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FIBER-REINFORCED GRAPHITE COMPOSITE
FABRICATION AND EVALUATION

F. Lambdin
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UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE   Y-12 PLANT

operated for the ATOMIC ENERGY COMMISSION under U. S. GOVERNMENT Contract W-7405 eng 26

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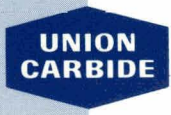
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Nuclear Division

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Contract W-7405-eng-26
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Oak Ridge, Tennessee

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ABSTRACT

Composites consisting of carbon fibers (2 microns in diameter by 10 mils long), and either of a thermoplastic or thermosetting resin, were spray formed onto graphite mandrels, carbonized to 1,000° C, and densified by repeated impregnation-carbonization cycles. Sections up to one inch in thickness and ranging in density from 0.2 to 1.7 gms/cc have been fabricated using spraying as the basic fabrication method. Isostatic and match-die compaction were used to increase the fiber population. Preliminary physical and mechanical properties of these composite materials were evaluated, and several were investigated to determine their performance under ablation conditions.

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SUMMARY

Composites consisting of carbon fibers (2 microns in diameter by 10 mils long) and having either a thermoplastic (coal tar pitch) or thermosetting (furfuryl alcohol) matrix were spray formed onto graphite mandrels. After carbonizing the sprayed matrix material, densification of the composite was attained by repeated infiltration with the desired matrix material and high-temperature carbonization cycles. Thick sections (~ 1 inch), ranging in density from 0.3 to 1.7 gms/cc, have been successfully fabricated using spraying as the basic fabrication method. Depending upon the intended use, spray-formed parts have been graphitized, infiltrated, or compacted in several ways to achieve the desired physical and mechanical characteristics. Isostatic and matched-die compactions were used to increase the fiber population of sprayed material and to accelerate the processing schedule.

Using spray forming, chopped Thornel and commercial graphite yarns were consolidated, but major efforts were devoted to the specially prepared two-micron-diameter graphite fibers. These materials were made by uniformly chopping unusually small-diameter viscose rayon yarns, pyrolyzing, and heat treating to 2,000° C by an appropriate furnace time-temperature cycle. These small-diameter fibers do not have the high strength and modulus usually associated with graphite fibers, but characterization of the composites containing these fibers has revealed significant property improvements. Mechanical and physical properties of the finished composites have been investigated for a variety of material and fabrication combinations. The data indicate that spray forming and compaction are useful and versatile methods for building efficient and light-weight graphite composites.

INTRODUCTION

Carbon-filament-reinforced graphite composites[a] are of interest because of their high strength-to-weight ratio and high-temperature strength-retention characteristics. These properties cause the composites to be attractive for refractory and weight-sensitive applications; and, considered with their high melting point, chemical inertness, and desirable mechanical properties attainable with the new high-strength and modulus fibers, make the long-range potential even more attractive.

One basic weakness in the continuous-filament-type composites, such as cloth layups and filament windings, is their severe limitations for applications where three-dimensional strength is needed. Methods of fabricating commercially available fibrous graphite composites involve using macerated graphite cloth or fibers of considerable length (1/32 to 1/4 inch). These materials are usually die pressed with a resin binder. This procedure usually results in considerable fiber alignment and an anisotropic structure.

Of particular interest have been some of the more specialized fabrication methods and alternatives which seem to be feasible with a carbon-filament-reinforced graphite body. In order to realize more fully the strength potential of the strong fibers in a composite, a system was devised for building graphite composites by spraying short fibers with resin and diluent onto a mandrel. Further processing of the composite from this point was optional, depending upon the desired characteristic and application of the final product. Isostatic-pressure carbonization of fibrous composites bound with phenolic and pitch resins was also developed for increased fiber population and more nearly random fiber alignment.

The objectives of the program were: (1) to characterize the physical properties of the consolidated materials, and (2) to correlate the fabrication parameters with these properties.

(a) In this report, the reinforcing fibers and filaments will be referred to as "carbon" and the matrix will be considered as "graphite". Since it is possible to alter the matrix from carbon to graphite, exceptions to the convention will be noted.

FABRICATION AND EVALUATION OF THE COMPOSITES

PREPARING THE COMPOSITE

Process Description

A flow diagram of the process by which short carbon fibers have been fabricated into test pieces and experimental hardware for evaluation is outlined in Figure 1. The process utilizes uniform lengths of carbon filaments sprayed from a continuously stirred mixture with one of a wide selection of resins in a carrier solvent. The resultant sprayed composite is then further processed in a variety of ways depending upon the selection of the resin and the desired properties of the final product.
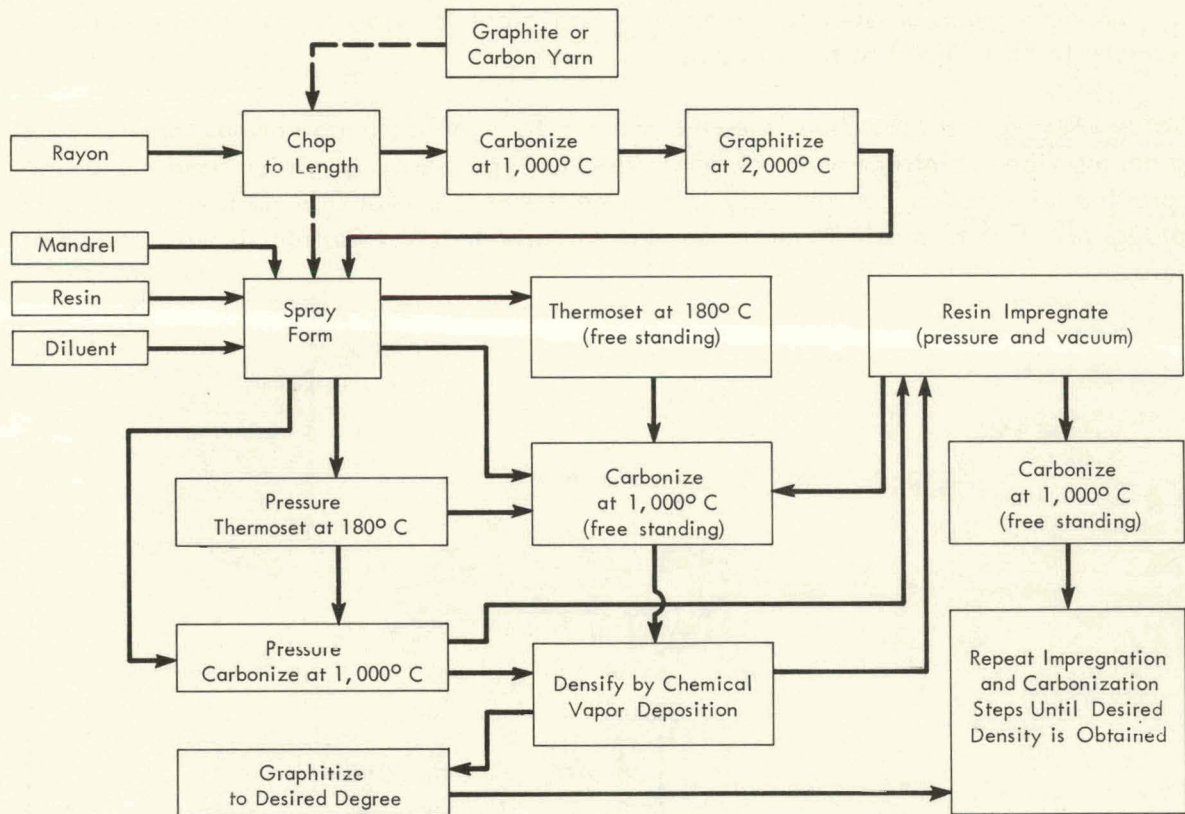
Figure 1   PROCESS FOR PRODUCING FIBER-REINFORCED GRAPHITE.

