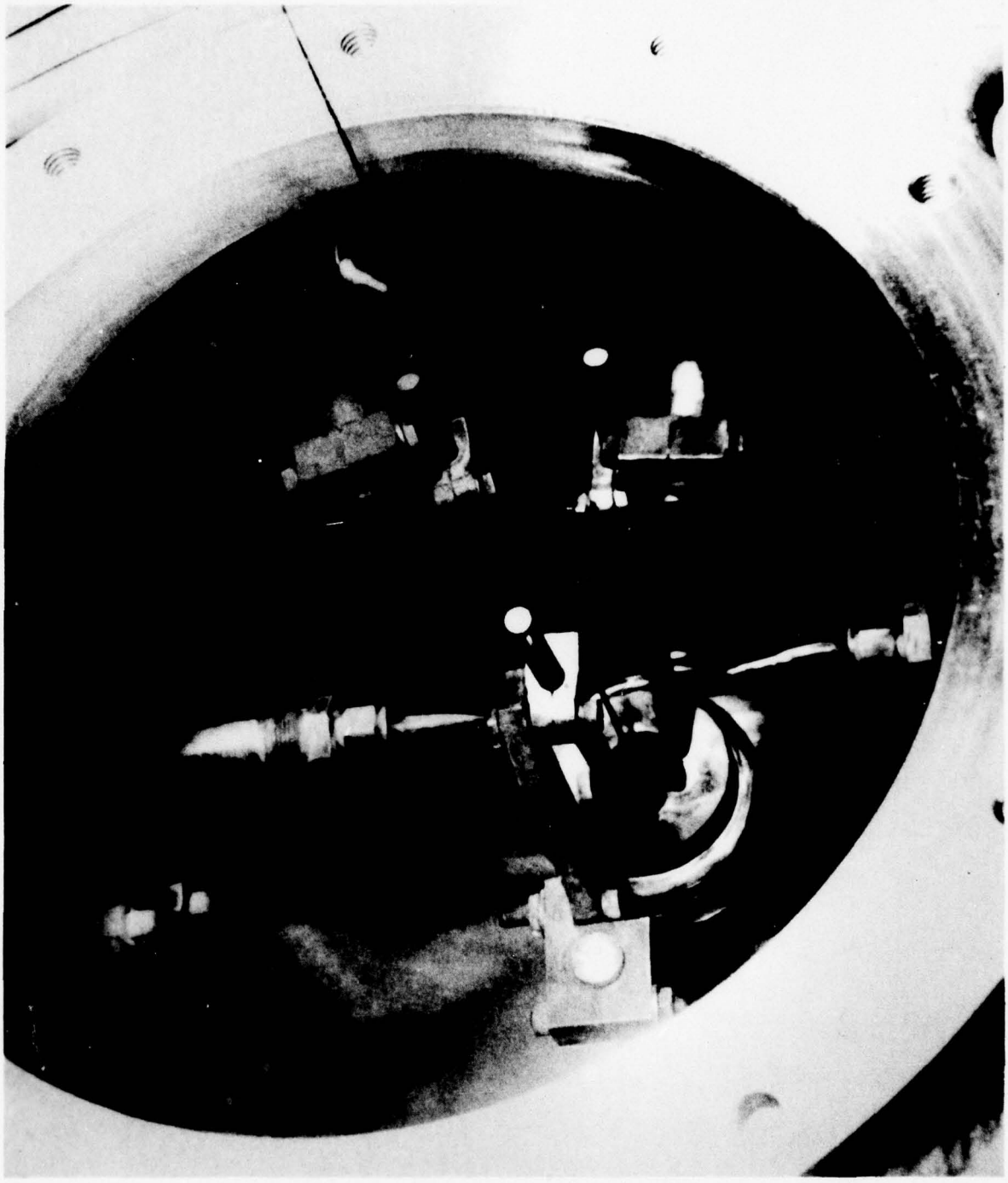
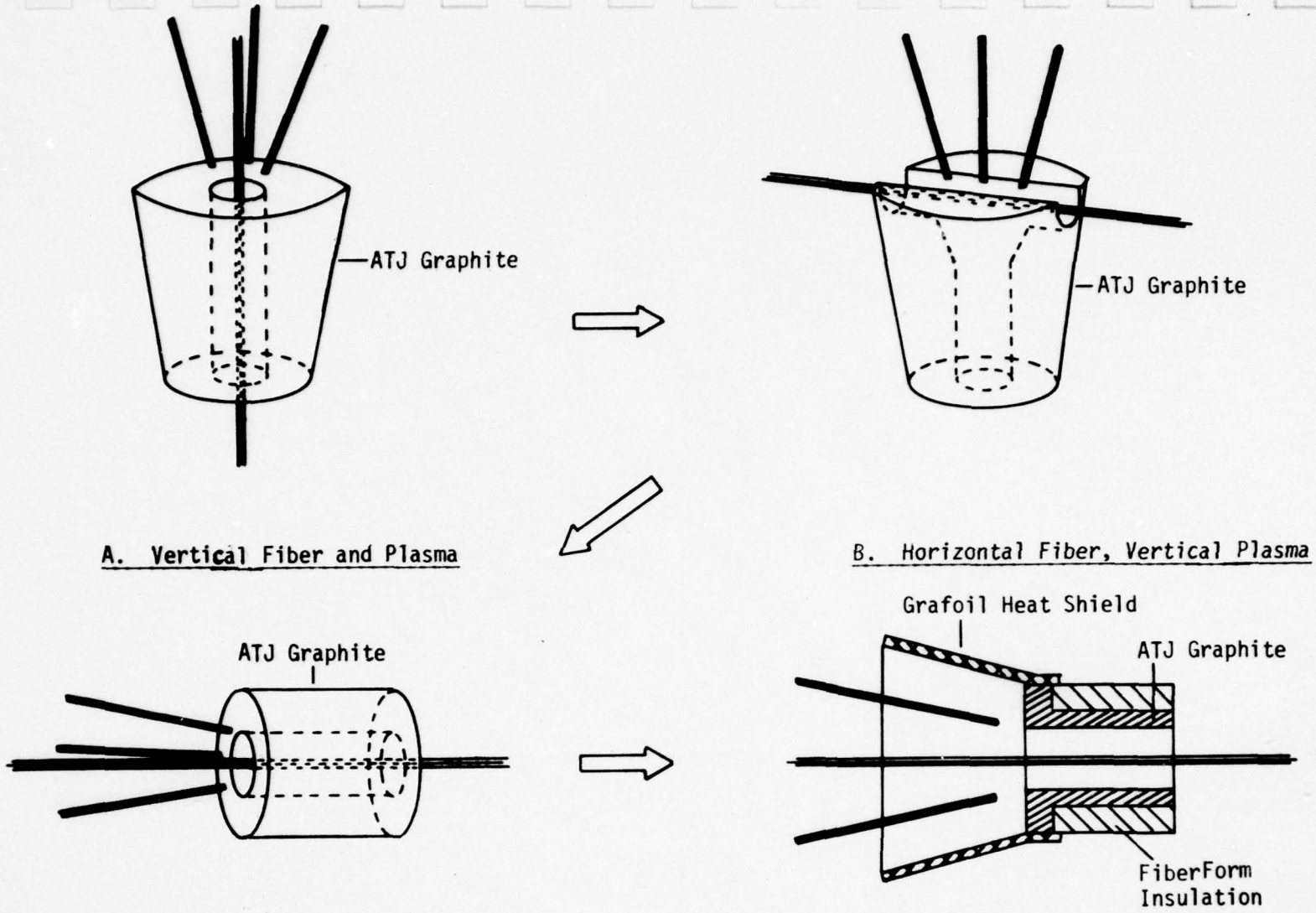


