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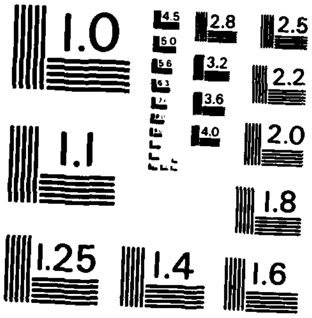

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FINAL TECHNICAL REPORT

"IMPROVED GRAPHITE FIBER"

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

CONTRACT NO. DAAK70-79-C-0209

PREPARED BY

R. PEPPER AND E. BREWSTER
ADVANCED MATERIALS DEVELOPMENT LABORATORY

OCTOBER 1982

SUBMITTED BY

FIBER MATERIALS, INC.
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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER FM-91178-2	2. GOVT ACCESSION NO. AD-A123141	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) "Improved Graphite Fiber"		5. TYPE OF REPORT & PERIOD COVERED Final Report 1 Oct. 79 - 31 Oct. 82
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Dr. Roger Pepper Ms. Elissa Brewster		8. CONTRACT OR GRANT NUMBER(s) DAAK70-79-C-0209
9. PERFORMING ORGANIZATION NAME AND ADDRESS Fiber Materials, Inc. Biddeford Industrial Park Biddeford, Maine 04005		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Army Mobility Equipment Research & Development Command Ft. Belvoir, VA		12. REPORT DATE
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) DCASR Boston 666 Summer Street Boston, MA 02210		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved For Public Release; Distribution Unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Graphite Fibers High Modulus, High Tensile Strength Fibers Boron Alloying Pilot Production Plant Graphite-Epoxy Composites		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The purpose of the program was to develop a production method for improved graphite fibers. A goal of 750 x 10^3 psi tensile strength at 60-65 x 10^6 psi modulus was set for the program. Improved 3-4 micron diameter boron strengthened graphite fibers were successfully prepared from Courtaulds SAF polyacrylonitrile fiber precursor in a pilot production plant which has the potential capacity to produce 1 lb/hour of graphite fiber.. An average tensile strength of 550 x 10^3 psi at the 60 x 10^6 psi modulus		

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level was achieved through a preliminary optimization of the plant processing conditions. The current state-of-the-art of HM grade high modulus graphite is 350 x 10^3 psi tensile strength at 55 x 10^6 psi modulus. The pilot plant is currently operated with a maximum of 24 tows and scale-up is underway for expansion to 96 tow capacity. Preliminary process conditions for a full-scale 96 tow plant were determined during the course of the program. Problems were encountered with the mechanical properties of graphite-epoxy composite panels. The data indicates that the surface treatment of the boron strengthened small diameter fibers is necessary for improvement of fiber-matrix interface bond strength and interlaminar shear strength in plastic matrix composites. The addition of a fiber surface treatment process following high temperature graphitization of the fibers is recommended.

SUMMARY

The purpose of the program was to develop a production method for improved graphite fibers. A goal of 750 x 10^3 psi tensile strength at 60-65 x 10^6 psi modulus was set for the program. Improved 3-4 micron diameter boron strengthened graphite fibers were successfully prepared from Courtaulds SAF polyacrylonitrile fiber precursor in a pilot production plant which has the potential capacity to produce 1 lb/hour of graphite fiber. An average tensile strength of 550 x 10^3 psi at the 60 x 10^6 psi modulus level was achieved through a preliminary optimization of the plant processing conditions. The current state-of-the-art of HM grade high modulus graphite is 350 x 10^3 psi tensile strength at 55 x 10^6 psi modulus. The pilot plant is currently operated with a maximum of 24 tows and scale-up is underway for expansion to 96 tow capacity. Preliminary process conditions for a full-scale 96 tow plant were determined during the course of the program. Problems were encountered with the mechanical properties of graphite-epoxy composite panels. The data indicates that the surface treatment of the boron strengthened small diameter fibers is necessary for improvement of fiber-matrix interface bond strength and interlaminar shear strength in plastic matrix composites. The addition of a fiber surface treatment process following high temperature graphitization of the fibers is recommended.

PREFACE

The Final Technical Report was prepared from work conducted on the "Improved Graphite Fiber" program. This manufacturing and technology program was performed at Fiber Materials, Inc., Biddeford, Maine, under Contract No. DAAK70-79-C-0209 issued by the U.S. Army Mobility Equipment Research and Development Command, Ft. Belvoir, Virginia. The technical monitor at MERADCOM was Mr. F. Harris. The program manager at FMI was Dr. R. Pepper with Ms. E. Brewster as project engineer. Engineering support was provided by Mr. D. Nelson and Mr. R. Patton.

TABLE OF CONTENTS

SECTION PAGE

TABLE OF CONTENTS CON'T

SECTION PAGE

LIST OF FIGURES

LIST OF TABLES

1.0 OBJECTIVE

The program objective was to demonstrate a production method for manufacturing high strength, high modulus graphite fiber at a rate of one (1) pound per hour. Specifically, the method should produce fibers with the following properties.

A. Tensile Strength, Min., psi 750,000

B. Modulus of Elasticity, psi 60 - 65 x 10^6

2.0 INTRODUCTION

Past work on improved graphite fibers (1 and 2) has shown that the tensile strength of graphite fibers can be increased by the presence of boron during high temperature graphitization. Fiber Materials, Inc. (FMI) has constructed a pilot plant for the production of graphite fibers from polyacrylonitrile (PAN) precursors which includes the boron treatment step during high temperature graphitization. The pilot plant has the potential capacity of 8000 lbs/year of high modulus graphite fiber.

FMI has also developed a process on internal R&D funding for the preparation of approximately 3-4 micron diameter graphite fibers from PAN precursors. Commercially available PAN fibers, drawn to the limit of standard technology, are drawn an additional three to four times in the FMI drawing process. The filament diameter is reduced from the conventional size of 11 microns (1.2 decitex PAN fiber) to approximately 6-8 microns. Small 3-4 micron diameter carbon and graphite fibers are made from the 6-8 micron PAN fibers using relatively conventional oxidation, carbonization, and graphitization techniques. The 6-8 micron diameter PAN fibers shrink to 3-4 microns diameter during carbonization.

2.1 Fiber Property Improvements With Small Diameter Fibers

Both the reduction in filament diameter and the increased alignment of the fiber crystal structure produced by the additional drawing result in higher graphite fiber tensile strength and modulus values. Past graphite-epoxy strand test data, Table I, shows that the fiber tensile strength increases from 460 Kpsi to 610 Kpsi with an increase in draw ratio from 1.1X to 3.0X.

More recent work has shown that a significantly higher fiber modulus can be obtained for a given graphitization temperature. For example, approximately 32 Mpsi modulus is typically attained at a temperature of 1350 - 1400°C on standard 7 micron diameter graphite fibers, whereas 38 - 42 Mpsi modulus is attained at the same temperature on 4 micron diameter graphite fibers. Four micron graphite fibers with a tensile strength of 680 Kpsi and 40 Mpsi modulus have been prepared on a pilot production basis. At higher graphitization temperatures and fiber modulus levels, the same beneficial effects of the small diameter fibers are observed. For example, 3.5 micron diameter graphite fibers of 60 Mpsi modulus and 550 Kpsi strength have been prepared at 2400°C as compared to 7 micron diameter graphite fibers of 50 - 55 Mpsi modulus and 350 - 400 Kpsi tensile strength produced at 2500 - 2600°C. Similarly, small diameter 70 Mpsi modulus 420 Kpsi strength graphite fibers have been prepared at 2600 - 2700°C as compared to 7 micron graphite fibers of 70 Mpsi modulus and 220 - 270 Kpsi produced at 2800 - 3000°C.

2.2 Composite Property Improvements With Small Diameter Fibers

In addition to improved fiber tensile properties, improved interlaminar shear strength has been observed in graphite-epoxy composites. Table II shows a shear strength value of 12.3 Kpsi on 3X drawn unsurface treated graphite fiber. Eight Kpsi is a typical shear strength value for standard size untreated 32 Mpsi modulus fiber. These results indicate the potential for a 50 percent increase in interlaminar shear strength with a graphite fiber diameter reduction from 7 microns to 4 microns.

Fiber handling and weaving characteristics are significantly improved with the small diameter fibers due to the

TABLE I

Impregnated Strand Properties of FMI 1400°C Fired Carbon Fibers

Precursor Fiber	Amount of Drawing	Strength (Kpsi)	Modulus (Mpsi)	Torsional Shear Strength (Kpsi)
Courtaulds 6k	1.1X	460	32.0	12.8
Courtaulds 6k	2.0X	560	34.6	13.9
Courtaulds 6k	3.0X	610	34.1	14.0

TABLE II

Composite Properties of FMI 32 - 34 Mpsi Modulus Carbonized Fiber Made With Epoxy Resin

Amount of Drawing	Strength* (Kpsi)	Sec. Modulus* (Mpsi)	Strain-to-Failure (%)	Transverse Tensile Strength (Kpsi)	Short Beam Shear Strength (Kpsi)
1.1X	248	19.6	1.23		
2.0X	257	19.9	1.26		
3.0X	287	19.6	1.36	5.1	12.3

*Normalized to 60 volume % fiber.

increased strain-to-failure of the fibers at all modulus levels and the reduction in the individual filament diameters. For example, the 60 Mpsi modulus 550 Kpsi strength 3.5 micron diameter fibers have comparable handling and weaving characteristics to commercially available T300.

The above discussion concerns organic matrix composites but similar property improvements have been attained with metal matrix composites and are expected with carbon/carbon composites. Excellent properties have been attained with graphite-aluminum wire composites. Average tensile strength values of 220 Kpsi have been attained with 34 $\frac{v}{o}$ of 60 Mpsi 3.5 micron diameter graphite fibers, with high strength values in excess of 300 Kpsi. The best values attained in the prior art with standard 7 micron diameter fibers are of the order of 150 Kpsi tensile strength.

2.3 Composite Compressive Properties With Small Diameter Fibers

Compressive properties at least equal to those achieved with standard 7 micron diameter PAN precursor graphite fibers are expected with the 4 micron diameter graphite fibers. The improved alignment of the fiber structures, demonstrated to give higher tensile strengths, should also give improved fiber compressive properties. However, the smaller fiber diameters may result in a slight lowering of the compressive strength values in composites and the overall effect may result in comparable compressive properties to composites prepared with standard size PAN precursor graphite fibers. Compressive properties substantially better than those achieved with high modulus pitch based fiber are anticipated with small diameter PAN precursor graphite fibers at the 60 Mpsi fiber modulus level.