To prepare a sample, as outlined in Figure 1, rayon-derived carbon fibers could be combined with a solvated thermosetting resin, sprayed onto a suitable mandrel, dried and thermoset at 180° C, carbonized to 1,000° C, impregnated with resin, and carbonized again to 1,000° C. The impregnation-carbonization cycles could be continued until a specified sample density was reached. Other alternatives will be discussed in the sections that follow.

Fibers – The carbon fibers which have been used came from two main sources: Fibers were initially supplied by chopping 7 to 10-micron-diameter commercial graphite yarn to lengths of ten mils. Later, a small-diameter graphite fiber supply was attained by chopping viscose rayon to short lengths followed by carbonization and graphitization to 2,000° C. It was desired that the fiber should be as short as possible to achieve random orientation in the sample yet maintain a high aspect ratio (length-to-diameter ratio) for optimum reinforcement.

Resins – Two main types of resins have been used, but the spraying process could be used with many solvated binder systems, including "dry" materials. Phenolic resins, diluted with a suitable solvent such as methyl ethyl ketone (MEK), and thermoplastic resins, such as coal tar pitch diluted with benzene, have been employed. Generally, the resins were successively added to the spraying mix in quantities from 23 to 60 weight percent. A resin diluent addition of 1,000 to 1,500 cubic centimeters per one hundred grams of fiber to the mix was sufficient to allow the resin-fiber-diluent mixture to be pumped to the spray gun.

Spray Forming – Figure 2 outlines the process for spray forming various samples with graphite fiber reinforcement. A recirculating-type spray gun was used, and the spraying mixture was continuously agitated in order to prevent the delivery lines from plugging. If the sample to be made was circular in cross section, it was rotated at
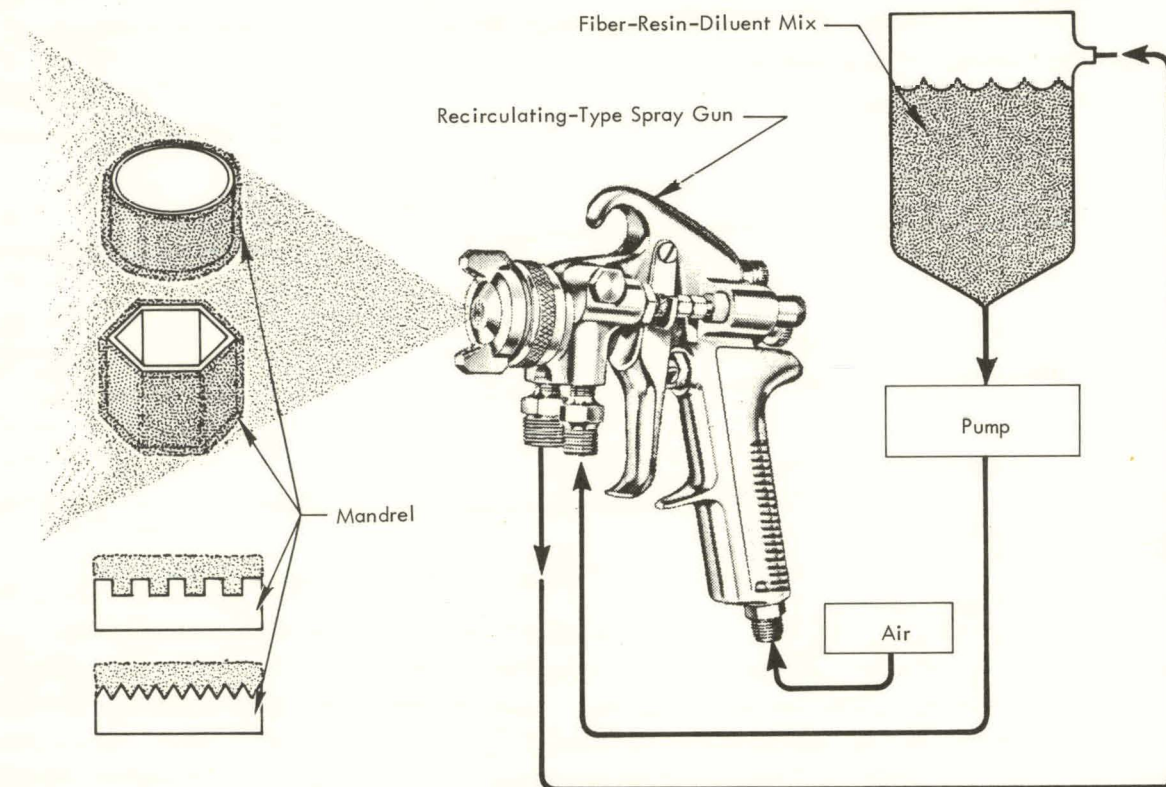
Figure 2. TYPICAL SPRAY-FORMING PROCEDURE.

approximately 10 rpm for a more even distribution of the sprayed fibrous material. Spraying usually was performed in a dry filter-type commercial paint spray booth. Wall thicknesses in the range of 15 mils to 3.000 inches were attained.

Controls for various process parameters were incorporated into the spray-forming system, namely: air pressure from 5 to 60 psi, mandrel rotation rates from 12 to 20 rpm, and spray-to-surface distances from 1 to 5 inches. Generally, if the samples had a large surface area (greater than one square foot), the spraying process was continuous; but, for smaller areas, sufficient drying time had to be allowed during the spraying operation for the excess diluent to evaporate. Continuously evacuated mandrels were tried on a small scale to shorten the drying time and improve sprayed uniformity, but these devices were not used for the samples described in this report.

Compaction - Compaction is a method of increasing the fiber population in the final sample above that which is attained in the spray-formed sample. Compaction of spray-formed material was accomplished for pressures ranging from 15 psi (vacuum bag technique) to 30,000 psi (gas autoclave), depending upon the resin system used and the desired end product.