FIGURE 11. INSIDE VIEW OF THE ARC-PLASMA CHAMBER



A. Vertical Fiber and Plasma

B. Horizontal Fiber, Vertical Plasma

C. Horizontal Fiber and Plasma

D. Horizontal Fiber and Plasma with Heat Shield and Insulation

Figure 12. PROGRESSION OF THE ANODE DESIGN OPTIMIZATION

tungsten cathodes became hot enough to alloy with carbon in the reaction atmosphere and form tungsten carbide. This resulted in a lowering of the melting point of the cathode tips which caused arc instability.

The anode design went through a number of major changes during the beginning of the program. Originally, the fiber was drawn through the chamber vertically and the anode was in the vertical position. Due to problems with the fiber handling system, changes were made so that the fiber would run horizontally. Several attempts were made to combine a vertical anode with the horizontal fiber. This approach was abandoned due to the fiber being damaged by the high velocity gases emitted by the arc-plasma. The tri-arc-plasma components were rearranged so that the arc-plasma could flow parallel to the fiber.

The first anodes also had extremely good copper coil cooling with no insulation. This was done to prevent erosion, however it also limited the maximum temperature in the hot zone to 2600°C and the length of the hot zone to less than 1 inch. In several runs, increased fiber processing temperatures had resulted in increased fiber properties, so the anode was redesigned for high temperature operation. Optimization of the anode design involved reducing the number of copper cooling coils and adding insulation and radiation shields. The optimum design used on this program isillustrated in Figure 13. With this design, a 2 inch long hot zone was measured with an average temperature of 2900°C and a maximum temperature of 3100°C. This temperature profile was measured using the end of a graphite rod as a target for an optical pyrometer. Smoke present in the sight path and radiant heat loss made the measured temperatures lower than the actual temperatures by probably 100-200°C.

If the conditions are not right, the arc-plasma bounces back rather than traveling down the anode hole. The positioning of the cathodes to the anode and the size of the anode hole were determined to be critical factors affecting this.

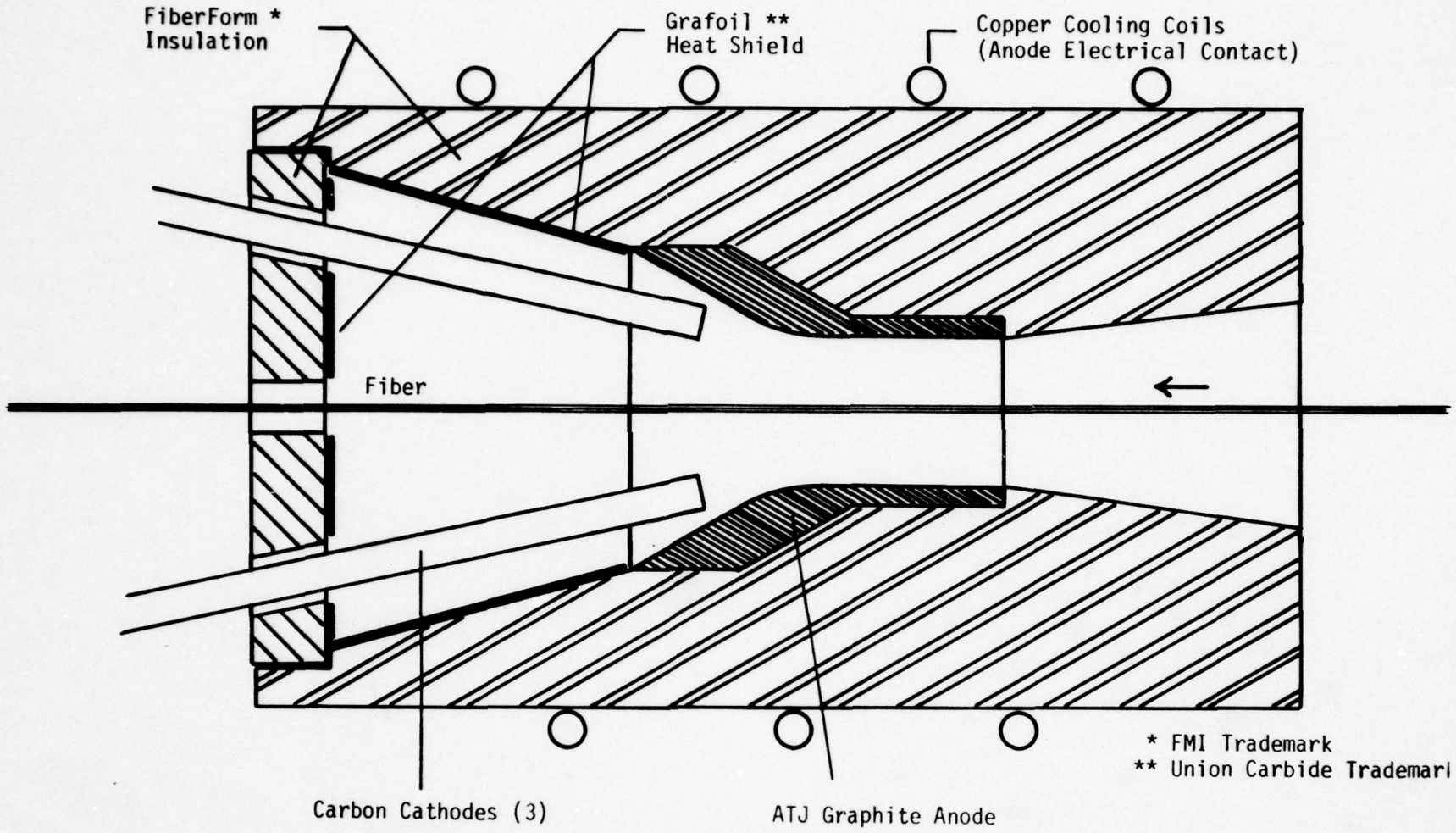


Figure 13. OPTIMUM DESIGN OF ANODE & CATHODES FOR ARC-PLASMA FIBER TREATMENT

It was found that the optimum position for the cathodes was at a 10° to 15° angle to fiber path, 1/8" to 1/4" from the anode surface. The arc-plasma bounce back problem was prevalent with 5/8 inch diameter anode holes. When the hole diameter was increased to 1 inch, it helped to alleviate this problem.