2.4 Small Diameter Fiber Costs

The fiber drawing is conducted prior to full oxidation of the PAN fibers and therefore does not lead to a reduction of the material through-put of the high temperature graphitization furnaces which is a major cost driver in the production of graphite fibers. Beneficial aspects of the small diameter fibers are higher permissible PAN fiber oxidation rates and higher carbonization rates leading to low costs for those process steps. The overall costs of producing 3 - 4 micron diameter PAN precursor graphite fibers in large-scale production are expected to be similar to the costs of producing standard 7 micron diameter PAN precursor graphite fibers. For example, fibers of 38 - 42 Mpsi modulus are anticipated to be in the $20 - 50/lb range, depending on fiber tow size, and 60 - 65 Mpsi modulus fiber is expected to cost $60 - 70/lb.

2.5 Fiber Property Goals

Realistic property goals with small diameter fibers are as follows:

Tensile Modulus (Mpsi)	Tensile Strength (Kpsi)
40 - 45	800 (without boron treatment)
60 - 65	600 - 750 (with boron treatment)

The above goals are recommended based on data achieved in a pilot production plant which has a potential capacity of 16,000 lbs/year for 40 Mpsi modulus small diameter graphite fiber and 8,000 lbs/year for 60-65 Mpsi modulus small diameter graphite fiber. There is a high probability that these property goals could be achieved on fiber produced in a full-scale production plant.

2.6 Boron Treatment During Graphitization

The higher the final graphitization temperature, the higher the modulus of the resulting graphite fiber. In the absence of boron treatment, the strength of graphite fibers derived from PAN generally goes through a maximum at approximately 1400°C, and surface and internal defects formed during graphitization cause a progressive lowering of strength with increase in graphitization temperature. Boron treatment during graphitization minimizes this strength loss at high graphitization temperatures by healing defects such as holes and cracks. The boron strengthening effect is largely a surface related phenomena, and the smaller 3-4 micron graphite fibers, which have larger surface areas than conventional 7-8 micron graphite fibers, show a bigger increase in tensile strength than the conventional fibers on boron treatment. Consequently, this program concentrated on the pilot production plant development of boron treated improved small diameter graphite fibers. Small diameter PAN precursor fiber was prepared for the program using the FMI PAN fiber drawing process.

Emphasis in the program has been in translating the research technology for the boron graphitization process to the pilot production scale. Preliminary optimization of graphite processing conditions was necessary to ensure the production of 20 lbs. of quality fiber for shipment to MERADCOM and prepare fiber for graphite-epoxy composite studies. The plant scale-up, production development, and preliminary plant optimization studies are described in detail in this report.

3.0 INVESTIGATION

3.1 Task I - Design and Construction of Pilot Plant

3.1.1 State-of-the-Art Technology for the Preparation of Graphite Fibers From PAN

The preparation of graphite fibers from polyacrylonitrile involves three distinct process steps: 1) oxidation; 2) carbonization; and 3) graphitization. Oxidation is generally carried out in air in the temperature range of 200-300°C; carbonization under nitrogen at 300-1200°C; and graphitization under nitrogen at 1200-2800°C. Boron treatment during high temperature graphitization, which is the subject of this program, is not state-of-the art practice. High performance graphite fibers for structural applications are made by continuous fiber processing through all three process steps, whereas moderate performance, ultra low cost commodity carbon fibers for nonstructural applications, such as thermal insulation and brake shoes, are generally batch-processed through the oxidation and carbonization steps. The interest here is in high performance structural fibers, and the following discussion is limited to continuous processing.

Stretching of PAN precursor fibers prior to oxidation leads to improved alignment of the PAN polymer fiber structure, which is in a large part inherited by the resulting graphite fibers. Improved alignment of the structure of graphite fibers leads to improved strength and modulus. FMI has devoted a substantial internal research and development effort to develop special techniques for fiber alignment and has demonstrated advanced high strength, high modulus fibers.

The objective of the oxidation (controlled burning in air) of the PAN precursor material is to render it infusible in order that it can be heated further for carbonization. Oxygen diffuses into the PAN structure and causes intermolecular crosslinking, stabilizing the structure and preventing excessive loss of carbonaceous and nitrile groups on heating. Loss of such constituents from the PAN should be minimized, since holes are left in the fiber structure leading to lower strength and modulus values in graphite fibers. Fiber stretching is not generally practiced during oxidation due to the fragile nature of the fiber at this stage, but care is taken to avoid longitudinal shrinkage which causes misalignment of fiber structure and loss of properties. The oxidation of PAN fibers is an intricate process calling for intimate knowledge of the process parameters for each different kind of PAN precursor. Oxidation rates vary widely for different precursors, and are related to their composition such as the type of comonomer or oxidation catalyst used.

Most of the gases evolved during the pyrolysis of PAN are given off during carbonization. Some minor amounts of water, ammonia and hydrocarbon groups are also given off in oxidation at 200-300°C, however. During carbonization in the 300-1200°C range, substantial quantities of CO_2, NH_3, H_2O, and HCN are given off. When large quantities of PAN are being processed, special scrubbers and ventilation systems are required for the disposal of the very poisonous HCN gas. Approximately half the weight of the PAN fiber is lost during the carbonization process, considerable fiber shrinkage occurs, and essentially an amorphous carbon fiber is formed. As the carbonization temperature approaches 1200°C, some graphitic structure is formed with a corresponding increase in modulus. Tension is maintained on the PAN fibers during carbonization, but fiber stretching is not generally practiced.

During graphitization, the turbostratic structure of the graphite fibers is formed. Relatively small amounts of residual gases such as CH_4, CO, and N_2 are evolved from the fibers. Fiber heating and processing rates can be high during graphitization as compared to oxidation and carbonization. Fibers of 450 Kpsi tensile strength and 32 - 34 Mpsi tensile modulus are typical of high quality carbon fibers prepared by graphitizing at 1300°C.

Fiber of properties 350 Kpsi tensile strength and 50-55 Mpsi tensile modulus are typical of fibers graphitized at up to 2500°C. Some tension is maintained on the fibers during graphitization, but stretching is not generally practiced during the graphitization process of PAN.

Considerable care must be taken throughout the overall processing of graphite fibers to eliminate defects such as kinked or joined fibers, and surface defects which arise from reactive dust particles.

3.1.2 Pilot Production Plant Design For The Boron Graphitization of PAN Fibers

Figure 1 shows the process steps employed in the pilot production plant and a general layout of the equipment is shown in Figure 2. In the plant layout, Figure 2, the line is shown to be separated into two separate steps: oxidation and graphitization. While complete in-line operation is the long term plan for the process for the purposes of the present contract, to expedite preliminary optimization of the various process steps, the oxidation and graphitization lines were separated and operated independently. The plant layout also shows an exhaust gas scrubbing tower. Hoods were installed at the ends of the furnaces in the plant and the toxic gases arising from the thermal decomposition of the PAN fibers were sucked through a series of duct work by the aid of a fan into the scrubber tower. These toxic gases were blown up through the tower, and a caustic solution was sprayed down the tower to purify the gas stream and in particular, to remove and neutralize the HCN from the oxidation and carbonization steps of the process. Detailed engineering drawings of the plant are provided in a separate report.

Oxidation

In the oxidation step of the process, 3X drawn PAN fibers of approximately 6-8 microns diameter were oxidized to approximately

3 MICRON GRAPHITE FIBER PROCESS STEPS

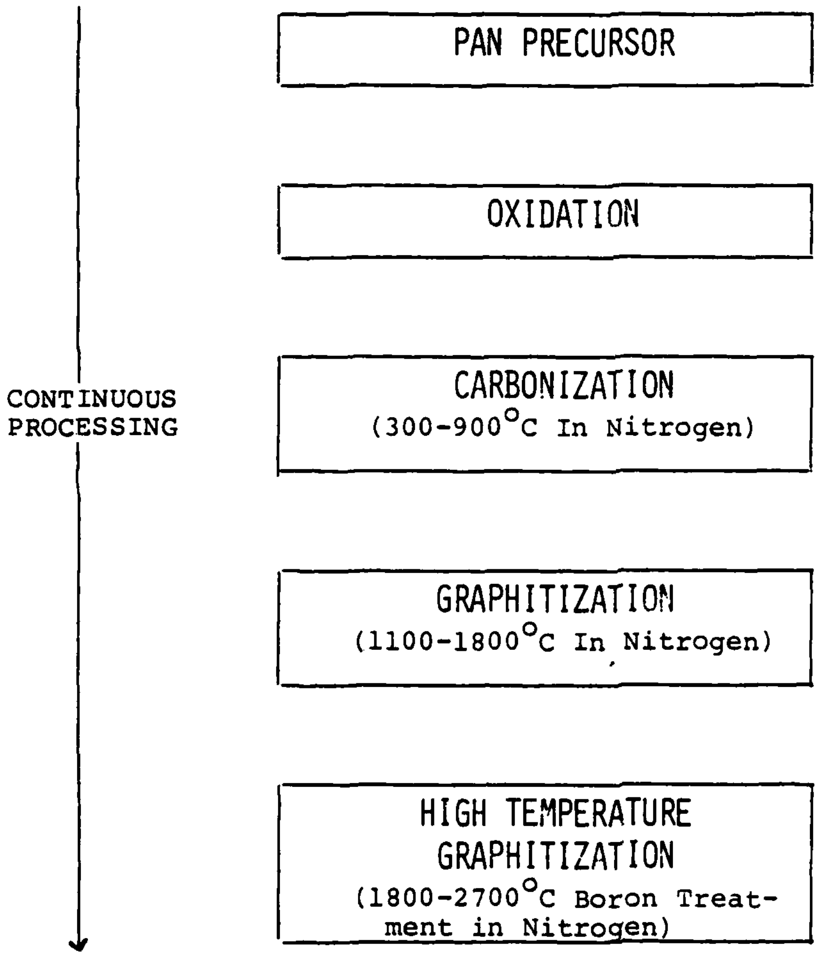

Figure 1

OXIDATION LINE

1. Feed Creel 500-0054
2. Nip Roll 500-0052
3. Oxidation Oven 500-0055
4. Nip Roll 500-0051
5. Oxidation Oven 500-0055
6. Nip Roll 500-0053
7. Winders (Take-up) 500-0060

CARBONIZATION - GRAPHITIZATION LINE

8. Feed Creel 500-0056
9. Nip Roll 500-0053
10. Carbonizer 500-0050
11. Low Temperature Graphitizer 500-0049
12. High Temperature Graphitizer 500-0048
13. Nip Roll 500-0051
14. Sizing Applicator 500-0059
15. Drying Oven 500-0061
16. Winders (Take-up) 500-0060