Compaction of spray-formed parts which used a phenolic resin as the binder was usually accomplished by thermosetting the resin at 180° C. Thermoplastic resin-fiber systems were compacted by pressure carbonization of the samples to 1,000° C, primarily in a gas autoclave. Continuous venting of the pyrolysis product of the resin was provided. In general, compaction of a phenolic resin-fiber system during thermosetting increased the fiber density by about 400 percent. One sample with a thermoplastic resin binder system increased the fiber volume by about 600 volume percent while undergoing pressure carbonization to 1,000° C.

Carbonization - Carbonization, as shown in Figure 1, is the complete pyrolysis of the binder resin to carbon in an inert atmosphere. In the carbonization of the non-compacted, spray-formed samples, the heat cycle to 1,000° C was programmed automatically for a 30 to 120-hour duration. The duration time varied with the type and amount of resin used and the size and shape of the sample. The program for the controller was derived to assure a constant weight loss per unit of time, as determined by a thermogravimetric analysis of the resin. Elimination of thermal shock in the samples was also a factor in determining the rate of heating and cooling in the carbonization cycle.

A typical carbonization furnace and its auxiliaries is sketched in Figure 3. Pressure carbonization of spray-formed samples required about 16 hours to heat to 800° C.

Densification - Densification of carbonized, spray-formed samples of fiber-reinforced graphite was generally accomplished by multiple coal tar pitch impregnations and carbonization cycles. This process is shown graphically in Figure 4. Densities in the range of 1.60 gms/cc were reached in 5 to 10 cycles, depending upon the initial carbonized density, concentration of the impregnant, and pressure used in the impreg-
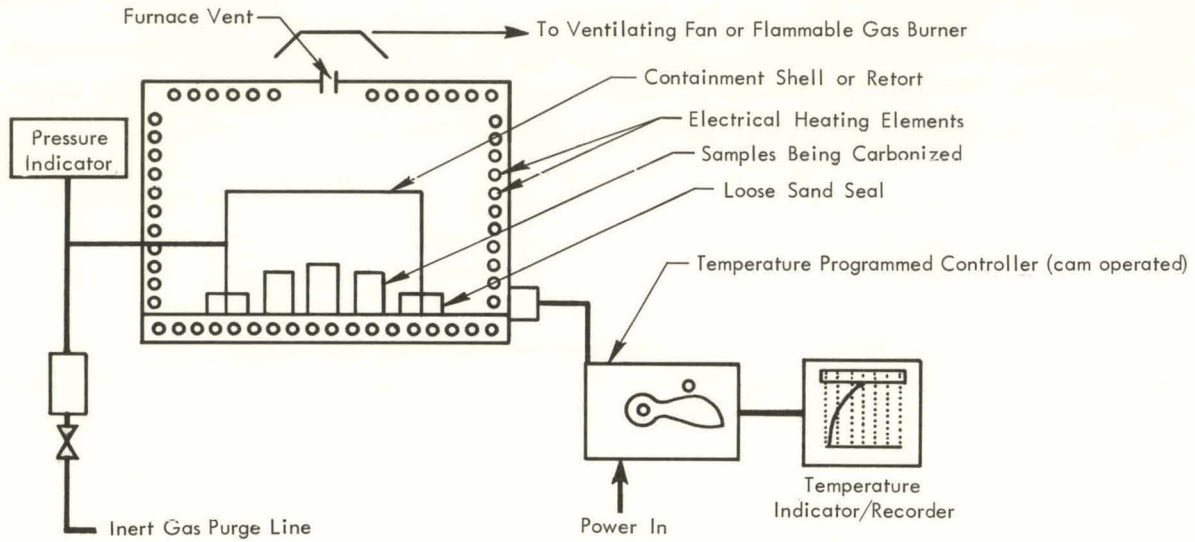
Figure 3. TYPICAL 1,000° C CARBONIZATION FURNACE AND ITS AUXILARIES.

Figure 4. METHOD USED TO VACUUM AND PRESSURE IMPREGNATE CARBONIZED, SPRAY-FORMED, AND FIBER REINFORCED GRAPHITE.

nating systems. Pressures from 100 to 5,000 psi were used, depending upon the sample size and density. Several samples were densified by carbon vapor deposition.

Graphitization - Graphitization, as shown in Figure 1, refers to heating the composite, including the carbonized matrix or impregnated carbon, to effect some degree of crystal reorganization and such associated property changes as a lowering of the modulus. Heating was accomplished in an induction-type furnace and usually involved heating the samples between 2,500 and 3,000° C in an inert atmosphere.

RAW MATERIALS DEVELOPMENT

Graphite Yarn-Derived Fibers

High-twist, first-quality graphite yarn, cut to 10-mil lengths[b] had less than one weight percent of the yarn remaining on a 30-mesh screen after sieving. This material was sprayed successfully using the recirculating-head spray gun. Figure 5 is a photomicrograph of a cross section of the commercial graphite yarn.

Low-twist graphite yarn, cut in the same way, yielded only about 50 weight percent of the minus 30 mesh material. Furthermore, this screened material was very agglomerated and could not be sprayed.

Rayon Yarn-Derived Fibers

Due to the short supply of high-twist graphite yarn, a second supply source of short graphite fibers was sought. As a result, a commercial type of rayon was found.[c] This material was chopped into ten-mil lengths and then carbonized and graphitized. Graphite fibers were produced which were sprayable without prescreening. The fibers were ten mils in length and seven microns in diameter (shown in Figure 6). The diameter of commercially available graphite yarn filament is approximately ten microns. A quantity of 0.15 denier/filament rayon was supplied by the same vendor and chopped, carbonized, and graphitized. This rayon, which has a filament diameter of approximately 3.7 microns, produces graphite fibers in the 1 to 2-micron-diameter range, as shown in Figure 7. Figure 8 indicates the length uniformity obtained in precision-cut seven-micron-diameter graphite fibers prepared from precut rayon.

Figure 9 presents a graph showing the theoretical-size relationship of Villwyte rayon yarn with its denier. Also shown is the average size of the rayon filament after carbonization to 1,000° C. Villwyte rayon of several deniers was carbonized and graphitized under various heatup rates and pyrolysis conditions. Since the quality of the chopped graphite yarn was very questionable for spraying (primarily, due to the nonuniform lengths), the tensile strength of various-sized yarns carbonized by different methods was investigated.

(b) By Microfibres, Inc., Pawtucket, Rhode Island.