4.1.4 Reaction Atmosphere

An argon atmosphere was found to allow the generation of a stable arc-plasma. However, severe oxidation of the tungsten cathodes was occurring, possibly due to moisture evolved from the fiber surface during processing. Hydrogen was added to the argon atmosphere to help prevent the oxidation by providing a reducing atmosphere. Concentrations of H_2 in Ar were kept well below 5% by volume to insure exhausting of a non-explosive gas mixture. The addition of the H_2 was also found to increase the fiber and arc-plasma temperature obtained due to the energy released from the dissociation of the hydrogen molecules. The use of Ar/H_2 atmosphere proved to be excellent for plasma stability and long term running.

The use of nitrogen as an atmosphere was assessed to increase the heat transfer to the fiber from the arc-plasma and yield higher fiber temperatures. Arc-plasmas were difficult to initiate and unstable in the nitrogen atmosphere as well as in an argon/nitrogen mixture.

4.1.5 Electrical Requirements

Stable tri-arc-plasmas were generated with currents ranging from 200 to 600 amps, voltages ranging from 35 to 70 volts and individual cathode ballast resistance ranging from 0.7 to 1.0 ohms. Each of the arcs in the tri-arc must be stabilized independently by a ballast resistor in series with its cathode. Without the ballast resistance, only one arc would be generated from the cathode with the lowest gap resistance. The upper limit on the current level was determined by the cooling capacity of the development unit.

4.2 FIBER TREATMENT

4.2.1 Ultra High Temperature Stretch Graphitization

Initial fiber processing with the arc-plasma concentrated on ultra high temperature stretch graphitization in an argon/hydrogen atmosphere. The objective was to improve the strength and modulus of graphite fibers by improving the alignment of the crystal structure, increasing the degree of graphitization, and/or collapsing microvoids in the graphite fibers. The carbon furnaces normally used to manufacture graphite fibers have a maximum operating temperature of approximately 2800°C. By using the arc-plasma to heat graphite and carbon fibers, the goal was to increase the degree of graphitization in the fibers working at very high temperatures. The purpose of applying a load to the fiber during this graphitization operation was to improve the alignment of the crystal structure and collapse voids. It was believed that with the improved alignment and collapse of voids, stretching might be measured in the fiber. Stretching was measured by comparing the rpm of a wheel rotated by the fiber before it entered the arc-plasma chamber with the rpm of a similar wheel after the chamber.

The processing conditions and results of the initial ultra high temperature stretch graphitization runs are listed in Table III. Fiber temperature, tension, and residence time were the major variables involved. HM/PVA 3000 filament tow was processed in a Ar/H_2 tri-arc with temperatures ranging from 2950 to 3150°C. The residence time was varied from 0.33 to 0.55 seconds and the load was varied from 1 to 2 pounds.

As a result of the fiber treatment, increases in modulus were observed that roughly correlated with increases in the processing temperature. No improvement in ultimate tensile strength or significant stretching was measured in this series of experiments. The highly graphitic state of HM fiber before treatment was thought to be preventing additional alignment. Lower modulus Celion 6000 was processed under

TABLE III. ULTRA HIGH TEMPERATURE STRETCH GRAPHITIZATION RESULTS

Sample	Fiber	Current (amps)	Temp (C^{o})	Residence Time (sec)	Load (lbs)	% Stretching	UTS (10^3 psi)	Average Modulus (10^6 psi)
As Received	HM/PVA	--	--	--	--	--	382	53.5
028-6-1	HM/PVA	250	3000	.33	1.0	0	333	54.4
028-6-2	HM/PVA	250	3000	.33	1.5	0	341	51.9
028-6-3	HM/PVA	250	2950	.33	2.0	0	353	54.0
028-6-4	HM/PVA	450	3150	.33	1.0	0	319	56.3
028-6-5	HM/PVA	500	3000	.33	1.5	0	357	56.1
028-8-1	HM/PVA	500	3000	.33	1.5	0	325	55.5
028-8-2	HM/PVA	500	2900	.33	1.75	0	330	54.5
028-8-3	HM/PVA	500	2850	.33	2.0	0	334	55.6
028-8-5	HM/PVA	500	2950	.55	1.5	0	343	53.9

All runs made with an Ar/H_2 atmosphere

Properties reported are average of 6 samples

similar conditions in the hopes that it would show higher deformation with better alignment of the graphite planes. However, no promising results were observed using the Celion fiber.

4.2.2 Carbon Coatings

During past work at FMI, the deposition of carbon coatings on graphite fibers had shown evidence of fiber strengthening. Optimization of the pyrocarbon coating of graphite fibers was carried out using arc-plasma heating under this program. The arc-plasma was used to decompose methane (CH_4) which had been added to the Ar/H_2 reaction atmosphere. With the high electronic wind of the arc-plasma, a uniform chemically vapor deposited pyrocarbon coating was applied throughout the fiber bundle. Table IV shows the mechanical properties of HM yarn after various pyrocarbon treatments in the arc-plasma.

The pyrocarbon coating provided no improvement in properties above the as received fiber values. However, the coating did help to prevent fiber degradation in the arc-plasma caused by surface evaporation due to the high temperature and erosion due to dust particle impacts. It also reduced fiber fuzzing after plasma treatment by acting as a fiber sizing. For these reasons, pyrocarbon coating was a standard operation and CH_4 was added to the Ar/H_2 atmosphere for the remainder of the program.

Work was also performed with a glassy carbon coating to improve fiber handleability. A phenolic resin sizing was applied to the fiber. The resin was cured at 1000°C in an inert atmosphere to leave a thin glassy carbon coating on the fiber prior to processing in the arc-plasma. Figure 14 shows the equipment used. The glassy carbon coating provided good handleability for HM fiber both before and after firing. Work and use was discontinued on this coating because improvements in the fiber handling system eliminated the need for it.