OTHER

17. Exhaust Gas Scrubber 500-0058
18. Temperature, Nip Speed and Scrubber Control Panel
19. Graphitizer Control Panel
20. Graphitizer Control Panel
21. Fiber Surface Treatment Gas Cylinders
22. Twister 500-0062
23. Twisted Fiber Winder (Take-up) 500-0063

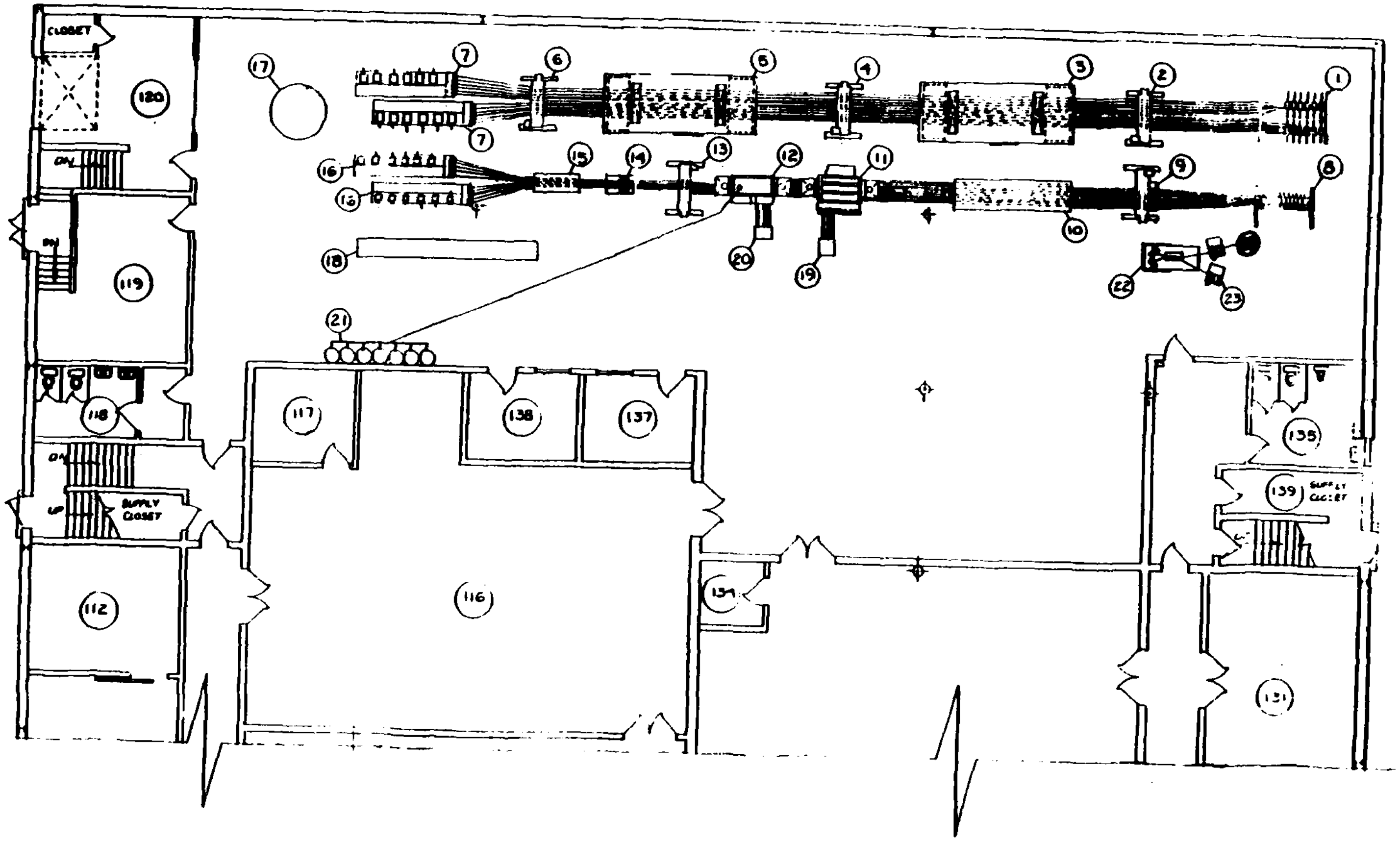

Figure 2. General Layout of Pilot Production Equipment

10-11 wt. % oxygen content at 250-270°C. The oxidation box ovens were purchased from the Gruenberg Co. Each oven has a work zone approximately 7 x 5 x 10 feet. The ovens are operated in the temperature range 250-300°C. Air is blown through the ovens by fans and heated by passing over strip heaters mounted in the top sections of the ovens. Guide rolls are mounted at both ends of each oven, allowing a maximum of seventeen passes of fiber through each oven. With a typical line speed of 1.4 feet per minute for the oxidation process, a total residence time of up to approximately 2½ hours is available in the hot zones of the ovens. Nip rolls are provided at the end of each oven to control the elongation of the fiber during the oxidation process. The fiber path in the oxidation line is approximately four feet wide, and is designed to accommodate the simultaneous processing of up to 96 tows of PAN fiber. A bank of Leesona 965 winders is located at the take-up end of the line and a fiber delivery creel is located at the beginning. Typical problems encountered during the oxidation processing are tearing and failure of the fiber tows in the box ovens, and build up of fuzz at the fiber guides and winder stations. The severity of the problem of the tearing of the fiber tows in the ovens was reduced by minimizing the velocity of the air blown through the ovens while still maintaining an acceptably low thermal gradient across the ovens. Ideally, the ovens should have a uniform temperature across the width of the fiber tow path. The use of steel guide rolls and ceramic pulley guides minimized fiber handling damage during transport through the oxidation line.

Carbonization

Carbonization was conducted in line with the graphitization furnaces, and a nip roll drive system was placed at each end of the entire line.

A resistance heated gradient slot furnace was designed and built by FMI for carbonization. The furnace has a slot 2 x 9 x 144 inches long and has four separate heating zones. Various thermal gradients were studied during the program and are described in section 3.2.3 of this report. A stainless steel retort/liner was provided in the furnace. Nitrogen cover gas from a bulk storage liquid nitrogen tank was supplied to the furnace through specially designed entrance and exit ports. Build-up of tarry deposits, particularly at the ends of the furnace were found to be a problem. Regular shut down and cleaning of the furnace was carried out during the program, but for larger scale production of graphite fibers continuous removal of tars from the furnace would be necessary. Oxidized PAN fibers were carbonized with approximately 0% elongation applied during processing.

Graphitization

Graphitization of the fibers was carried out in line with the carbonization step described above. Two furnaces were used. A carbon block/resistance heated graphite bar element slot furnace made by Astro Industries (operating temperature 1350-1450°C), and a resistance heated graphite tube furnace made by Pereny (operating temperature 2300-2500°C).

Both furnaces were operated under a protective atmosphere of nitrogen and specially designed end ports were used to prevent contamination of the furnace atmosphere with air. Boron containing gases were used in the high temperature graphitization tube furnace, and the pre-graphitization step at 1400°C was conducted without boron additions. 0% elongation was maintained between the nip rolls placed at each end of the carbonization and graphitization line during processing. Since graphitization was carried out in line with carbonization without a nip roll drive station between the "carb" and "graph" steps, the tension applied during the graphitization steps was minimal (200-300 grams for a 6k tow), and equal to the natural shrinkage tension of the PAN fiber produced during 0% carbonization by 0% elongation.

The 1400°C Astro graphitization furnace was found to suffer from bowing and arcing of the heater bars to the graphite block chamber walls, and general erosion of the graphite hardware. The former problem was corrected by using a dense grade of graphite for the heater bars, adjusting the electrical contacts on the heater bars to minimize the applied bending stress on the bars, and electrically insulating them from the graphite block chamber by wrapping them with boron nitride fiber. Erosion of the graphite hardware was minimized by adjusting the nitrogen cover gas flows. With these modifications the furnace lifetime was extended to approximately 12 weeks.

The Pereny high temperature graphite tube furnace was found to have two major problems limiting furnace life and productivity. Oxygen leaks into the furnace case through such areas as the seals between the casing and the electrodes caused severe erosion of the outside diameter of the furnace element and the sight tube used for measuring furnace temperature. The erosion was tolerable at a 2400°C operating temperature where furnace life was three to four weeks duration but at higher temperatures erosion of the graphite hardware was very rapid. For example, at 2700°C the furnace lifetime was 1 day, making continuous production impractical. The furnace performance has been considerably improved by sealing leaks in the casing, but further design and construction work to eliminate oxygen containing refractory bricks and electrical insulating boards from the interior of the furnace may be necessary to completely solve the problem

The boron containing gas added to the high temperature graphitization furnace atmosphere caused a rapid build-up of soot and hard deposits in the furnace tube, leading to tearing and fuzz build-up on the fiber tows being passed through the furnace. The problem has been minimized by replacing the triethylborane gas used in the past program(1) with a diborane/methane gas mixture which deposits less carbon. Regular cleaning of the furnace tube by dragging a graphite bar through the hot zone has also increased the life of the furnace tube. A complete solution to the problem has not yet been worked out. Optimization of the furnace gas flows is needed to reduce the total amount of material deposited while maintaining effective boron surface treatment on the fibers.

3.2 Task II - Optimization of Pilot Plant Process

3.2.1 Initial Shake-Down Trials of Pilot Plant

To simplify development of the plant, the oxidation and graphitization lines of the plant were operated independently of each other.

Furnace Temperature Calibrations

A study of the temperature profiles of the Gruenberg oxidation ovens was made with a chromel-alumel thermocouple and it was found that the sides of the ovens were cooler than the middle sections. This would mean that fiber tows running through the oven center sections would receive more oxidation exposure than fiber tows running near the sides. The oven has a multitude of approximately 2 inch diameter baffles set in the two side walls which can be adjusted to control the flow of hot air which provides the heat source. Adjustment of the baffles minimized the problem for the initial work. Twenty four winders were available and the temperature distribution across 24 tows in the oxidation oven was judged as acceptable. Determination of densities/oxygen contents of the tows as described below in section 3.2.2 verified this judgment. A series of "readout" chromel-alumel thermocouples were placed in the side zones of the ovens to record the temperature profiles of the ovens during fiber processing.

The thermal gradient in the carbonization oven was measured using a chromel-alumel thermocouple and the furnace was adjusted to give a very gradual gradient from 300°C-400°C for the first six feet of the oven and then a steeper gradient to 825°C for the last four feet. Little difference was found in temperature between the sides and middle of the oven.