(c) IRC Fibers Division of Midland-Ross Corporation supplied their Villwyte rayon of 2.29 denier/filament (~ 18-micron) size.
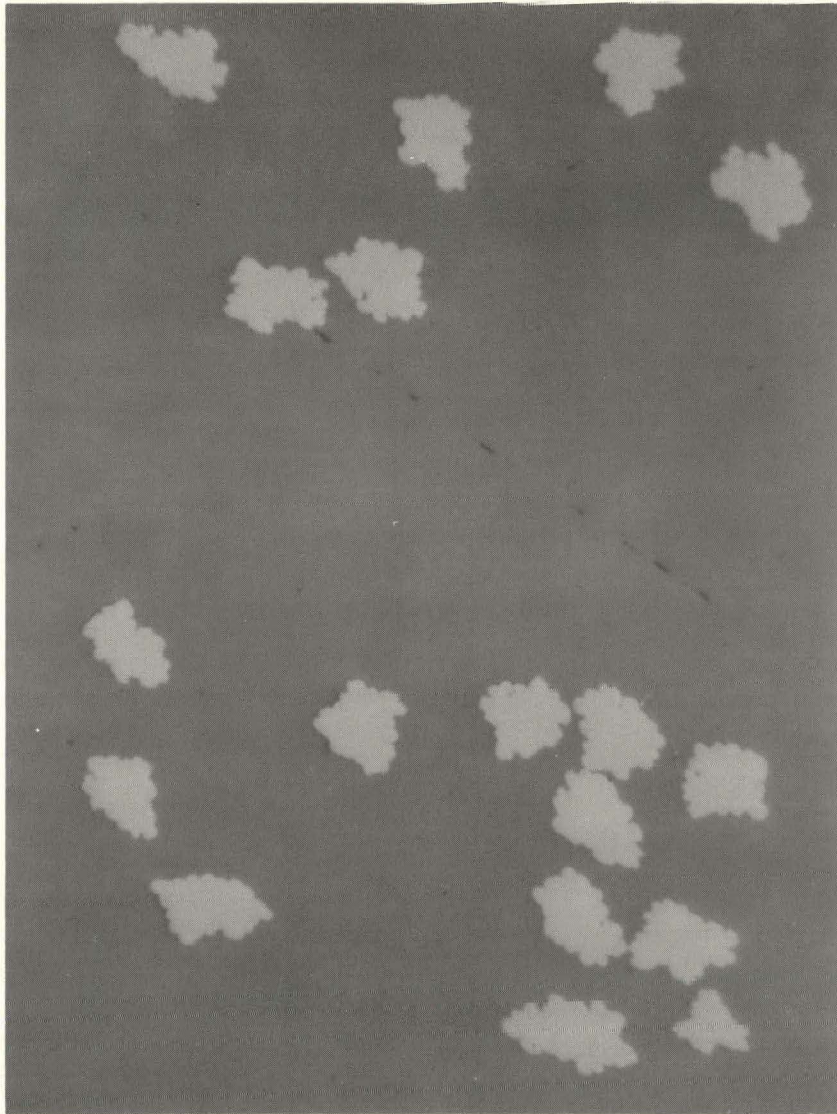
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Figure 5. PHOTOMICROGRAPH SHOWING THE CROSS SECTION OF COMMERCIAL GRAPHITE YARN. (1,000X; Bright Field Illumination; As Polished)

Table 1 lists the carbonization conditions and strength of the appropriately sized filament. For comparison purposes, the results are shown on ten-micron filaments from commercial graphite. The tests were made using an Instron test machine with Load Cell A (0 - 50 grams). The crosshead speed was 0.05 inch/minute. The fiber (1.0-inch test length) was mounted vertically on a cardboard fixture with household cement.[d] The cross-sectional area was determined by microscopic diameter

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(d) Manufactured by Ross Chemical and Manufacturing Company, Detroit, Michigan.

Table 1

STRENGTHS OF GRAPHITE YARN OF VARIOUS SIZES AND CARBONIZING CONDITIONS
(Tensile Strengths in psi)

	Rayon Denier/Filaments			
	1,100/100	450/60	1,100/240	1,100/480
Rayon Denier Filament Ratio	11.0	7.50	4.58	2.29
Rayon Filament Size (microns)	30.2	26.4	20.6	14.4
Graphite Filament Size (microns)	17.0	13.6	10.9	7.0
Carbonizing Conditions of Materials				
High Twist, Commercial[1]			66,000	
TGA–Derived Heat Cycle (30 hrs), N_2 Purge (graphite)	42,300			
TGA–Derived Heat Cycle (60 hrs), N_2 Purge (graphite)	44,800	62,700	58,700	39,800
(carbon)		72,700		78,000
TGA–Derived Heat Cycle (150 hrs), N_2 Purge (graphite) (carbon)	51,000			
TGA–Derived Heat Cycle to 400° C in Six Hours in Hydrocarbon Oil Remainder of Decomposition in 60 Hours (graphite)	39,000			
TGA–Derived Heat Cycle to 400° C in 60 Hours in Hydrocarbon Oil. Remainder of Decomposition in 60 Hours. N_2 Purge (graphite)	41,000			
Air at 100° C for 24 Hours, 100 to 200° C at 5° C/hr, then TGA–Derived Heat Cycle in 60 Hours, N_2 Purge (graphite)	37,000			
TGA–Derived Heat Cycle in 60 Hours. Less Than 50 Microns Hg Vacuum (graphite)		Not Testable Due to Brittleness		
To 190° C in 60 Hours in Vacuum then TGA Derived. Heat Cycle 60 Hours in N_2 Purge (graphite)	37,000			
200° C/hr to 2,300° C with one-Hour Hold in Argon Purge (graphite)		51,700	52,000	36,000
100° C/hr to 2,300° C with one-Hour Hold in Argon Purge (graphite)				29,000
30° C/hr to 650° C then 50° C to 900° C in N_2 Purge (graphite)		49,500	54,500	Too brittle
(carbon)		72,000		45,000
25° C/hr to 150° C, 16-Hour Hold in Air, then 30° C/hr to 650° C and 50° C/hr to 900° C in N_2 Purge (graphite)				41,000
(carbon)				48,500

(1) Union Carbide Corporation's WYB-85. 90,000 psi at 1.0-inch test length.

measurements. The diameter measurement was not correlated with the metallographic specimen; therefore, the area probably was 20 to 25 percent lower than the diameter measurement indicated due to the irregularity in shape. Although these tests were

D181

Figure 6. PHOTOMICROGRAPH SHOWING THE CROSS SECTION OF SEVEN-MI-CRON-DIAMETER GRAPHITE FIBERS PREPARED FROM PRECUT RAYON YARN. (1,000X; Bright Field Illumination; As Polished)

not accurate or precise enough to show size-strength relationships, they do show the differences expected from process conditions. They also show, in a relative manner, that rayon fibers processed in batch conditions are generally as strong as commercial