TABLE IV PYROCARBON COATING OF HM FIBER IN THE ARC-PLASMA

SAMPLE		CURRENT (amps)	TEMP (^{o}C)	RESIDENCE TIME (sec)	LOAD (lbs)	SPECIAL CONDITIONS	UTS (10^3 psi)	MODULUS (10^6 psi)	% TOTAL STRAIN
HM/PVA Lot #75-4			As Received Fiber		--	--	382	53.5	.71
028-40	#1	550	> 3000	.33	1	--	361	54.2	.67
	2	550	> 3000	.33	3	--	359	52.8	.68
	6	400	≃ 2700	.33	1	No Sizing Burnoff	363	54.7	.66
	7	400	≃ 2700	.55	1	No Sizing Burnoff	371	51.5	.72
	8	400	≃ 2700	.33	1	--	362	51.8	.70
	9	400	≃ 2700	.55	1	--	360	51.7	.70

NOTES: All runs made with $Ar/H_2/CH_4$ atmosphere

Properties reported are average of 6 samples

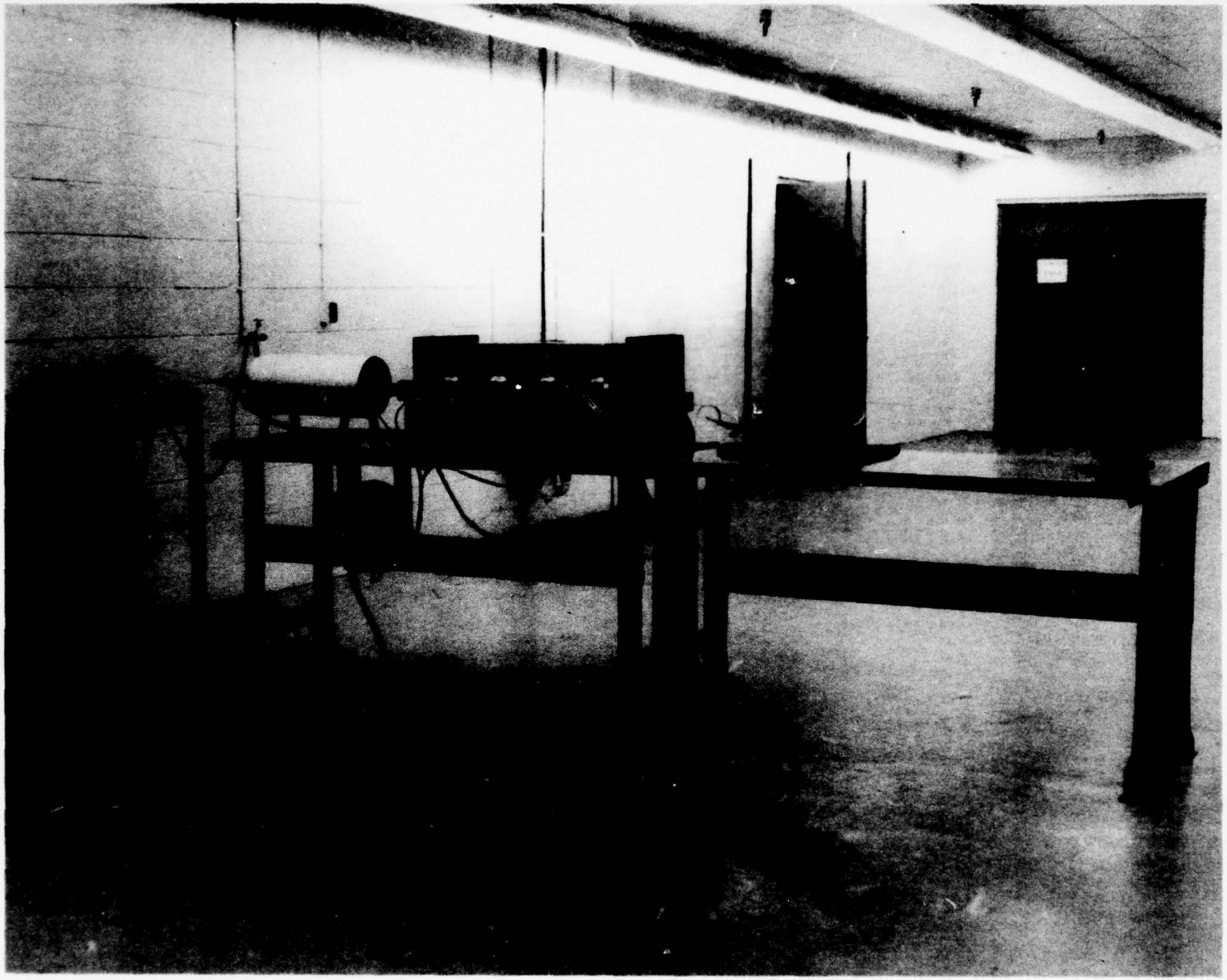


FIGURE 14. GLASSY CARBON COATING EQUIPMENT

4.2.3 Utilization of Arc-Plasma In Chemical Treatments

Carbon fibers that had been previously intercalated with various chemicals were processed in the arc-plasma facility. The effect of these chemicals on the mechanical properties of the graphitized fibers was observed. Br_2 and CrO_2Cl_2 were used to demonstrate the effect of removing a fugitive intercalant during processing, leaving only trace amounts in the final fiber. In this manner, the effect on graphitization of any atomic rearrangement by intercalation was observed.

$FeCl_3$ and $MoCl_5$ were also intercalated into HM fiber samples, however before processing in the arc-plasma the compounds were reduced to Fe and Mo by reduction in H_2. Fiber samples prepared in this manner, with elemental Fe and Mo dispersed throughout the fiber, were processed in the arc-plasma facility. Iron and molybdenum are known catalysts for bulk graphitization and this technique was used to study their effect on fiber graphitization characteristics.

Samples were processed in an Ar/H_2 arc-plasma flame at various temperatures and residence times. Severe fiber degradation was observed in processing the CrO_2Cl_2 and Br_2 samples. No fiber samples for mechanical property testing were obtained from these treatments. The Fe and Mo treated samples were processed and tested for mechanical properties. Both treatments caused a 50 % loss in fiber ultimate tensile strength from original fiber properties.

Recent work in the Russian literature indicates that a thin layer of Ni on pyrocarbon coated graphite fibers would improve mechanical properties. A nickel rod was vaporized in the arc-plasma facility while simultaneously processing HM fiber. In this manner, a thin Ni layer was deposited on the fiber surface from condensation of Ni vapor. Slight fiber degradation was observed in mechanical test results, as shown in Table V.

TABLE V. NICKEL PLATING ON HM FIBERS TEST RESULTS

Ni PLATING DURING PG DEPOSITION - ALL RUNS 400 AMPS, 2700°C, $Ar/H_2/CH_4$ ATM IN PLASMA FURNACE

SAMPLE		RESIDENCE TIME (sec)	TENSION (lbs)	UTS (10^3 psi)	MODULUS (10^6 psi)	% TOTAL STRAIN
028-44	#2	.33	3	322	54.2	.64
	#3	.55	1	287	50.8	.57
	#4	.55	4	331	52.1	.64

4.2.4 Boron Treatment

Previous work by Ezekiel [17] had shown that boron increases the rate of graphitization in carbon fibers and results in an increase in fiber properties. Under this program, the boron treatment of graphite fibers resulted in significant improvements in both strength and modulus. Table VI provides a list of the processing conditions and mechanical properties of several of the significant runs. Two things should be kept in mind when analyzing this data. First, the properties of the as received fiber varied substantially, as shown in Table VII. It is therefore important to examine the percent change in the processed fiber compared to the as received fiber, as well as the actual values for tensile strength and modulus. Second, the temperatures reported are the ones that were actually measured by using an optical pyrometer, sighting on the end of a graphite rod in the hot zone. Due to smoke in the reaction chamber and end conduction loss from the graphite rod these temperatures are probably 100 to 200°C lower than the actual fiber temperatures.