The gradients in the 1400°C and 2400°C graphitization furnaces were not measured but accurate verification of the maximum temperatures of the hot zones was obtained. A Leeds and Northrup portable optical pyrometer was used for this work. Temperature readings were taken by sighting the pyrometer directly down into the hot zone through the furnaces entrance and exit slots.

Fiber Drive and Handling Systems

The speeds of the nip rolls on the oxidation and graphitization lines were calibrated using a stopwatch to time roll speeds. Some problems were encountered with jerky motion on the oxidation oven guide rolls during shake down trials. This was traced to overtightening of the drive chains and the newness of the drive system. Adjustment of the tension of the chains and running the drive system improved smoothness of the drive system. Additionally, the motor gear reducer ratio was changed from 150:1 to 500:1 to improve the smoothness of the drive and accuracy of the speed control system. The motor gear reducer ratio of the nip rolls on the graphitization line was also changed from 150:1 to 600:1 to improve the accuracy of the fiber drive speed control.

A ceramic pulley guide system was devised for both the oxidation and graphitization lines for direction change points from the line level to the winder bank entrance level. Problems with fuzz build-up were encountered with pulleys located immediately following the sizing drying oven of the graphitization line, and a driven polished steel roll was installed to replace the pulley eliminating the problem. Fiber tows were spaced across the width of the furnaces using a glass pin guide system. Fuzz build-up on these guide pins was a continual problem throughout the program, however, and a complete solution to the fiber spacing problem has not yet been found.

The nip rolls pressures on the oxidation line were not adequate to prevent tow slippage during processing. The pneumatic pressure cylinder size was increased in order to increase the force on the nip roll from 1000 to 2700 lbs to solve the problem. Fiber slippage was also observed through the nip rolls on the graphitization line. Increasing the force on the rolls did not prevent slippage owing to the slippery nature of the fiber surfaces after graphitization and a satisfactory solution to the problem was not found during the program. This resulted in lower line tensions being used during graphitization than were desired. The problem will be corrected with plant scale-up to approximately 96 tows by the installation of a "staggered" roll drive system in the graphitization line.

Oxidation Oven Problems

The excessively high wind velocity in the ovens was found to shred fiber tows leading to fiber fuzz build-up and occasional tow failure. The fan drive systems were geared down, the wind velocity in the ovens was reduced, and the fiber damage problem was resolved. Frequent electrical problems were encountered with the box ovens. During normal operation the oven fuses and breakers were loaded to capacity and burning out of fuses and blowing of the breakers was a constant source of problems and production downtime during the program. Graphite fibers in the plant air were found to be a major cause of the problems. The problems were minimized by regularly vacuuming the whole area during operation and immediately disposing of fiber fuzz as it was removed from guide pins and pulleys, etc. In addition, the fuses and "hot terminals" were isolated with electrical insulating tape. The problem has not been entirely solved however.

Carbonization Furnace Problems

Insufficient electrical insulation was placed between the furnace elements and the stainless steel retorts in the original furnace design, and shorting/arcing out of the elements was a constant problem during the shake-down trials. The furnace was rebuilt and additional ceramic electrical insulators were installed to solve the problem.

Graphitization Furnaces

The 1400°C Astro graphitization furnace was designed by the manufacturer to be operated in a vertical position. This was found to be impractical during trials since the "chimney effect" of hot gases rising up the long slot shaped work zone caused air to be drawn into the bottom of the furnace. Even the use of very high nitrogen flows at the bottom entrance port did not prevent the problem. Severe erosion of the graphite heater bars of the furnace and the carbon block chamber walls was encountered, and degradation of the graphite fibers being processed was observed. The furnace was redesigned and placed in a horizontal position thus eliminating the "chimney" effect and the problem.

The 2400°C Pereny high temperature graphitization furnace element was observed to erode very rapidly around the outside and at the junction of the optical pyrometer sight tube. The problem was not entirely eliminated, but was minimized by sealing air leaks in the furnace casing and decreasing the nitrogen purge flows in the sight window tube. The original furnace was designed with an automatic optical pyrometer temperature control system. This did not work well on long term runs. Clogging of the sight tube and fogging of the sight window resulted in the automatic optical control system reacting to an "apparently" low temperature signal from the furnace and increasing the power input to rectify the situation. The actual furnace temperature would rise above the set level in response to the additional power input and cause further clogging of the sight tube and fogging of the sight window to compound the problem. On several occasions, the furnace went out of control overnight under these circumstances and reached actual temperatures as high as 3000°C. To correct the problem, the optical pyrometer automatic control system was abandoned, and a "watt converter" control system was installed. The "watt converter" control system keeps the power applied to the furnace element at a constant level and operates independently of the optical sight window. An Ircon continuous optical pyrometer temperature readout system was installed at the sight window to record process temperatures. The problem was successfully solved and a temperature control of ± 30°C has successfully been maintained on long production runs.

3.2.2 Preliminary Optimization of Oxidation Conditions

The objective of this work was to establish preliminary conditions for the oxidation of the Courtaulds 3X drawn PAN fiber to approximately 10-11% oxygen content. The oxidation line was run with a maximum number of fiber tows at feed speed of approximately 18 inches per minute. Approximately thirteen passes of fiber were made through each oven. The oven temperatures were set at various temperatures in the range of 240°C-300°C. Box Oven I was set at approximately 10°C less than Box Oven II to allow for a progressive increase in oxidation temperature as the fiber oxidation process proceeded. Samples of fiber from the trial runs were analyzed for oxygen content by the IRT Corporation using the neutron activation method and the denier and density of the samples were measured at FMI. A general relationship between fiber density and oxygen content was established and is presented in Figure 3. Table III shows typical denier and density values on samples of fiber oxidized to the 10-11% O_2 content range. Samples from the sides and middle of the oxidation ovens did not show too great a variation in density, indicating that the variations in oxygen content were not excessive.

3.2.3 Preliminary Optimization of Carbonization and 1400°C Graphitization Conditions

Tensile tests* were conducted on a series of samples carbonized under various conditions and graphitized at 1400°C in the Astro graphitization furnace. The carbonization furnace gradient was varied by changing the temperature of the zones, A (fiber entrance), B, C, D(fiber exit) and in some cases turning the zones off. The philosophy was to obtain the strongest and highest modulus fiber possible at the 1400°C graphitization step on the assumption that such a fiber would convert to the strongest high modulus fiber possible at the high (2400°C) graphitization step. The data is presented in Table IV, and interpretation of the data is presented in the discussion section of this report.

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*ASTMD 2343-67 (72) Strand Test

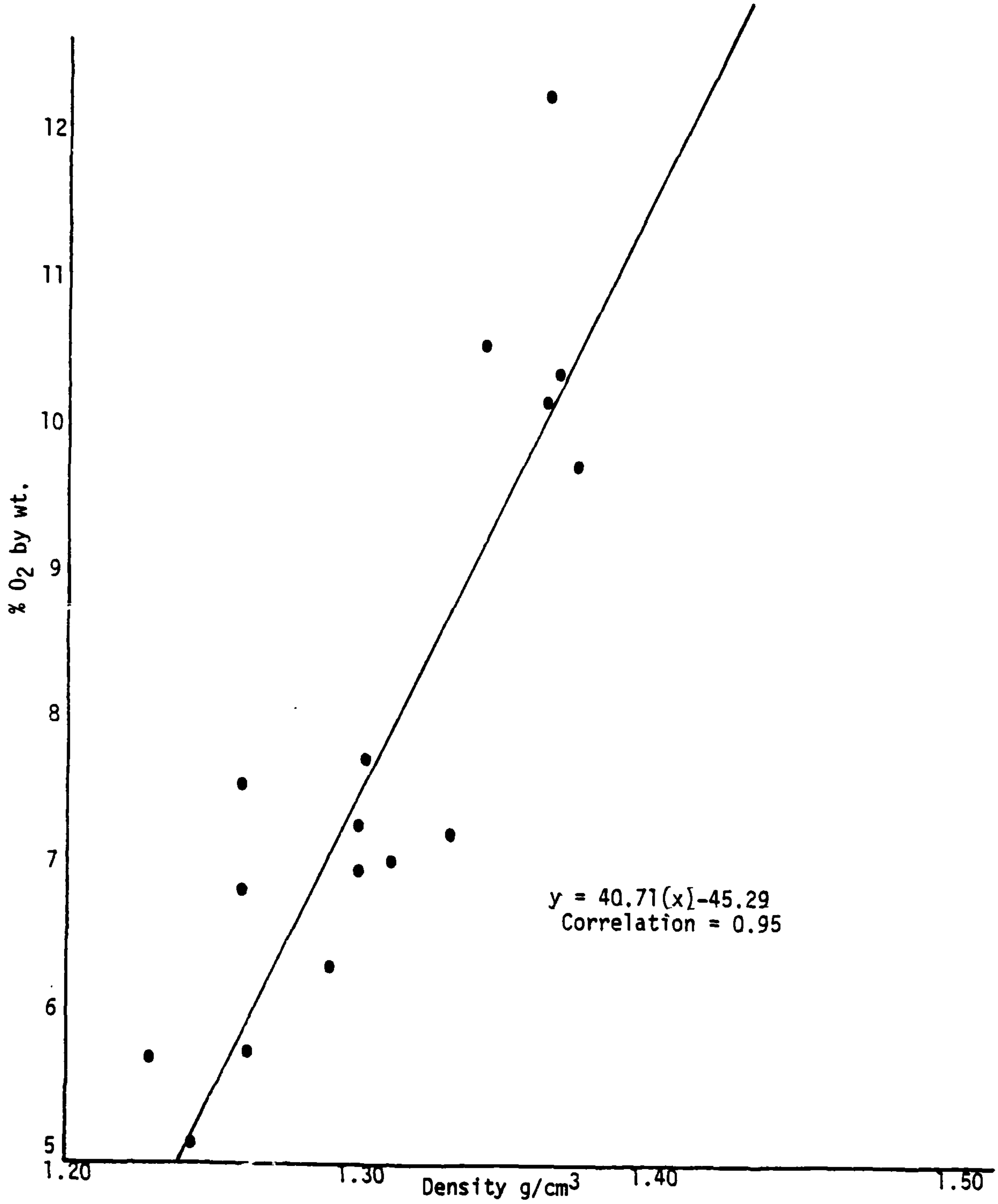

Figure 3. O_2 VERSUS DENSITY

OXIDIZED FIBER DATA

Sample	Avg. Denier	Avg. Density
0-55 9-2	2760	1.39
0-51 11-1	2755	1.39
0-51 8-1	2770	1.40
0-49 23-1	2701	1.38
0-49 24-1	2686	1.37
0-46 20-1	2699	1.40
0-46 20-2	2646	1.40
0-43 11-1	2702	1.39
0-43 23-1	2647	1.37
0-43 3-1	2750	1.42
0-37 8-1	2563	1.38
0-37 14-1	2520	1.38
0-36 1-1	2416	1.43
0-36 23-1	2556	1.41
0-35 6-1	2523	1.43
0-35 13-1	2588	1.40
0-34 9-1	2443	1.39
0-34 23-1	2316	1.39
0-33 7-5	2468	1.39
0-33 18-3	2542	1.37
0-31 1-1	2475	1.40
0-31 17-5	2408	1.39
0-42 12-1	2678	1.43
0-42 14-1	2859	1.42

Sample number shows the position of the fiber tows in the oxidation oven. For example, 0-31 1-1 is from the side of the oven, and 0-42 12-1 is from the center. The number underlined indicates the position of the tows. 1 and 24 are on the sides.