graphite yarn fibers which are processed in a continuous manner. (e) As a result of these tests, the TGA-derived 60-hour heat cycle was used as the standard process condition for the production of short graphite fibers from chopped Villwyte rayon.
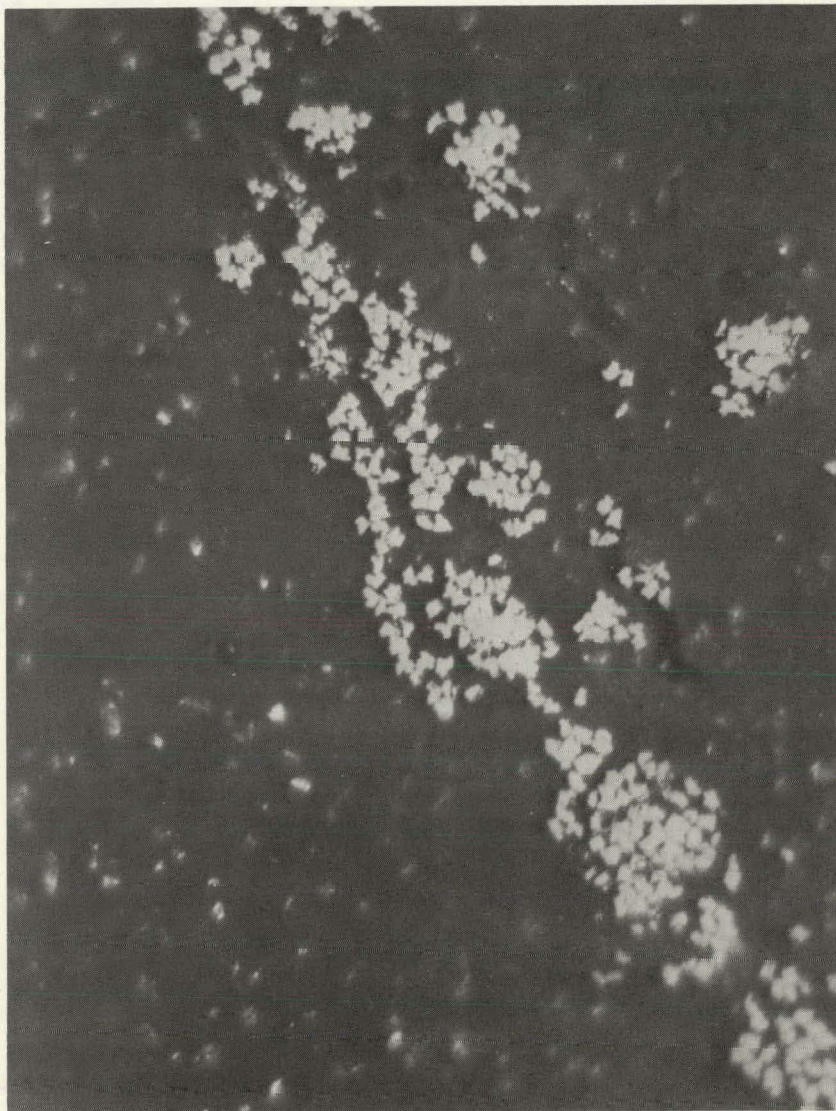
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Figure 7. PHOTOMICROGRAPH SHOWING THE CROSS SECTION OF TWO-MICRON-DIAMETER GRAPHITE FIBERS PREPARED FROM PRECUT RAYON YARN. (1,000X; Bright Field Illumination; As Polished)

(e) Since the testing method has considerable influence on the results of particularly high-modulus materials such as these filaments, a more sensitive testing procedure will have to be used. In particular, a slower crosshead speed and closer correlation of the area with filament diameter would be desired.

Graphite fibers from the 2.7-micron-diameter rayon (0.15 denier/filament) were not tested in this investigation due to the inability to physically mount the 1.4-micron fiber specimen.

Figure 8. PHOTOMICROGRAPH SHOWING PRECISION-CUT, SEVEN-MICRON-DI-AMETER GRAPHITE FIBERS PREPARED FROM PRECUT RAYON YARN. (15X)

Table 2 summarizes the physical characteristics of ten-mil-long carbon and graphite fibers from various sources. The table also gives the average fiber diameter, screen fractions (if screened), bulk density, tap density, helium density, and surface area. As the table indicates, the low-twist commercial graphite yarn did not chop to the short lengths very uniformly and had to be passed over a series of screens in order to
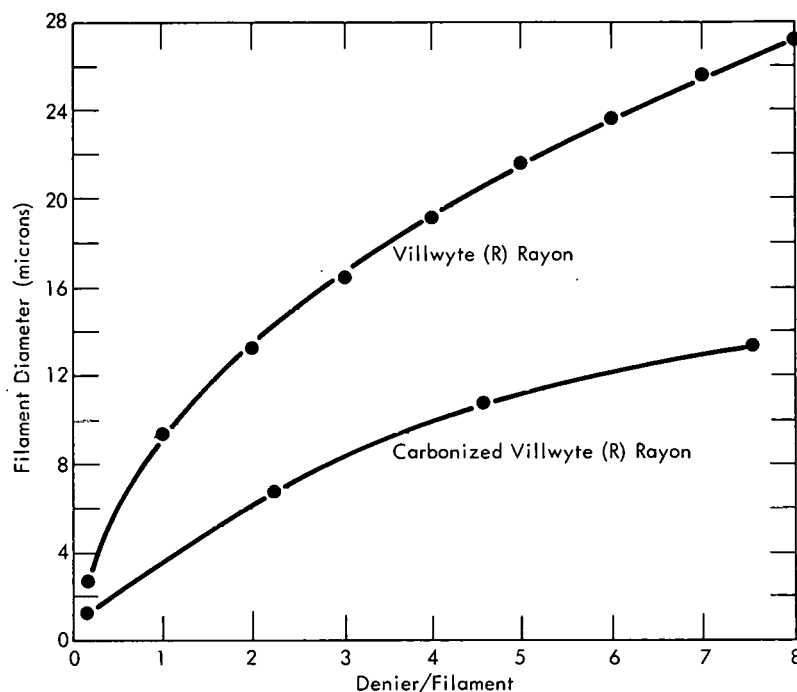
Figure 9. SIZE RELATIONSHIP OF VILLWYTE RAYON BEFORE AND AFTER
CARBONIZATION TO 1,000° C.

separate the material which could be sprayed using a spray gun. Approximately 50
weight percent of this material passed through a 30-mesh sieve and was usable. The
high-twist commercial graphite yarn chopped somewhat more uniformly with only about

Table 2

PHYSICAL CHARACTERISTICS OF VARIOUS FIBER SUPPLIES
(Ten-Mil Lengths)

Material	Fiber Diameter (μ)	Screen Fraction (mesh)	Density (gms/cc)			Surface Area (m^2/gm)
			Bulk	Tap	Helium	
Graphite Yarn, High-Twist Commercial (UCC's WYB-85)	10	-30	0.200	0.294	1.43	2.32
Graphite Yarn, Low-Twist Commercial (The Carborundum Company)	10	+30	0.034	0.054	1.43	2.32
	10	-30	0.158	0.282	1.43	2.32
	10	-30 +80	0.050	0.080	1.43	2.32
	10	-80	0.262	0.462	1.43	3.34
Villwyte Rayon (1,100/480) Derived (1,000° C) Carbonized	7.0	All	0.140	0.220	1.87	0.30
Graphitized (2,300° C)	7.0	All	0.150	0.230	1.44	0.98
Villwyte Rayon (1,100/480) Derived (1,000° C) Carbonized	2.0	All	0.067	0.108	1.90	1.89
Graphitized (2,300° C)	2.0	All	0.067	0.108	1.39	2.04

one weight percent removed with a 30-mesh screen. The graphite fibers made from chopped rayon were very uniform and, although slightly agglomerated, were capable of being sprayed uniformly (see Figure 8).