The first boron treatments in the arc-plasma were performed by adding BCl_3 to the $Ar/H_2/CH_4$ reaction atmosphere. The addition of boron resulted in up to a 6% increase in the tensile strength of HM 3000 graphite fiber, however, this increase was accompanied by a slight decrease in modulus (see run #028-46-2, Table VI). Further work on the CH_4/BCl_3 coating system did not yield improvements. The chemical intermediates which form during the pyrolysis of boron trichloride and methane have been found to interfere with deposition processes [26].

Boron trichchloride was replaced by triethylborane, $(C_2H_5)_3B$. This gas system, using organoboranes and hydrocarbons, does not form the harmful intermediates during pyrolysis. The initial results utilizing the triethylborane gave properties of 450 x 10^3 psi average tensile strength and 55.2 million psi average modulus on HM/PVA 3000 fiber. These are increases over the as received fiber of 11% and 2% respectively, see run # 028-64-4, Table VI. The graphite yarn had been processed in the arc-plasma at approximately 2600°C with a residence time of 0.3 seconds in

TABLE VI. BORON TREATMENT OF GRAPHITE FIBERS

		Tensile Strength (10^3 psi)		Modulus (10^6 psi)		% Change from As Received Fiber	
		Average	High	Average	High	Tensile	Modulus
#028-46-2	Boron Addition - BCl_3 Measured Temperature - ~2700°C Residence Time - 0.3 sec. Tension - 3 lb Fiber - HM	406	422	52.2	55.9	+6.3%	-2.4%
#028-64-4	Boron Addition - $(C_2H_5)_3B$ Measured Temperature - ~2600°C Residence Time - 0.3 sec. Tension - 1lb Fiber - HM	450	472	55.2	57.7	+11.3%	+2.4%
#032-62-4	Boron Addition - $(C_2H_5)_3B$ Measured Temperature - ~2650°C Residence Time - 0.7 sec. Tension - 3 lb Fiber - HM	420	451	59.3	60.4	+11.1%	+12.7%
#032-28-1	Boron Addition - $(C_2H_5)_3B$ Measured Temperature - ~2900°C Residence Time - 1.4 sec Tension - 3 1/2 lb. Fiber - HM	426	450	64.4	66.2	+14.8%	+24.6%
#032-22-3	Boron Addition - $(C_2H_5)_3B$ Measured Temperature - ~3000 Residence Time - 0.7 sec Tension - 4 lb. Fiber - HM	360	379	69.5	71.5	-3.0%	+34.4%

NOTES: All runs made with $Ar/H_2/CH_4$ atmosphere, Temperature Measurements are probably low by 100 to 200 C. Properties reported are the average of six tests.

the high temperature zone. The back tension was held at 1 pound. The ratio of carbon to boron in the $Ar/H_2/CH_4/(C_2H_5)_3B$ atmosphere was 20:1.

During further optimization of the boron treatment of graphite fibers, many combinations of the operating parameters were made. The temperature of the fiber during processing was found to be the major variable affecting fiber properties, as shown in Table VI. Increases in the modulus values were found to correspond with increases in fiber processing temperatures. At temperatures of 2600°C and below, no significant increases in modulus was observed. At temperatures of 3000°C, the modulus was increased over 20% from the as received fiber up to values of 70 million psi. The ultimate tensile strength values did not show a direct correlation with fiber processing temperatures. Between measured temperatures 2600°C and 2900°C, the increase in tensile strength varied from 5 to 15%. At measured temperatures above 2900°C, tensile strength values usually declined.

By analyzing the changes in weight, density and cross-sectional area of the processed fibers, it was determined that significant evaporation of material from the fiber surface was taking place at measured temperatures above 2900°C, see Table VIII. The low tensile strength values of fiber processed above 2900°C may be accounted for by the evaporation loss. Carbon evaporation was also evident on the cathodes and anode hardware, limiting running time. The strongest portion of PAN precursor graphite fibers is the highly aligned outer layer of the filaments which is damaged at these extreme conditions.

To overcome the evaporation problem, a sacrificial coating was applied to the fiber before the high temperature processing. The sacrificial coating was borocarbon deposited at 2800°C. When the fiber was reprocessed at 3000°C no net change in cross-sectional area occurred, since the coating evaporated rather than the actual fiber surface. However, in the three double processing runs that were made, no increase in mechanical properties was seen.

TABLE VII. VARIATION IN AS RECEIVED FIBER PROPERTIES
(FMI TEST DATA)

HM-PVA LOT #75-4

SPOOL #	TENSILE STRENGTH (10^3 psi)			TENSILE MODULUS (10^6 psi)		
	Average	High	Low	Average	High	Low
225	409	428	374	52.7	53.1	50.1
226	369	384	348	52.7	54.0	51.9
227	341	363	300	51.7	54.6	49.8
228	399	422	358	53.9	55.8	50.9
229	344	388	275	48.1	50.1	47.1
230	371	401	326	51.7	55.1	50.1
231	372	393	349	53.6	55.3	51.9

TABLE VIII. FIBER SURFACE EVAPORATION DATA

FIBER EXPERIMENTAL DESIGNATION	MEASURED PROCESSING TEMPERATURE	CROSS-SECTIONAL AREA	AVERAGE ULTIMATE TENSILE STRENGTH	AVERAGE TENSILE MODULUS
032-62-4	2650°C	$19.6 \times 10^{-5} in^2$	420×10^3 psi	59.3×10^6 psi
032-28-1	2900°C	$17.1 \times 10^{-5} in^2$	426×10^3 psi	64.4×10^6 psi
032-22-3	3000°C	$15.6 \times 10^{-5} in^2$	360×10^3 psi	69.5×10^6 psi

Optimization of single processing conditions has shown that measured temperatures of $\sim 2800^{o}C$ (actual fiber temperature > $3000^{o}C$), with processing speeds of 7 ft/min, yield consistently good fiber properties. The higher temperatures appear critical for attainment of further improved properties, however, the evaporation loss is limiting the attainment of property increases.