TABLE III

Table IV. Preliminary Optimization of Carbonization and 1400°C Graphitization Conditions

Sample No.	Fiber Type	Carbonization Furnace					Astro Furnace		Line Speed	Fiber Sizing	Fiber Tensile Properties			
	3X Drawn	Furnace Zone Temperature				N_2* Flows	Temp.	N_2* Flows		E=Epoxy P=PVA	Density	E	UTS	Strain
		A °C	B °C	C °C	D °C	Ent. Exit	°C	Ent. Exit	Ft/Min.		g/cc	X 10^6 psi	X 10^3 psi	%
0-43 5-4-1	Oxidized	308	422	530	680	100 100	1400	100 100	1	E	1.72	37	435	1.25
0-43 5-4-2	Oxidized	308	422	530	680	100 100	1400	100 100	2	E	1.72	37	516	1.51
0-43 5-4-3	Oxidized	308	422	530	680	100 100	1400	100 100	3	E	1.72	36	507	1.51
0-43 5-4-4	Oxidized	308	422	617	822	100 100	1400	100 100	1	E	1.72	34	307	0.90
0-43 5-4-6	Oxidized	308	422	617	822	100 100	1400	100 100	2	E	1.72	34	346	1.05
0-43 5-4-6	Oxidized	308	422	617	822	100 100	1400	100 100	3	E	1.73	37	579	1.66
0-43 19-1-20	Oxidized			617	822	150 50	1400	100 100	1	E	1.71	38	550	1.57
G-58 9-5	Oxidized			617	822	150 50	1400	100 100	2	E	1.74	39	673	1.85
G-58 13-1	Oxidized			617	822	150 50	1400	100 100	2	E	1.76	40	643	1.79
G-58 9-1	Oxidized			617	822	150 50	1400	100 100	2	E	1.75	39	657	1.79
G-58 15-1	Oxidized			617	822	150 50	1400	100 100	2	E	1.74	40	659	1.74
G-46 11-1	Oxidized			617	822	150 50	1400	100 100	3	E	1.75	39	550	1.48
G-46 13-1	Oxidized			617	822	150 50	1500	100 100	2	E	1.76	39	541	1.49
G-46 11-1	Oxidized			617	822	150 50	1270	100 100	2	E	1.71	39	570	1.57
G-46 21-1	Oxidized			617	822	150 50	1400	100 100	2	E	1.75	38	498	1.40
G-47 7-1	Oxidized			617	822	150 50	1400	100 100	2	E	1.75	39	556	1.49
G-45 5-3	Oxidized			617	822	150 50	1400	100 100	2	E	1.76	42	587	1.50
G-45 10-1	Oxidized			617	822	150 50	1400	100 100	2	E	1.76	41	600	1.52
G-45 7-1	Oxidized			617	822	150 50	1400	100 100	2	E	1.74	39	552	1.49
0-43 19-1-21	Oxidized			617	822	150 50	1400	100 100	2	E	1.73	40	614	1.59
0-43 19-1-22	Oxidized			617	822	150 50	1400	100 100	3	E	1.73	39	611	1.67
0-55 4-4-29	Oxidized				822	150 50	1400	100 100	2	E	1.75	40	689	1.86
0-55 4-4-30	Oxidized				822	150 50	1400	100 100	4	E	1.75	35	609	1.82
0-55 4-4-31	Oxidized				822	150 50	1400	100 100	6	E	1.76	35	613	1.89

*Nitrogen Flows: 50= 13.5 liters/minute, 100= 30 liters/minute, 150= 50 liters/minute.

3.2.4 Preliminary Optimization of Boron Graphitization Conditions

During past work(1) triethylborane {$(C_2H_5)_3B$} was used to introduce boron into the graphitization atmosphere. The decomposition of triethylborane leads to the deposition of large amounts of undesirable soot and hard deposits on the fiber surfaces and in the furnace hot zone. Additionally, triethylborane is a liquid at room temperature and due to the rapid change of its vapor pressure with temperature, it was found very difficult to maintain a constant concentration of the gaseous specie in the graphitization furnace atmosphere. Nitrogen was bubbled through a tank of liquid triethylborane and the nitrogen was saturated with triethylborane vapor. During operation of the triethylborane delivery system for long periods of time, evaporative cooling of the liquid in the tank took place lowering the triethylborane content of the exiting nitrogen gas. A series of graphitization experiments were conducted in a research induction graphitization furnace, Figure 4. Graphitization runs were conducted in pure nitrogen, a nitrogen/diborane (B_2H_6) mixture, nitrogen/diborane/methane mixtures of various B/C ratios, and triethylborane. The tensile properties of the samples were determined*, and observations were made on the condition of the fiber surfaces and the furnace hot zone during and following each experiment. A general conclusion from the work was that nitrogen/diborane/methane gas mixtures could be used to produce boron strengthening of graphite fibers instead of triethylborane. The problems of soot, hard deposits, and control of the boron content of the furnace atmosphere were minimized by the use of the diborane instead of triethylborane. A detailed discussion of the results presented in Figure 5 is made in section 4.2 of this report.

An extended series of preliminary optimization runs were conducted in the 2400°C graphitization line of the pilot production plant. 3X drawn fiber oxidized to 10-11 wt.% O_2 was used as a

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*ASTMD 2343-67 (72) Strand Test

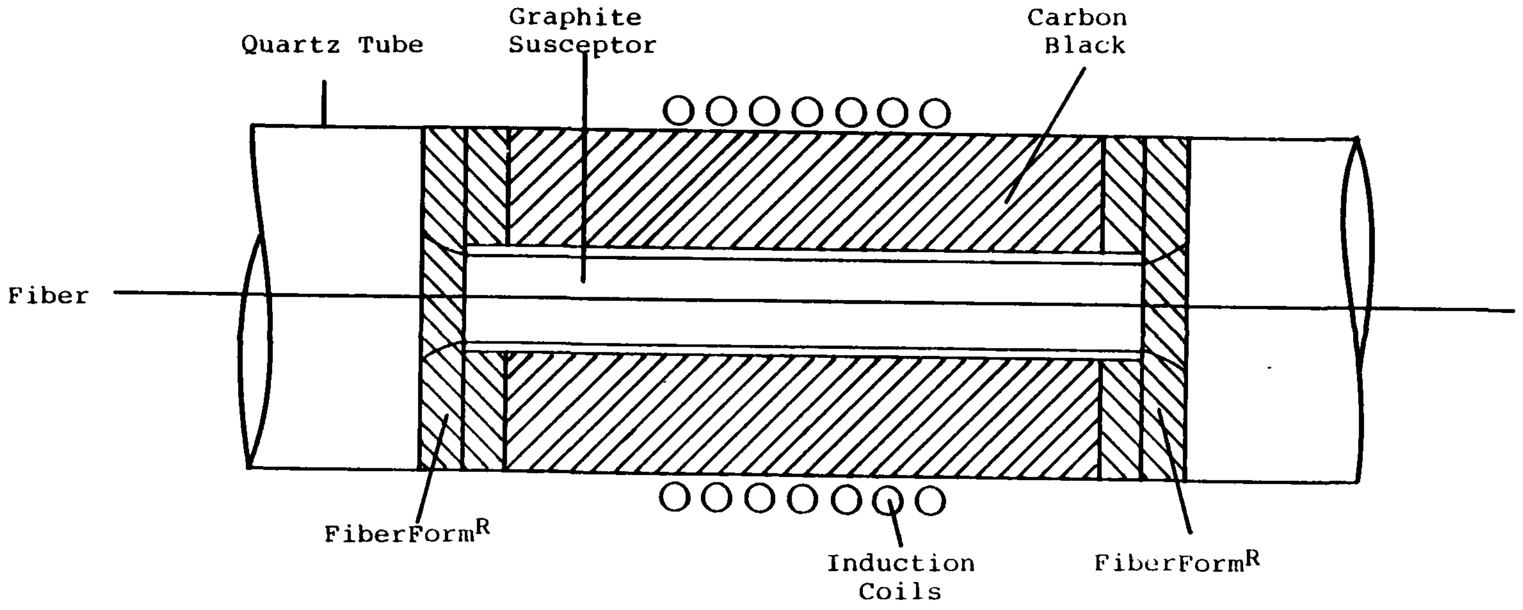

FIGURE 4

RESEARCH INDUCTION GRAPHITIZATION FURNACE
SECTION VIEW

FIGURE 5. The Effect of Gas Composition on Fiber Properties During 2400°C Graphitization.