Ten-inch lengths of cuprammonium rayon yarn, Nomex[f] nylon yarn, and Villwyte rayon yarns were heated for two hours at temperatures from 100 to 900° C in a flowing argon atmosphere. After cooling, the lengths were measured. Figure 10 gives a plot of the length of the ten-inch pieces after two hours at the appropriate temperatures. New pieces of yarn were used for the determination of each temperature shown in the plot.

In Figure 10, the Villwyte rayon is shown to yield approximately 58 percent of its original length after a 900° C carbonization. This value corresponds to an average of about 52 percent yield on the diameter (Figure 9); however, the diameter measurements were probably not as accurate as those of length.
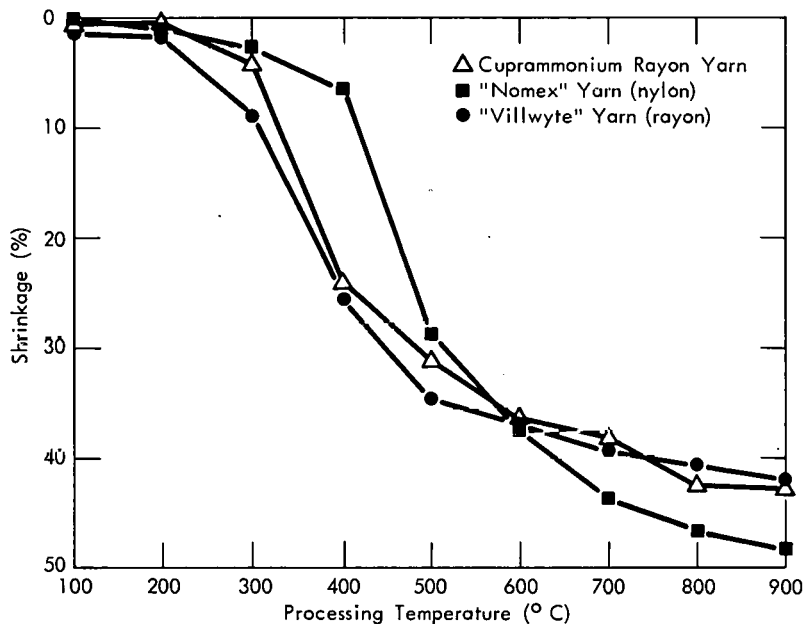
Figure 10. EFFECT OF HEAT ON TEN-INCH LENGTHS OF VARIOUS YARNS.

Pitch and Phenolic Resin

Spraying was accomplished equally well with coal tar pitch,[g] the characteristics of which are given in Table 3, or phenolic resin.[h] For spraying purposes, only the

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(f) Manufactured by E. I. Du Pont de Nemours and Company, Inc.

(g) Allied Chemical Corporation's CP-227-15V.

(h) Type 91-LD, manufactured by American Reinforced Plastics Company, Los Angeles, California.

benzene-soluble portion (filtered) of the pitch was used in the mixture, but impregnation operations generally used either molten (100%) or benzene-solvated (unfiltered) pitch.

EQUIPMENT DEVELOPMENT

Manual Spray Forming

The feasibility of spraying the fiber-resin diluent from a commercial, recirculating-head-type paint spray gun was determined in cooperation with the manufacturer. A hand-held gun[i] was set up with a four-liter stainless steel recirculating tank and a pump.[i] The 70-mil opening in the spray gun was found to spray the material suitably when held three to ten inches away from the spraying surface, depending upon the surface finish desired, the amount and kind of fibers being sprayed, the amount of drying air being used, and the pressure and amount of air supplied to the spray gun for atomization.

Automatic Spray Forming

The need for better process control was apparent from the experience with hand-held guns. A large number of parameters were found to affect the quality of the sprayed

Table 3

CHARACTERISTICS OF A COMMERICAL PITCH

Characteristic[1]	Value[2]
Softening Point, CIA	90 - 95° C
Specific Gravity at 25° C	1.26 - 1.32
Benzol Insoluble (wt %)	12 - 16
Quinoline Insoluble (wt %)	2 - 6
Coking Value	
7 minutes at 950° C (wt %, min)	26
10 minutes at 700° C (wt %, min)	30
Conradson (wt %, min)	35
Ash (wt %, max)	0.25
Distillation (wt % to 360° C, max)	9

(1) Pitch was Allied Chemical Corporation's Grade CP=227-15V.
(2) Data supplied by the vendor.

(i) The DeVilbiss Company MBC-5028-704-EE.
(j) Eastern Industries Model D-11.

sample, for example: gun-to-surface distance, transversing speed, and spray angle. The simultaneous manual control of all of these variables to within narrow limits was not possible.

An automatic, vertical-carriage spraying machine[k] was designed, procured, and set up to spray mixes of short, chopped graphite fibers, resin, and diluent onto stationary or rotating mandrels for use in sample preparation and to develop fabrication techniques. The machine uses an automatic recirculating-type spray head and can be adjusted for any sample shape. Figure 11 shows a plan view and Figure 12 a side view of the automatic spray machine.

The design includes a hydraulic pressure-actuated traversing mechanism and turntable. The spraying arm slides on a precisely machined track and is lifted by a continuous belt arrangement. The spray arm is held in contact with a contoured cam by a spring (Figure 11), and the cam positions the spray gun a predetermined distance from the mandrel. The speed of the spray head, as it traverses a part with a varying surface area, is changed by the traversing speed cam (Figure 11).

This adjustable cam positions a hydraulic-fluid-valve lever which varies the pressure to the hydraulic motor; which, in turn, changes the speed required to provide a constant dwell time per unit of surface area. The sweep rate is variable along the seven-foot maximum stroke from about 500 to 1,800 ft/min. Speed is maintained in both directions of travel. The direction change is accomplished by a direction-reversing rod (Figure 11) which is fastened to the direction-reversing valve and is actuated by the spray arm through adjustable stops attached to the rod.

Impregnation Equipment

The vacuum-pressure impregnation cycles with coal tar pitch, shown in Figure 4, were carried out as separate operations in the majority of the densification work; that is, the samples were first vacuum impregnated (oven) in molten pitch at 200° C and 25 inches of vacuum, then pressure impregnated (autoclave) in molten pitch at 200° C and 5,000 psi. This equipment limited the size of the impregnated samples to about four inches in diameter. A larger facility, consisting of two interconnected tanks (22" D x 40" L), provided a capability for evacuating parts and impregnant separately, transferring liquid impregnant to the evacuated part under pressure, heating to 400° C, and pressurizing to 50 psi. Later, a single-tank, automatic-impregnation system[l] was purchased. This unit has an impregnating tank that is 2 1/2 feet in diameter and 7 feet in depth, and is capable of subjecting multiple samples to dry vacuum, wet vacuum, and wet pressure. The unit also has interchangeable impregnant tanks and the capability of operating to 475° F with a 28.5-inch mercury vacuum or 100-psi pressure.