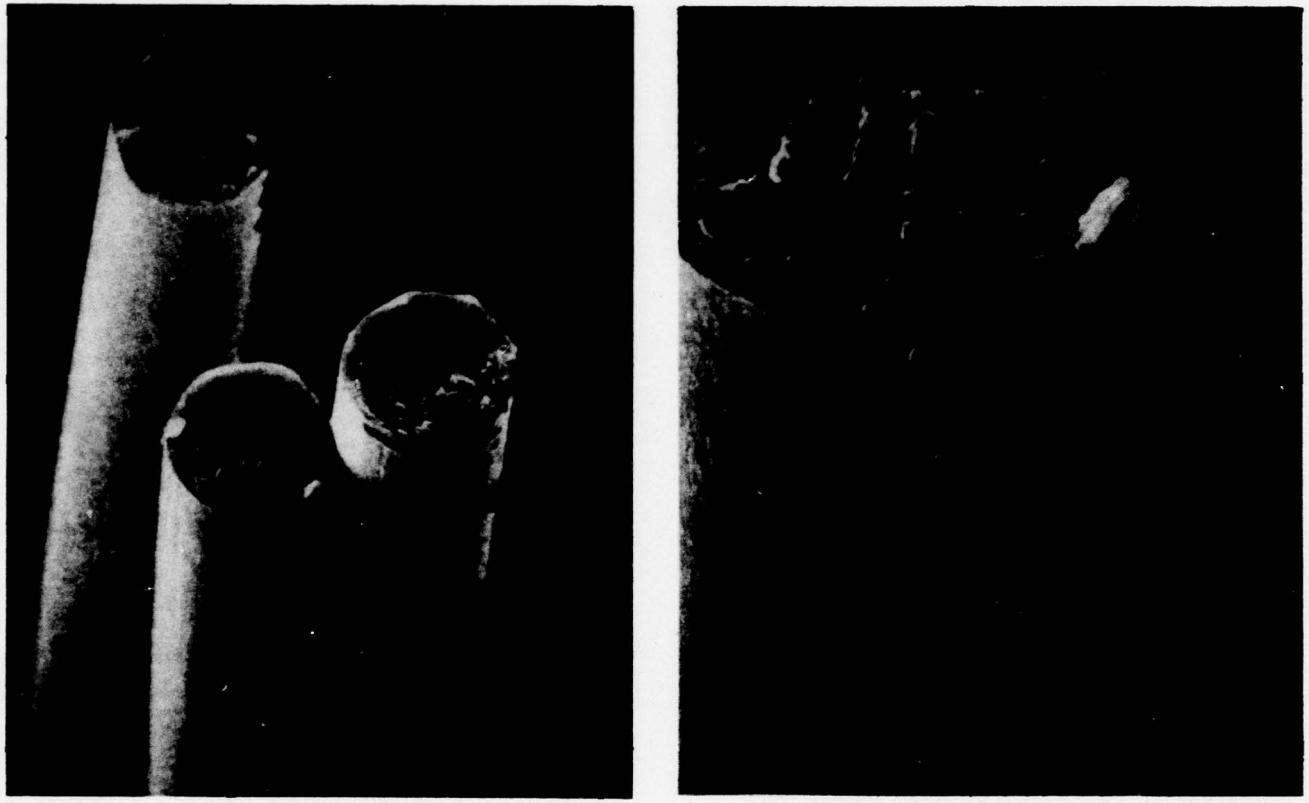
Analysis of FMI boron strengthened fibers by SEM has shown that the fiber surfaces are very smooth as compared to untreated fibers. Figure 15 shows the good surface finish of the boron doped fiber. The analyzed fiber showed no decrease in diameter which indicates that surface defects were healed rather than removed as in most chemical surface treatments.

Detailed microanalyses of the improved boron doped fibers are currently in progress at the Aerospace Corporation* using Ion Microprobe Mass Analysis (IMMA) and Scanning Auger Microscope (SAM) analyses. Preliminary work with the IMMA has shown that the fibers contain boron distributed throughout the fiber cross-sections. Fibers located both on the outside and inside of yarn bundles were found to contain similar amounts of boron, indicating that boron deposition and diffusion into the fibers occurred uniformly throughout the yarn bundles during the boron strengthening process. Additional work is being carried out to estimate the boron concentrations and distributions from the surfaces to the centers of the fibers.

4.2.5 Fiber Precursor Study

Various fibers other than the Hercules HM/PVA were tested in the arc-plasma boron strengthening process. Carbonized rayon, low modulus PAN, high modulus PAN, and Pitch graphite fibers have all been processed with varied success. Table IX summarizes the results of these fiber treatments. Improvements in properties were observed in graphitizing the carbonized rayon yarn (VYB/PVA), however, they are well below the properties available by commercially graphitized rayon fibers. The

* Work being conducted outside the contract scope under the auspices of Dr.M.F. Amateau.



3000 X

10,000 X

FIGURE 15. BORON STRENGTHENED FIBER SURFACES BY SEM

TABLE IX. EFFECT OF FIBER PRECURSOR ON ARC-PLASMA BORON STRENGTHENING PROCESS

SAMPLE #	FIBER	AS RECEIVED PROPERTIES		TREATED FIBER PROPERTIES	
		UTS (10^3 psi)	E (10^6 psi)	UTS (10^3 psi)	E (10^6 psi)
028-62-6	VYB/PVA	120	6	190	20.6
028-64-3	T-300	382	32.5	254	27.5
032-36-9	VSA-11	178	50	166	53.1
028-64-5	GY 70	260	62.4	340	70.5
032-28-1	HM/PVA	370	51.7	426	64.4

low modulus PAN fiber (T-300) exhibited a loss in mechanical properties as a result of the ultrahigh temperature treatment. The poor results of the above trials are probably due to the outgassing and thermal shock in the fiber as it is rapidly heated to temperatures well above what they had been previously processed at.

The Pitch precursor graphite fiber (VSA-11) showed little change in mechanical properties by treatment in the arc-plasma boron strengthening process. This may be due to the large number of internal flaws in the fiber which are not being healed in this surface treatment. Recent advances in the state-of-the-art for Pitch fiber manufacture may produce a fiber more amendable to this process than the fiber used in this study.

In addition to the HM/PVA, Celion GY70, another high modulus PAN fiber, has been processed with significant improvement in properties. This fiber is of a dogbone cross-section rather than round as in the HM/PVA. The filament size is approximately 5 x 13 microns giving a larger surface area of fiber with the same cross-sectional area as the HM/PVA. This increased amount of surface area may be responsible for the larger improvement in tensile strength as compared to the HM/PVA fiber. Other internal defects within the fibers are most likely limiting the absolute values of the tensile strength.