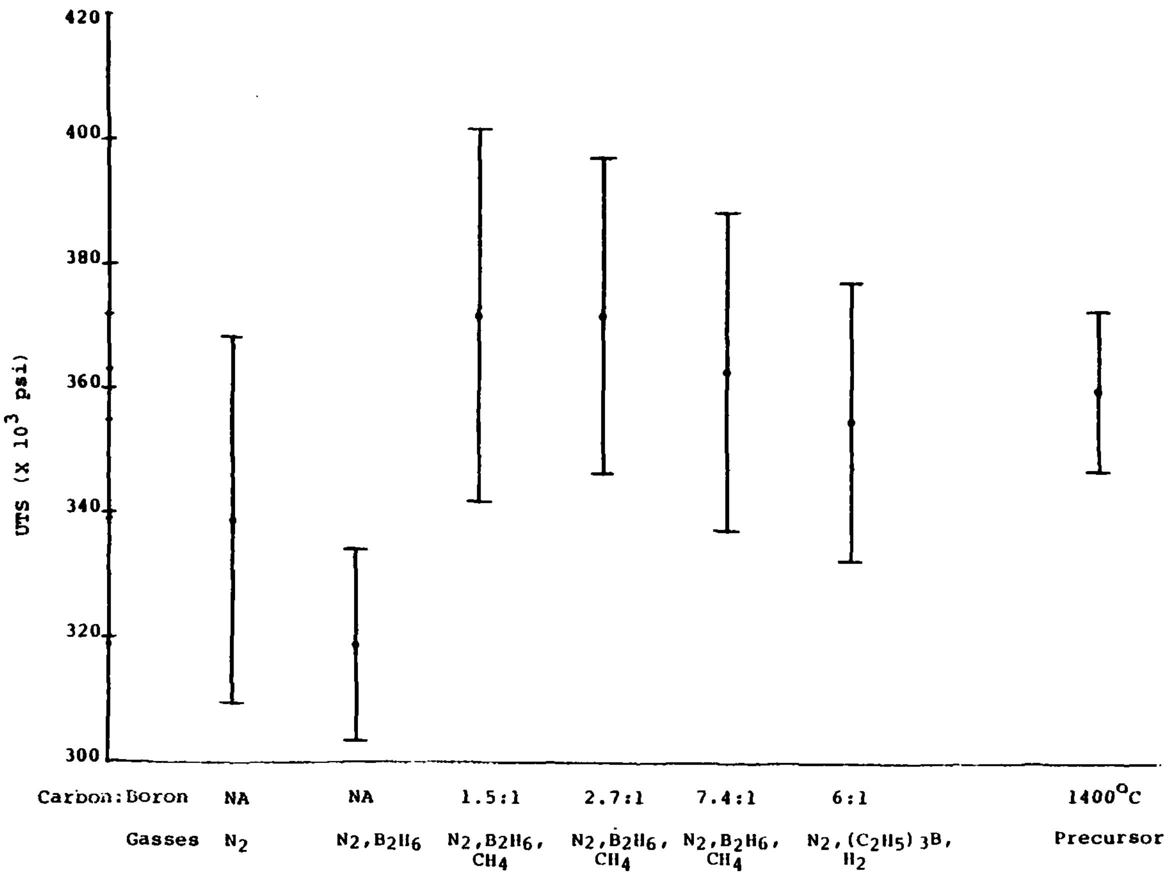

Table V. Preliminary Optimization of 2400°C Graphitization Conditions

Sample No.	Fiber Type	Carbonization Furnace						Astro Furnace			Pereny Furnace					Line Speed	Fiber Sizing	Fiber Tensile Properties			
	3X Drawn	Furnace Zone Temperature				N_2* Flows		Temp.	N_2* Flows		Temp.	N_2* Flows		Boron** Addition			E=Epoxy P=PVA	Density	E	UTS	STRAIN
		A °C	B °C	C °C	D °C	Ent.	Exit	°C	Ent.	Exit	°C	Ent.	Exit	Diborane	Methane	Ft/Min.		g/cc	x 10^6 psi	x 10^3 psi	%
0-43 19-1-7	Oxidized	308	422	530	680	50	150	1400	100	100	2400	100	110	41	100	1	E	1.83	55	432	0.81
0-43 19-1-8	Oxidized	308	422	530	680	50	150	1400	100	100	2400	100	110	41	100	2	E	1.80	56	440	0.84
0-43 19-1-9	Oxidized	308	422	530	680	50	150	1400	100	100	2400	100	110	41	100	3	E	1.78	56	468	0.86
G-42 7-2	Oxidized	308	422	617	822	90	90	1400	100	100	2400	90	110	41	100	1	E	1.80	55	468	0.90
G-34 21-8	Oxidized	308	422	617	822	90	90	1400	100	100	2300	90	110	41	100	1	P	1.81	60	473	0.79
G-47 18-1-10	Oxidized	308	422	617	822	150	50	1400	100	100	2400	100	110	41	100	1	E	1.85	60	471	0.79
G-49 11-13	Oxidized			617	822	150	50	1400	100	100	2500	103	100	41	100	2	E	1.87	62	514	0.87
G-49 14-5	Oxidized			617	822	150	50	1400	100	100	2500	103	100	41	100	2	E	1.86	60	485	0.86
G-49 11-10	Oxidized			617	822	150	50	1400	100	100	2500	103	100	41	100	2	E	1.82	63	542	0.93

*Nitrogen Flows: 50= 13.5 liters/minute, 90= 26 liters/minute, 100= 30 liters/minute, 103= 31 liters/minute, 110= 34 liters/minute, 150= 50 liters/minute.

**Diborane/Methane: 41= 0.8 liters/minute, 100= 0.10 liters/minute.

precursor for the work. The major variable studied during the 2400°C graphitization work was the carbonization conditions of the fibers. For example, as with the 1400°C graphitization studies, the thermal gradient in the carbonization oven was increased by changing the temperatures of the furnace zones and in some cases turning the zones off. The results of the work* are summarized in Table V, and are also discussed in detail in section 4.2 of this report.

3.2.5 Fiber Twisting For Metal Matrix Composites

Past work on the liquid metal infiltration of graphite fiber tows has shown that twisted fiber tows yield high fiber content aluminum composite wire. A major portion of the high strength and modulus small diameter fiber prepared under this program was required for work in metal matrix composites, and consequently fiber twisting studies were conducted. As a result of the studies, 6000 filament tow twisted fiber with a twist of ½ turn per inch was successfully produced for the MERADCOM metal matrix composites work.

A twisting machine was designed and constructed which consisted of a rotating fiber storage creel, a nip roll drive unit and 2 Leesona fiber winders. The twisting machine was capable of producing twisted fiber at a rate of approximately 20 feet per minute. Studies of twisting fully graphitized fiber were started, but were discontinued owing to the considerable visible damage occurring to the fiber tows on twisting. It was found that the oxidized PAN fiber could be twisted with little damage occurring during the twisting operation. Oxidized fiber samples were twisted at the ¼, ½, and 1 turn per inch levels, and were subsequently graphitized in the pilot production plant to the 2400°C stage. The results* of the studies are presented in Table VI, and are discussed in detail in section 4.2 of this report.

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*ASTMD 2343-67 (72) Strand Tests.

Table VI. Tensile Properties of Twisted High Modulus Graphite Fibers

Sample No.	Fiber Type	Carbonization Furnace						Astro Furnace			Pereny Furnace					Line Speed	Fiber Sizing	Fiber Tensile Properties			
	Oxidized 3X Drawn	Furnace Zone Temperature				N_2* Flows		Temp.	N_2* Flows		Temp.	N_2* Flows		Boron** Addition			E=Epoxy P=PVA	Density	E	UTS	STRAIN
	Twist (Turns Per Inch)	A °C	B °C	C °C	D °C	Ent.	Exit	°C	Ent.	Exit	°C	Ent.	Exit	Diborane	Methane	Ft/Min.		g/cc	x 10^6 psi	x 10^3 psi	%
G-42 7-2	½	308	422	617	822	90	90	1400	100	100	2400	90	110	41	100	1	E	1.80	55	468	0.90
G-31E 14-1	½	308	422	617	822	90	90	1400	100	100	2400	90	110	41	100	1	E	1.73	48	548	1.20
G-31E 15-1	½	308	422	617	822	90	90	1400	100	100	2400	90	110	41	100	1	E	1.74	47	532	1.16
G-33 3-1	1.1	308	422	617	822	90	90	1400	100	100	2200	90	110	41	33	1	P		41	264	0.78
G-33 4-1	1.1	308	422	617	822	90	90	1400	100	100	2200	90	110	41	33	1	P		46	415	0.92
G-35 19-4	½	308	422	617	822	90	90	1400	100	100	2300	90	110	41	100	1	P		50	391	0.78
G-35 13-9	½	308	422	617	822	90	90	1400	100	100	2300	90	110	41	100	1	P		49	393	0.80

*Nitrogen Flows: 90= 26 liters/minute, 100= 30 liters/minute, 110= 34 liters/minute.

**Diborane/Methane: 33= 0.05 liters/minute, 41= 0.8 liters/minute, 100= 0.10 liters/minute.

3.2.6 Fiber Sizing Studies

Sizing of the graphitized fiber is necessary to facilitate fiber handling during the winding operation and subsequent use. Unsized high modulus graphite fiber is very easily damaged and can not be successfully removed from spools or subjected to further processing operations such as weaving.

Polyvinyl alcohol (PVA) sizing was used for fiber for metal matrix composite studies and Shell Chemical Co. Epon 834 resin was used for fiber for epoxy matrix composites. Data from Material Concepts, Inc.,(3) indicated that a PVA sizing content of 0.25 wt.% was the most desired for use in metal matrix composites. To apply the sizing, the fiber was passed through a dip tank containing the sizing solution as it emerged from the final nip roll drive station of the graphitization line. Following application of the sizing, the fiber was passed through a drying oven, run at approximately 150°C, and then on to the winding station.

Distilled water was used as the solvent for the PVA sizings. An organic solvent was initially used for the epoxy compatible sizing (EPON 834), but problems with the sizing tank igniting led to the use of a water-based emulsion. The emulsion consisted of 100 parts by weight of EPON 834, 16.6 parts of ALIPAL EP-120 emulsifier, and 88.4 parts of water. It was prepared with vigorous stirring and diluted to a 1% solution for use. Analyses of the sizing content on graphite fibers showed it to be in the approximate range of 0.5 - 1.0%.

3.3 Task IV - Pilot Production Demonstration of Improved Graphite Fiber

Twenty pounds of improved small diameter graphite fibers were prepared and shipped to MERADCOM. This fiber was made towards the latter end of the program, but at too early a time to incorporate the improvements made in the carbonization techniques described in sections 3.2.3 and 3.2.4. Conditions similar to sample no. G-34 21-8,

Table V, were used for the production demonstration. Each roll of fiber was tested as part of the quality control testing conducted in Task III of the program, and the results are given in Table VII. Details of the quality control testing and the test methods are given in the Production Plan which accompanies this Final Technical Report.

3.4 Task V - Test and Evaluation of Best Effort Fibers Into Unidirectional Composites

Two uniaxial graphite-epoxy plates were prepared for testing. One 10 x 10 x 0.125 inches and one 6 x 10 x 0.25 inches. The fiber used for the preparation of the plates was typical of that supplied to MERADCOM, Table VII, and had the epoxy compatible sizing on it.