(k) Designed and manufactured by The Process Equipment Company, Tipp City, Ohio.
(l) Designed and manufactured by Sinter-Seal Division of the N. B. Newcomb Company, Inc., Buffalo, New York.

Filter Bank (9 1/2 ft high)

Baffle

Air Pump

Mix Tank

Telescopic
Spray Arm

Rotary
Turntable

To Gun

Return

Contour Cam

Recirculating
Head-Type
Spray Gun

Traversing Speed Cam

Direction Reversing Rod

Spray Booth

6'

44"

8' 4"

On	On	On
Off	Off	Off
Table rpm	Table Control	Gun Control	Air Supply

24"

Hydraulic Control Cabinet
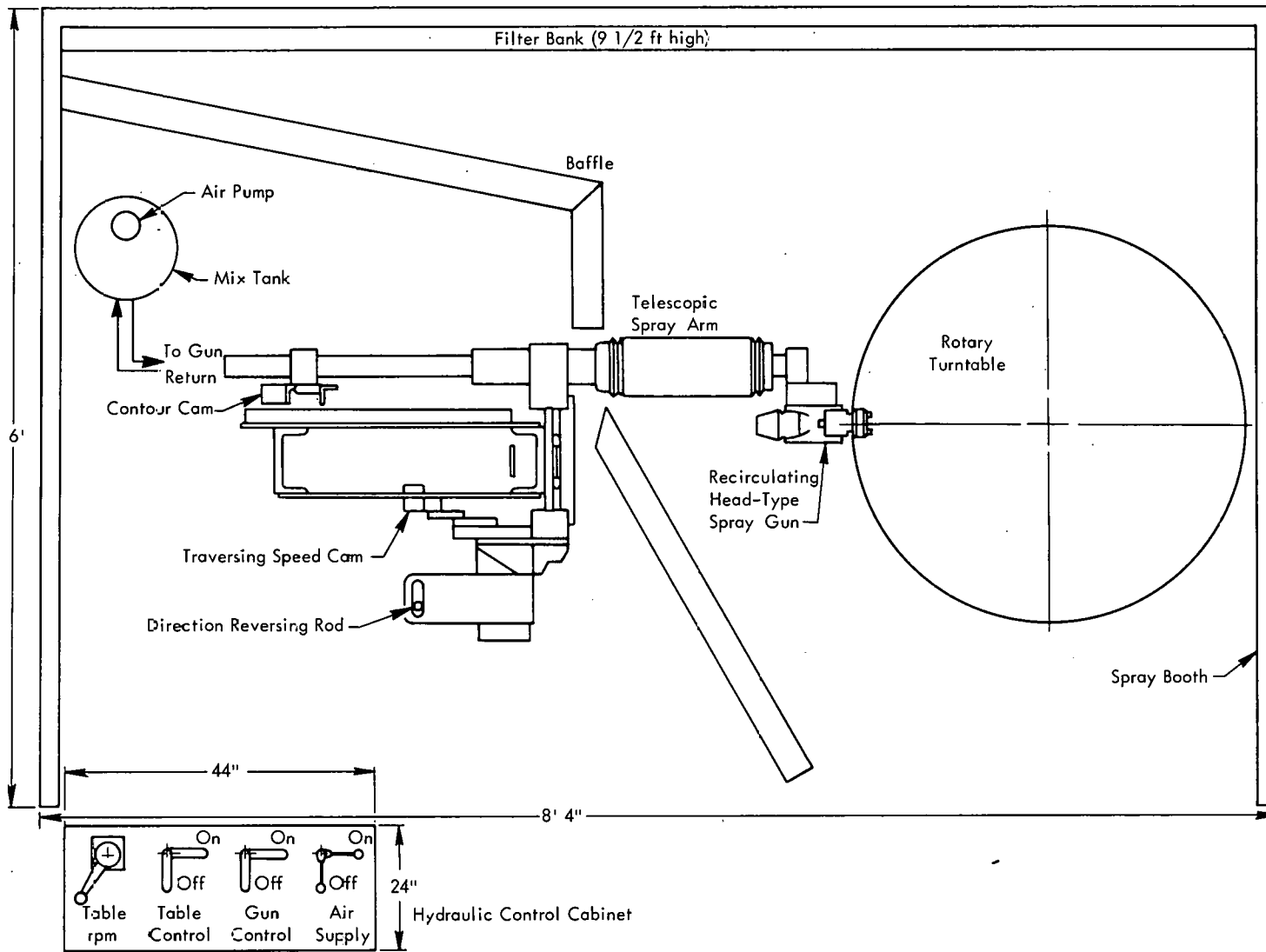
Figure 11. PLAN VIEW OF THE AUTOMATIC SPRAY MACHINE.
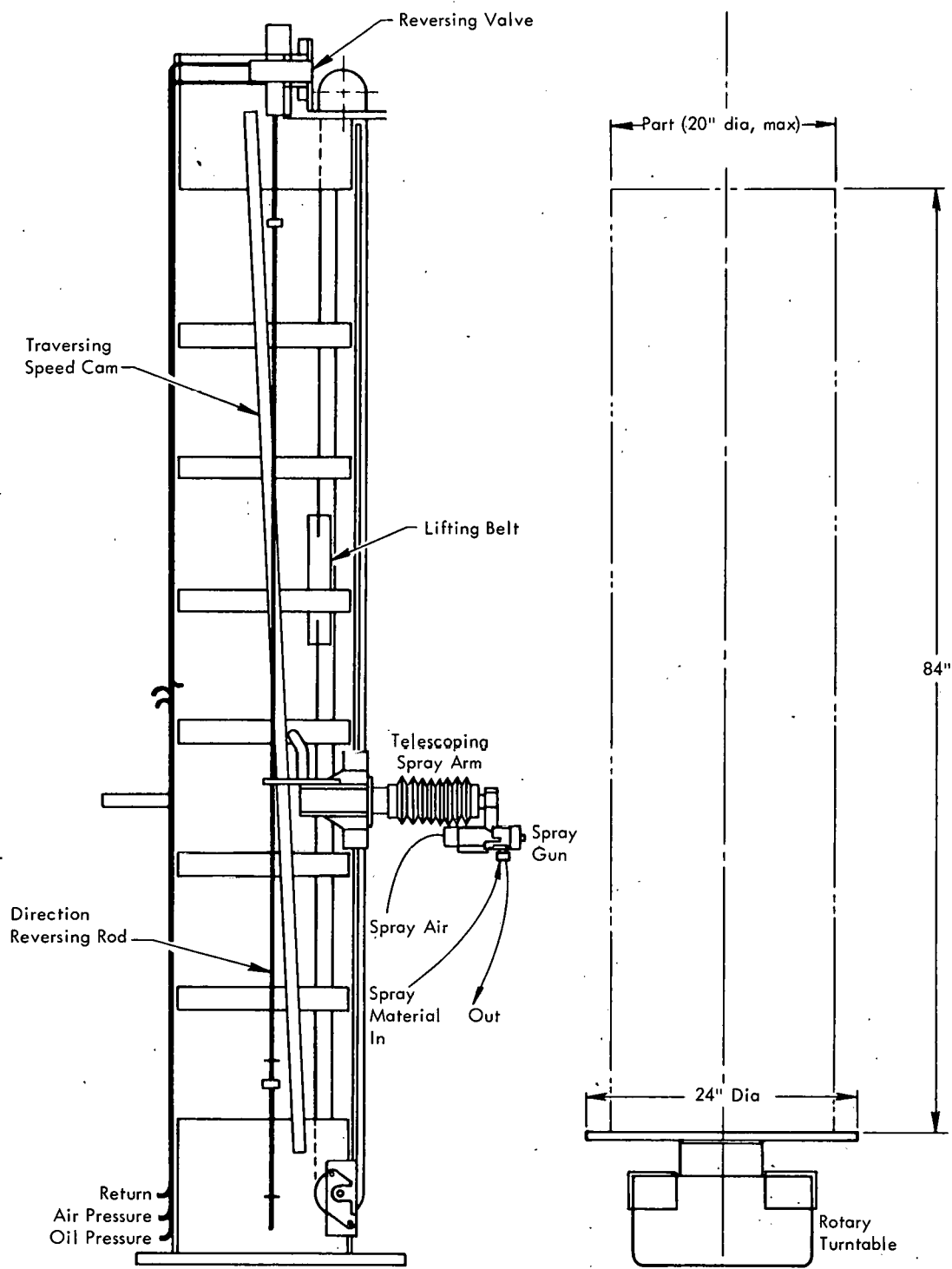
Figure 12. SIDE VIEW OF THE AUTOMATIC SPRAY MACHINE.