5.0 DISCUSSION

Achievements during the program have confirmed the findings of Diefendorf [16] and Ezekiel [17] on the effects of boron on graphite and demonstrated a potentially low-cost high-speed production oriented process for the boron strengthening of fibers. Fibers are continously processed under tension in an arc-plasma flame, and fiber temperatures in excess of 3000°C can be attained if desired. Graphitization of carbon fibers in an arc-plasma was demonstrated prior to the FY 78 program [27], and graphitization of boron doped fibers in the reducing cone of an oxy-acetylene flame was demonstrated by Ezekiel [17]. An intense electrical wind generated in the plasma gives uniform heating and boron deposition throughout fiber bundles. The arc-plasma flame is generated between three carbon cathodes and a cylindrical annular graphite anode, and the fiber is passed through the anode hole with the flame. Handling damage to the fibers is minimized with an in-line orientation of the arc between the fiber feed and take-up reels. Significant improvements in fiber properties have been observed with the above boron strengthening process. High values of 473×10^3 psi tensile strength at 63 million psi modulus have been achieved with HM fiber with starting properties of 399×10^3 psi and 53.9 million psi, respectively. Preliminary design considerations for scale-up of the boron strengthening process have shown that the simultaneous processing of seven strands of a typical fiber such as HM 3000 would meet the future pilot production goal of 1 lb/hr.

Data generated at FMI in the boron strengthening process indicates that the predominant strengthening mechanism is the healing of fiber surface flaws. In addition, the modulus of fibers was observed to be significantly increased (from approximately the 50 million psi to 70 million psi level) on the application of tension during boron treatment

at temperatures in excess of approximately 2800°C. This modulus increase is thought to be due to straightening of the layer planes of the graphite fiber structure. Most significant here is the increase in fiber modulus without the customary loss in strength usually experienced in fiber manufacture. The retention and improvement of strength while processing for increased modulus may be due to the simultaneous healing of surface flaws during graphitization. Fiber properties of 450×10^3 psi strength at 66 million psi modulus have been achieved. The best commercially available 70 million psi modulus fiber has an average tensile strength of 270×10^3 psi. Comparative data of MERADCOM/FMI boron strengthened fibers and commercial fibers is shown in Table X. Other possible beneficial influences of the boron treatment process may be increase of the graphitization rate of fibers by boron catalysis [17] and solid solution hardening of the graphite fiber structure by boron atoms.

Whilst significant improvements have been made in fiber strengths and moduli with the boron strengthening process, full attainment of the program goal of 750×10^3 psi strength at 60-70 million psi modulus will probably require additional measures. For example a limiting factor determining fiber strengths is the presence of large internal flaws such as voids and inorganic inclusions. Carbon precursor fibers containing substantially less flaws may be needed to achieve the maximum benefit of the boron strengthening process. Figure 16 [28] shows a model of the defect structure of high modulus graphite fibers. Voids and inclusions are present in rayon, PAN, and pitch precursors which are trapped in fibers during the spinning process. Reduction in void content has been achieved in PAN fibers by drawing up to 22x prior to oxidation and carbonization [29]. Further complications resulting in voids and flaws arise in PAN fibers due to excessive material loss and shrinkage during the stabilization, carbonization and graphitization steps which result in a defect loaded core structure of

TABLE X. FIBER PROPERTY COMPARISON

	HM/PVA*	GY 70*	Pitch Type P*	MERADCOM/FMI Boron Alloyed Fibers		
			VSA-11	028-76-6	032-28-1	032-22-3
TENSILE STRENGTH (10^3 psi)	350	270	175	473	450	379
TENSILE MODULUS (10^6 psi)	55	75	55	63.1	66.2	71.5
DENSITY (g/cm^3)	1.85	1.96	1.99	1.86	1.82	1.87

* Manufacturers Test Data

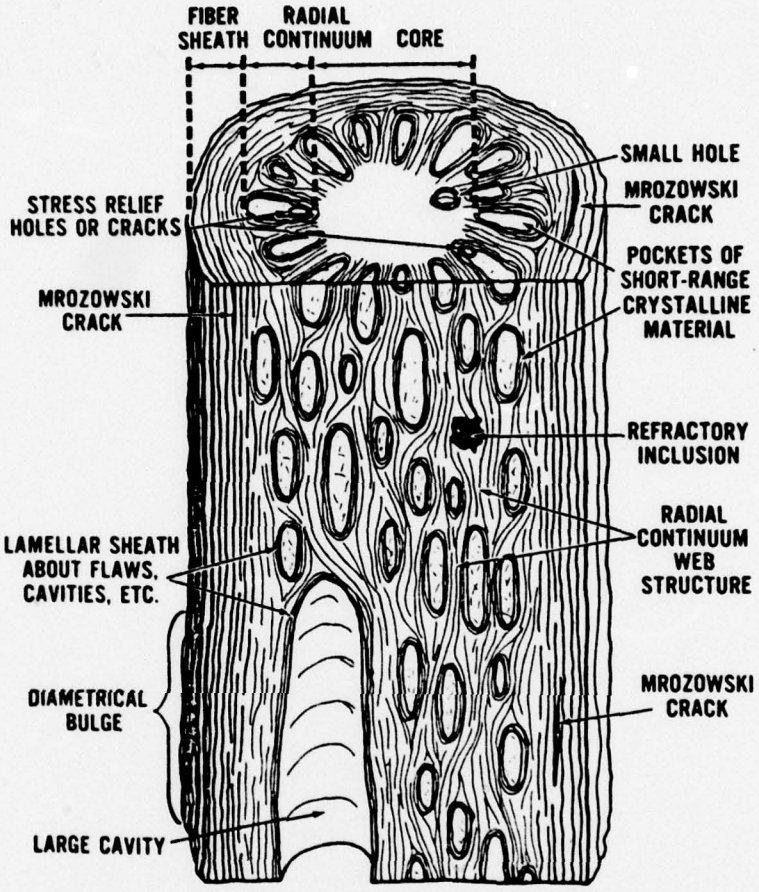


FIGURE 16. MODEL OF FIBER DEFECTS

a low degree of alignment. Figure 17 illustrates a typical high modulus fiber structure, and Figure 18 illustrates the nature of the residual stresses which probably arise from the variations of fiber alignment. In view of the lack of perfection of currently available commercial high modulus fibers, it is not surprising that their strengths are low and that improvements due to the boron strengthening process when using such fibers as precursors appear limited to the 500 x 10^3 psi strength level. Shorshorov [30] discussed new PAN graphite fibers of 2 micron diameter of 800 x 10^3 psi tensile strength at the 50 million psi modulus level. Attempts have subsequently been made to obtain samples of these small diameter Russian fibers for evaluation but have been unsuccessful. It is however believed that the development is genuine. Fibers of such small diameter may have much better aligned structures, and in particular have a more orderly core structure containing less defects such as voids. The Russian observations confirm well established theories [31] that decrease in fiber diameter leads to a corresponding decrease in the number of flaws and an increase in fiber strength.

The chemical treatments of graphite fibers utilized under this program have shown little promise in fiber strengthening. Successful intercalation of chemicals, such as Br_2, ICl, $FeCl_3$ and $MoCl_5$ have been demonstrated in the highly graphitized fibers, such as the HM/PVA. Only in isolated cases were minor improvements in strength observed with Br_2 treatments and no increases in modulus were observed. All other chemical treatments caused a loss in mechanical properties. It appears that the highly graphitized fibers, that will allow intercalation, have a too well defined crystal structure to allow for healing of internal defects in that state. This is supported by the lack of stretching of fibers during tensioning with intercalation.