To form a unidirectional prepreg, graphite fiber was wound on a drum and the epoxy resin matrix was metered onto the yarn during winding. Dow Epoxy Resin 324 was used with Allied Resin Corp. NMA and BDMA hardeners (Nadic Methyl Anhydride and Benzyl Dimethylamine). The composition of the resin was 100 parts by weight of DER324, 90 parts NMA, and 1 part BDMA. Unidirectional sheets of prepreg were cut from the drum, and stacked in a hot pressing mold. 20 layers of prepreg were used for the 0.125 inch thick plate and 46 layers of prepreg for the 0.25 inch thick plate. A layer of Teflon coated fiberglass cloth (green bleeder) was placed at the bottom and top of the stack to facilitate separation of the plate from the mold. Approximately 55$\frac{v}{o}$ resin was metered onto the fiber during prepregging, and resin was expressed during pressing giving a final composition of approximately 60$\frac{v}{o}$ fiber and 40$\frac{v}{o}$ resin for both plates. The plates were pressed at 100 psi and 121°C for 1½ hours until the resin gelled, and were post-cured at 166°C for 17 hours.

0° tensile tests, 90° tensile tests, 45° tensile tests, 0° short beam shear tests, and 0° flexure tests were conducted on the plates. 0° and 45° tensile tests were conducted on the 0.125 inch thick plate, and the 90° tensile tests, 0° short beam shear tests, and 0° flexure tests were carried out on the 0.25 inch thick

TABLE VII

TYPICAL TENSILE PROPERTIES* OF THE DEMONSTRATION FIBER SHIPPED TO MERADCOM

FIBER	DENIER	DENSITY (g/cc)	ULTIMATE TENSILE STRENGTH (X 10^3 psi)	TENSILE MODULUS (X 10^6 psi)
G-42 10-1	1318	1.81	480.0	59.4
G-42 12-1	1322	1.80	465.8	55.0
G-42 17-1	1357	1.82	412.0	54.2
G-42 18-2	1362	1.80	443.0	54.4
G-42 7-2	1387	1.80	467.8	55.0

*ASTMD 2343-67 (72) Strand Test.

plate. The results of these tests are shown in Table VIII. Chemical analyses showed the 0.125 inch thick plate the 0.25 inch thick plate to have fiber contents of 58.1 volume percent and 62.5 volume percent, respectively. 0^{o} tensile specimen No. 1 moved on one end while the tabs were cured which resulted in uneven loading in the grip area during tensile testing. Tensile 2 appeared to be well aligned and is considered a valid test. The fibers near the edge of the 0.125 inch thick plate where tensile 3 was taken were observed to be nonaxial and thus tensile 3 is not considered representative of the true tensile strength of the composites. No problems were encountered with the 45^{o} and 90^{o} tensile tests. Very successful classical horizontal shear failures were observed in the 0^{o} short beam shear tests. Single shear failure was most evidenced. A span of 4 inches was tried on the 0.25 inch thick plate for the 0^{o} flexure tests but resulted in a short beam type of shear failure. The 0^{o} flexure span was increased to 9 inches and good flexural failures were obtained. Compression tests and high strain rate flexural impact tests were not conducted due to the lack of availability of suitable test fixtures and lack of time available for the testing phase of the program.

TABLE VIII

MECHANICAL PROPERTIES OF UNIAXIAL GRAPHITE/EPOXY PANELS

DATA TABLE

Tension 0°

	Ten-1	Ten-2	Ten-3
Young's Modulus E (x 10^6 psi)	27.0	29.5	24.4
Ultimate Tensile Stress σ(x 10^3psi)	84.5	135.5	65.1
Total Strain ε(%)	.312	.477	.435

Tension 90°

	Ten-1	Ten-2
E (x 10^6 psi)	1.05	1.03
σ (x 10^3 psi)	2.37	2.96
ε (%)	.224	.286

Tension 45°

	Ten-1	Ten-2
E (x 10^6 psi)	1.54	1.45
σ (x 10^3 psi)	5.68	4.98
ε (%)	.377	.322

Short Beam Shear 0° (Interlaminar Shear)

	SBS-1	SBS-2	SBS-3
Shear strength (x 10^3psi)	6.825	6.768	5.796

Flexure 0°

	Flex-1	Flex-2
Young's Modulus E (x 10^6 psi)	29.7	29.3
Modulus of Rupture (Flexure Strength) (x 10^3 psi)	94.1	90.1

4.0 DISCUSSION

The preparation of graphite fibers from polyacrylonitrile is a complex process and the results of this program are very promising and represent a major step towards translating past research results on the strengthening of graphite fibers by boron treatment during graphitization into a practical end item application. Development of the pilot production plant proved to be a larger task than anticipated, and was not advanced to the point originally expected on this program. A considerable amount of process optimization was necessary to produce improved graphite fibers at the intermediate plant scale-up level of 24 tows. Future work planned for the final plant scale-up to 96 tows will complete the development, and should lead to a further improvement in the tensile properties of high modulus graphite fibers. Some important process steps were not accomplished in the present program. For example, studies of the effect of tension during graphitization were not conducted due to difficulties with the existing fiber drive system of the plant, and the improved graphite fibers were not surface treated for improvement of fiber-matrix interface bonding in plastic matrix composites. These additional process steps will be resolved in the forthcoming future work on the graphite fiber pilot plant.

4.1 Plant Design

Oxidation Process

Temperature variations in the Gruenberg box ovens remain a problem. Improvements were made in the uniformity of the temperature distribution in the ovens during the program, but further improvements are needed. For example, one side of the ovens is cooler than the other which gives rise to a variation of oxygen content from one fiber tow to another. At this point in the development, the accuracy is ± 1-2% which is not adequate for consistent properties in graphite fibers. At the present time, considerable variation in graphite fiber tensile strength is found between different rolls of fiber, and the problem may originate in the oxidation ovens. Plans are currently in hand to insert additional horizontal baffles in the ovens to further improve the temperature uniformity during oxidation.

The oxidation of PAN fibers occurs at slow rates and in general is the rate limiting step of the graphite fiber production process. The use of high oxidation temperatures also requires study with the objective of shortening oxidation residence times, and increasing line speeds and the productivity of the process. The present line speed of 18 inches translates into a production rate of 1.9 lbs. per hour of oxidized 6000 filament tow 3X drawn (1.23 decitex) PAN fiber with a 96 tow plant. One pound of oxidized PAN converts to approximately a half a pound of graphite fiber therefore an increase in oxidation line speed to 2 feet per minute is needed to comfortably meet the overall program goal of 1 lb/hr of graphite fiber.

Carbonization and Graphitization Process

Scale-up on the carbonization line will require a system for the trapping or removal of tars from the furnace. In the present furnace, tarry deposits gradually build-up the entrance and exit slots, eventually causing fuzz build-up and damage to the fiber tows. In the present work with 24 tows, the problem is not serious, but will become important with the proposed plant scale-up. The overall present line speed of 2 feet per minute is acceptable and meets the goals of 1 lb/hour capacity for the pilot production line.

The reliability of the 1400 and 2400°C graphitization furnace needs considerable improvement. Particularly that of the 2400°C Pereny furnace, where the erosion problem with furnace element tube must be resolved. Re-design of the furnace box will be necessary to achieve vacuum furnace quality air tightness, and the elimination of all oxygen containing refractory bricks and thermal/electrical insulating boards will be necessary. For efficient long-term production runs, a furnace life of 3 months is judged as necessary. The present maximum life span of the heater element tube in the Pereny furnace is three weeks. Rebuilding of the furnace takes several days, which at best results in spasmodic operation of the graphitization line. Studies need to be conducted to determine if the 1400°C graphitization furnace step is necessary for high modulus 2400°C fired graphite fiber production. Past literature recommends slow heating of the fibers at intermediate temperatures to allow the removal of trapped gases such as nitrogen and oxygen from the carbonized fibers. This may, however, not be necessary with small diameter fibers since such gases may escape readily without damaging the fiber structures. Prior to scale-up of the plant to 96 tows, experimental pilot production runs will be carried out feeding the as-carbonized fibers directly into the 2400°C graphitization step. The properties of the fibers directly graphitized to 2400°C will be compared to those processed with the additional 1400°C graphitization step.

Improved fiber drive and guiding systems are needed. Past literature indicates that increased strength and modulus can be achieved by applying tension to the fibers during graphitization. Replacement of the nip roll drive system on the graphitization line with a staggered roll drive system will be necessary to accomplish this with the planned 96 tow scale-up. Such a drive system is currently used in the production of commercially available high modulus fibers. Improved fiber guiding and spacing systems are also needed to completely eliminate the fuzz build-up with the high modulus level graphite fibers.

Considerable progress was made on the program to the production adaptation and development of the boron treatment strengthening process. Further steps need to be taken, however, to reduce the flows of diborane and methane gases used and to correspondingly reduce the deposits of soot and boron doped pyrocarbon formed in the hot zone of the furnace and on the fiber surfaces. Detailed studies of these gas flows are planned in the future production development of the plant.

4.2 Process and Fiber Tensile Property Optimization

Oxidized Fibers

In general, past work on the preparation of graphite fibers from "undrawn" PAN has shown that approximately 10 wt.% is the optimum oxygen content for stabilization of the fiber during the carbonization process and maximum strength and modulus in graphitized 6-8 micron diameter fibers. In these standard size fibers, a skin and core type of structure is frequently observed in the fibers in the oxidized state, where the skin is of greater than 10 wt.% oxygen and the core is deficient in oxygen. Fibers with such an inhomogenous structure are difficult to process and must be carbonized at relatively slow rates. This processing at relatively slow rates may lead to a partial loss of the aligned structure resulting from the aligned polymer chains in the original PAN fiber. The small diameter PAN fibers which are drawn an additional 3X beyond the state of standard PAN fibers do not show this skin and core structure in the oxidized state, but rather oxidize both rapidly and uniformly. Consequently, the accepted optimum level of 10 wt.% oxygen may not apply to the small diameter fibers and a production development study of the effect of oxygen content on the tensile properties of the resulting 3-4 micron diameter graphite fibers is needed. This study was not in the scope of the present program, and the lack of knowledge in this area may account for the scatter in properties seen between different rolls of fiber. Present indications are that oxygen contents greater than 10% may lead to improved strength and modulus in small diameter graphite fibers.

Carbonized and 1400°C Graphitized Fiber

As stated above, higher heating rates in carbonization may be possible with the small diameter fibers. The data shown in Table IV shows a substantial increase in 1400°C fired graphite fiber tensile strength, of approximately 400-690 x 10^3 psi, with modifications to the carbonization oven increasing the thermal gradient. It is estimated that the heating rate of the fibers during carbonization at a line speed of 2 feet per minute was increased from approximately 50°C/min. to 300°C/min. by changing from zones A, B, C, and D to only zone D of the oven. Work is continuing on studies of the effects of the gradients during carbonization on the properties of resulting graphite fibers. Little is documented in the literature of the mechanisms of the pyrolysis of PAN fiber and their effects on the properties of the resulting graphite fibers. The present work, however, does indicate that to preserve the alignment of the oxidized PAN fibers, processing must be conducted at as high a heating rate as possible. As stated above, processing at high rates is possible with the small diameter fibers. The thermal gradient of the present carbonization furnace is very steep, and through the use of furnaces with more shallow gradients, line speeds could be increased well beyond 2 feet per minute giving a significant increase in productivity of the plant. The limitation here may be the length of the furnace hot zone available at the high temperature graphitization step necessary for the attainment of high modulus.