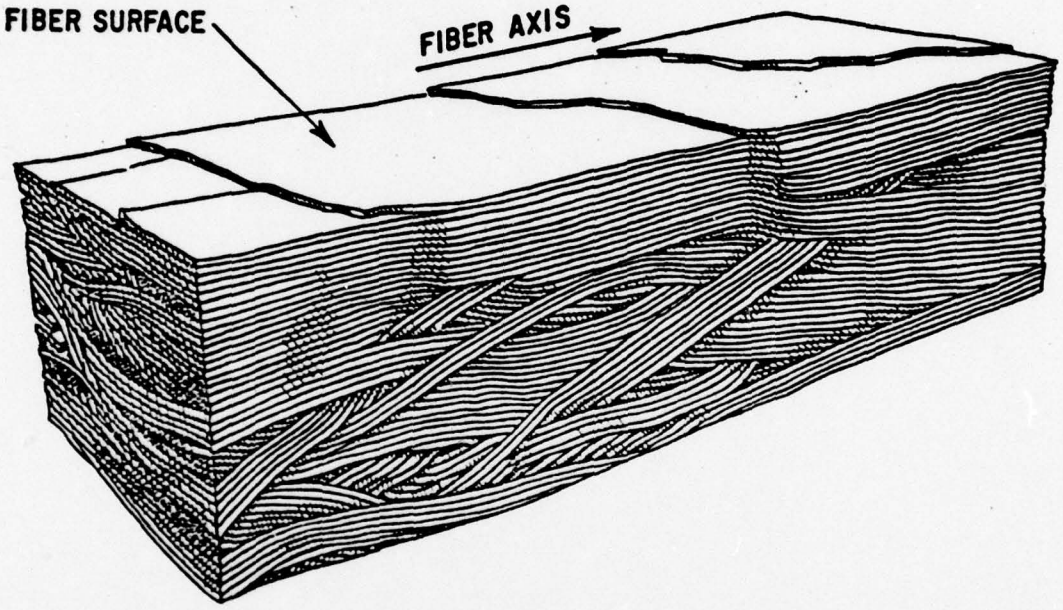
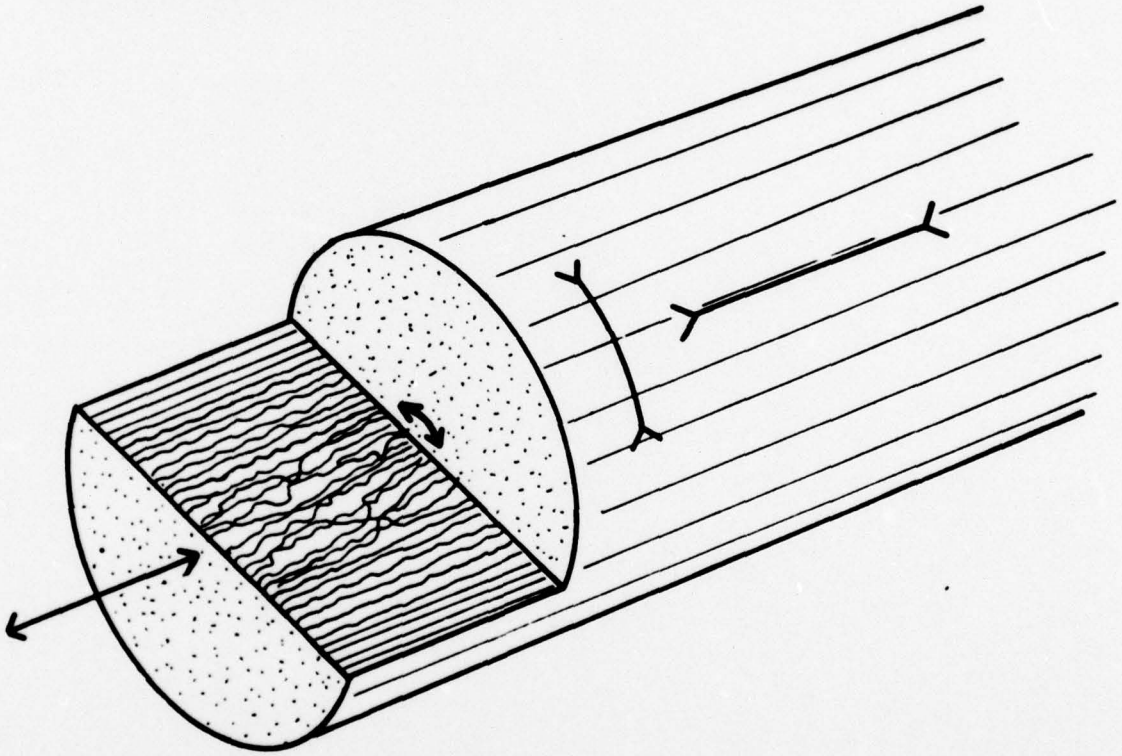


FIGURE 17. TYPICAL HIGH MODULUS FIBER STRUCTURE

PROBABLE RESIDUAL STRESS DISTRIBUTION IN HIGH MODULUS GRAPHITE FIBERS



FIBER SURFACE LAYERS IN COMPRESSION.
FIBER CORE IN TENSION.

FIGURE 18.

The elimination of defects in the fiber must come at as early a stage in processing as possible. Preventing formation of internal defects should be emphasized rather than treating existing defective fibers.

6.0 CONCLUSIONS

1. Graphite fiber processing temperatures above those used in current commercial graphitization furnaces are needed for improvements in fiber mechanical properties.
2. Healing of fiber surface flaws by ultrahigh temperature borocarbon deposition enhances fiber mechanical properties.
3. No significant improvement in fiber properties have been observed with chemical intercalation treatments.
4. Maximization of fiber surface area to fiber volume (reduction of fiber diameter) should maximize fiber properties when combined with an ultrahigh temperature borocarbon treatment.

7.0 RECOMMENDATIONS

The following recommendations are made based on the results of this program:

1. The arc-plasma boron strengthening process should be advanced with the building of a production plant capable of processing one pound per hour of graphite fibers. This ultrahigh temperature process would be capable of producing premium quality graphite fibers with a goal of properties as follows:
   a. Tensile strength min, psi 750,000
   b. Modulus of elasticity, psi 60-70 x 10^6
2. Small diameter PAN fibers should be incorporated into the program and the arc-plasma boron strengthening process should be used for graphitization. This would allow the maximization of fiber surface area as well as the addition of trace elements such as boron to catalyze graphitization.
3. Utilize additional methods of alloying graphite fibers. For example, the precursor PAN fiber could be treated with boron oxide prior to the carbonization step [17] to incorporate boron into the graphitized fiber.

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