2400°C Boron Treated Graphite Fibers

The data in Table V shows that increasing of the gradient of the carbonization furnace also improves the tensile properties of the 2400°C boron treated graphite fibers as well as those of the 1400°C fibers (Table IV). For example, a tensile strength of 440 x 10^3 psi at approximately 60 x 10^6 psi modulus is typical of the data with zones A, B, C, and D of the carbonization oven on, while 500-550 x 10^3 psi at 60 x 10^6 psi modulus is typical with only zones C and D on. Work was not conducted at 2400°C with only zone D of the carbonization oven on, but will be conducted in future work. Optimization of the boron containing gas used during high temperature graphitization was also not carried out in the present program, and together with the above recommended studies of the optimization of the oxygen content of the preox fibers may lead to a significant improvement in graphite fiber properties.

The boron treatment process is a surface related phenomena. Work conducted at MIT(4) on boron treated samples has definitely shown that the deposited boron is confined to a surface layer on the fibers approximately 150 angstrom units in thickness. It is thought possible that the boron and carbon deposited from the borane/methane gas mixture provides strengthening of the fibers by healing surface defects such as pits and cracks. An undesirable feature of the boron treatment process is the deposition of soot and hard deposits on the surfaces of the fibers. This may well lead to poor interlaminar shear strength in organic matrix composites, and should be reduced as much as possible through refinement of high temperature graphitization processing conditions.

Studies were conducted in a research induction graphitization furnace of the effects of varying the nature and composition of the boron/carbon containing gas on the properties of 2400°C graphitized fibers. In this work 1400°C fired fiber was further graphitized at 2400°C in the induction furnace. It should be noted that the tensile strength of the starting 1400°C fiber used for the study was relatively low due to the gradual heating employed in carbonization of the oxidized PAN at the time of the study. The results do, however, show very definite trends. The base-line sample graphitized at 2400°C in nitrogen only showed an average strength of approximately 340 x 10^3 psi. Treatment with a nitrogen/diborane gas mixture caused a significant lowering of the fiber's tensile strength. However, the addition of methane to the nitrogen/diborane gas mixture increased the strength of the fibers to an average value of approximately 370 x 10^3 psi. The use of a nitrogen/triethylborane gas mixture instead of the nitrogen/diborane/methane gas mixture gave similar results. The work showed that the boron strengthening treatment can be successfully conducted using diborane as the source of boron, provided that carbon is simultaneously deposited from a gas such as methane. Diborane was used for the boron strengthening of fibers in the pilot production plant since significantly less soot and hard deposits were generated than has been observed with triethylborane.

During the graphitization of PAN fibers at high temperatures, the turbostratic graphitic structure of the fibers becomes pronounced as the temperature increases. Increase of the bond strengths of the fibers occurs in the "a" direction of the hexagonal graphite structure while a dramatic reduction in strength to almost zero occurs in the "c" direction. Misalignment of this turbostratic layered structure in the fibers can therefore lead to a catastrophic loss in fiber tensile strength. For example, if the "c" direction of the graphite structure is placed in shear, initiation of a crack in the fiber and a resulting failure will take place at a low load. Maintenance of tension on the fibers during high temperature graphitization, which favors the alignment of the turbostratic structure has been shown to improve fiber tensile strength and modulus. As stated above, modification will be made to the pilot production plant to facilitate graphitization under tension.

It is interesting to note that tensile tests conducted on graphite-aluminum wire have demonstrated higher filament tensile strengths than are indicated by the epoxy impregnated strand tests. For example, average tensile strength values of 220×10^3 psi and many high strength values of the order of 300×10^3 psi have been recorded on graphite aluminum wire of 34 volume percent fibers which was prepared from similar fibers to those shipped to MERADCOM and described in Table VII. Rule-of-mixtures analysis of this graphite-aluminum wire indicates the average strength of the individual filaments to be of the order of 550×10^3 psi with high numbers of the order of 785×10^3 psi. This is considerably in excess of the values observed in the strand tests. This discrepancy between the epoxy and the aluminum matrix data is not well understood, but the appearance of "relatively" low strength values on the epoxy strand tests could be due to the lack of a surface treatment on the graphite fibers and interference with the fiber-organic resin bond by the sooty deposits from the borocarbon depositon treatment. Further studies are planned as soon as possible to resolve this important issue since the graphite-epoxy strand test data is being used as a guideline to the optimization of high modulus graphite fibers in the pilot production plant.

Twisted Graphite Fiber Tows For Metal Matrix Composites

Table VI shows that the tensile strength of the twisted fiber tows as measured with the epoxy impregnated strand test is considerably less than that of the untwisted tows, Table IV. It should be noted that the work on twisted tows was conducted with a low thermal gradient in the carbonization oven, and before the preliminary optimization of carbonization conditions was carried out. It could be that problems causing degradation of fiber strengths, such as fiber sticking, occurred because of the slow heating rates used during carbonization. Further work is planned on the graphitization of twisted fiber tows using the improved carbonization conditions (higher heating rates) developed during this program.

4.3 Composite Properties

The properties determined on the graphite-epoxy panels, Table VIII, were considerably lower than expected. For example, given an average fiber tensile strength of 453 x 10^3 psi from the graphite-epoxy test data on the fiber shipped to MERADCOM (Table VII), the 0° tensile strength of the plates at approximately 60 volume percent fibers should have been approximately 226 x 10^3 psi. This is assuming an 83% translation of properties which is typical of surface treated high modulus fibers. The 0°tensile modulus value is correspondingly low, and the 0° flexure properties of the composites are also low. A comparison of some of the data on the 3-4 micon diameter boron strengthened graphite fiber with data(5) from HMU (unsurface treated) and HMS (surface treated) fibers is made in Table IX. The comparative data indicates that very poor fiber-matrix interface bonding was achieved with the graphite-epoxy panels made on this program. The 90° tensile strength and modulus of the panels is lower than the values reported for unsurface treated HM. Obviously, surface treatment of the boron strengthened small diameter is mandatory for improved interface bonding in organice matrix composites. As has already

TABLE IX

COMPARISON OF COMPOSITE* DATA FOR 3-4 MICRON DIAMETER BORON STRENGTHENED FIBER, AND HMU AND HMS FIBER

	3 Micron Fiber	HMU	HMS
0° Tensile			
UTS x 10^3 psi	136	130	175
Modulus x 10^6 psi	29.5	27	32
90° Tensile			
UTS x 10^3 psi	2.96	5-10	12.5
Modulus x 10^6 psi	1.1	1.3	2.0
0° Short Beam Shear			
Shear Strength x 10^3 psi	6.8		10.5

*Uniaxial Graphite-Epoxy Composite Panels of Approximately 60 Volume Percent Fibers.

been stated, loose or brittle deposits on the fiber surfaces must also be minimized. Finally, no work has been done on the choice of the optimum resin system to maximize translation of fiber properties in the small diameter fiber composites. It is well known in the industry that the best composite results for a particular fiber can sometimes only be obtained with a specific resin system. Consequently, a graphite epoxy composite study with the objective of choosing a workable resin system for the small diameter boron strengthened fiber is recommended.

5.0 CONCLUSIONS

1. Improved 3-4 micron diameter boron treated graphite fibers can be made from the small diameter (3X drawn) Courtaulds SAF polyacrylonitrile precursor fiber.

2. The pilot production plant has the potential capability for the production of the improved fiber at a rate of 1 lb. per hour.

3. Small diameter graphite fibers of average tensile strength 550×10^3 psi (as measured by epoxy impregnated strand tests) at the 60×10^6 psi modulus level have been prepared in the pilot production plant as a result of the preliminary optimization studies. This is a considerable improvement over the current state-of-the-art of HM fibers which is 350×10^3 psi at the 55×10^6 modulus level.

4. Tensile strengths in excess of 600×10^3 psi can be achieved at the 60×10^6 psi modulus level on the boron treated small diameter fibers with further process optimization of the pilot production plant.

5. Excellent translation of the improved fiber properties occurs in aluminum matrix composites. An in situ average filament strength of 550×10^3 psi with high numbers of the order of 785×10^3 psi have been observed.

6. Increasing the heating rate during carbonization gave a significant increase in the tensile strength and modulus of the graphite fibers following processing at the 1400°C and 2400°C graphitization temperatures.

7. Diborane can be used as a source of boron for the boron strengthening during graphitization at 2400°C and produces less undesirable soot and deposits than triethylborane.

8. Surface treatment of the improved 3-4 micron diameter graphite fibers is required for improvement of fiber-matrix interface bonding and interlaminar shear strength in plastic matrix composites.

6.0 RECOMMENDATIONS

1. A detailed optimization of the processing conditions in the graphite fiber pilot production plant is recommended with the objective of further improving the fiber properties. Parameters to be studied include the temperature and residence times during oxidation, carbonization, and graphitization, the concentration of boron containing gases in the 2400°C boron treatment step of the process, and the line tension applied to the fibers during the overall graphitization process.

2. Scale-up of the pilot production plant to full capacity of continuously processing 96 tows of fiber is recommended in order to achieve the production goal of 1 lb./hour.

3. Improvement of the fiber drive and guiding systems is also recommended to reduce fuzz build-up and damage to fiber tows, and to facilitate the application of tension during the graphitization steps of the process.

4. Redesign of the carbonization furnace is suggested to eliminate tar build-up at the entrance and exit ports of the furnace during processing. This requirement for tar removal during processing will become especially important as the plant scale-up proceeds.

5. Graphitization studies are recommended to determine if an intermediate temperature graphitization step is necessary for the preparation of improved high modulus graphite fiber (a 1400°C step is presently used).

6. Studies to minimize the amount of soot and deposits built-up in the hot zone of the 2400°C graphitization furnace are recommended to prevent damage to the fiber tows and increase the effective life of the furnace.

7. The surface treatment of high modulus graphite fibers is necessary for improved fiber-matrix interface bonding and interlaminar shear strength in composites, and the inclusion of such a surface treatment step following the graphitization process is recommended.

8. Studies of boron strengthened small diameter graphite fiber composites prepared with various commercially available resin matrix systems are recommended. The objective of this work would be to select a resin system giving good translation of fiber properties into composites.

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8