FABRICATION TECHNIQUES

Process Histories

Spray-Formed Samples – Process histories of fibrous spray-formed samples are listed in Table 4. The table presents the manufacturing process, final temperature, fiber diameter, initial binder type and amount, number of impregnation-carbonization cycles, final fiber content, and final density. All samples were initially fabricated by spray forming onto a suitable mandrel. All volume percentages were calculated using 1.4 gms/cc as the density of the fiber and 2.0 gms/cc as the density of the matrix carbon.

Samples C-8 and C-8G, after spraying, were bagged in polyvinyl chloride, evacuated, preheated to 150° C, and pressed in cold oil at 5,000 psi until cold. The samples were then carbonized to 1,000° C, unrestrained. This deviation in the manufacturing cycle was made in an attempt to achieve a higher fiber density by compacting the sprayed samples at a temperature near the melting point of the binder pitch. This pressing procedure reduced the thickness of the sample by about one half, but the subsequent carbonization cycle caused the thickness to expand by about 20 percent from the pressed condition. As a result of the pressing and expansion during carbonization, the fiber density was increased by about 50 percent over that normally achieved by unrestrained carbonization (0.2 gm/cc). It will be noted from the table that these samples contained more pitch in the initial sprayed binder. This additional amount was used to prevent crushing damage to the fibers during the pressing operations.

All other samples shown in Table 4 were sprayed with a hand-held spray gun, air dried to remove the benzene diluent, and carbonized free standing to 1,000° C in an inert atmosphere. Spray-formed samples which were not physically supported (as were flat plates) were supported by blocks of graphite inserted underneath these sections. This procedure was found necessary due to the softening of the thermoplastic resin (pitch) used in the spray mix which caused the samples to sag or drape out of shape.

Duration times of the initial carbonization heat cycles of the spray-formed samples were from 30 to 120 hours. Figure 13 shows a thermogravimetric analysis of the 15-V pitch used as the resin in spray forming. The temperature rate of rise of the carbonization cycle for samples with this binder was derived from the graph by dividing the weight loss (ordinate) into 2.5 weight percent increments. This procedure gave separate temperature readings for each of 40 increments of weight loss. A total time scale was then assigned to the 40 increments so that individual temperature-time relationships could be determined.

After initial carbonization to 1,000° C, the spray-formed samples of 70 pph pitch and two-micron-diameter fibers exhibited a density of 0.20 ± 0.02 gm/cc. Samples made from seven-micron-diameter fibers had carbonized densities of 0.45 gm/cc; those of ten-micron diameter had a density of approximately 0.58 gm/cc.

Table 4

DESCRIPTION OF MATERIALS AND PROCESSING FOR SPRAY-FORMED SAMPLES

Sample Number	Manufacturing Process	Final Processing Temperature (°C)	Fiber Diameter (μ)	Initial Binder	Binder Content on a Weight Basis (parts binder/100 parts fiber)	Number of Pitch Impregnations[1]	Final Fiber Content (vol %)	Final Fiber Content (wt %)	Final Density (gms/cc)
C-8	Isostatically Pressed Warm and Carbonized Free Standing	1,000	2	Pitch	100	8	17.9	15.5	1.61
C-8G	Same as for Sample C-8	2,500	2	Pitch	100	8	17.9	15.1	1.66
SC-12-3C	Sprayed and Carbonized Free Standing	1,000	2	Pitch	70	13	17.9	13.8	1.45
F-4	Same as for Sample SC-12-3C	1,000	2	Pitch	70	8	14.3	18.2	1.10
F-4G	Same as for Sample SC-12-3C	2,500	2	Pitch	70	8	14.3	18.9	1.06
D-10	Same as for Sample SC-12-3C	1,000	2	Pitch	70	2	14.3	53.0	0.38
10-1	Same as for Sample SC-12-3C	1,000	2	Pitch	70	2	14.3	53.0	0.38
10-2	Same as for Sample SC-12-3C	1,000	2	Pitch	70	4	14.3	38.6	0.52
10-3	Same as for Sample SC-12-3C	1,000	2	Pitch	70	6	14.3	20.7	0.97
8-6	Same as for Sample SC-12-3C	1,000	2	Pitch	70	4	14.3	22.8	0.88
8-6G	Same as for Sample SC-12-3C	2,500	2	Pitch	70	4	14.3	22.0	0.91
SC-12-11-C	Same as for Sample SC-12-3C	1,000	2	Pitch	70	2	14.3	57.1	0.35
SC-12-11-D	Same as for Sample SC-12-3C	1,000	2	Pitch	70	2	14.3	57.1	0.35
SC-12-G	Same as for Sample SC-12-3C	1,000	2	Pitch	70	10	14.3	14.1	1.42

(1) All parts were impregnated with Allied Chemical Corporation's Type CP-227-15V pitch.
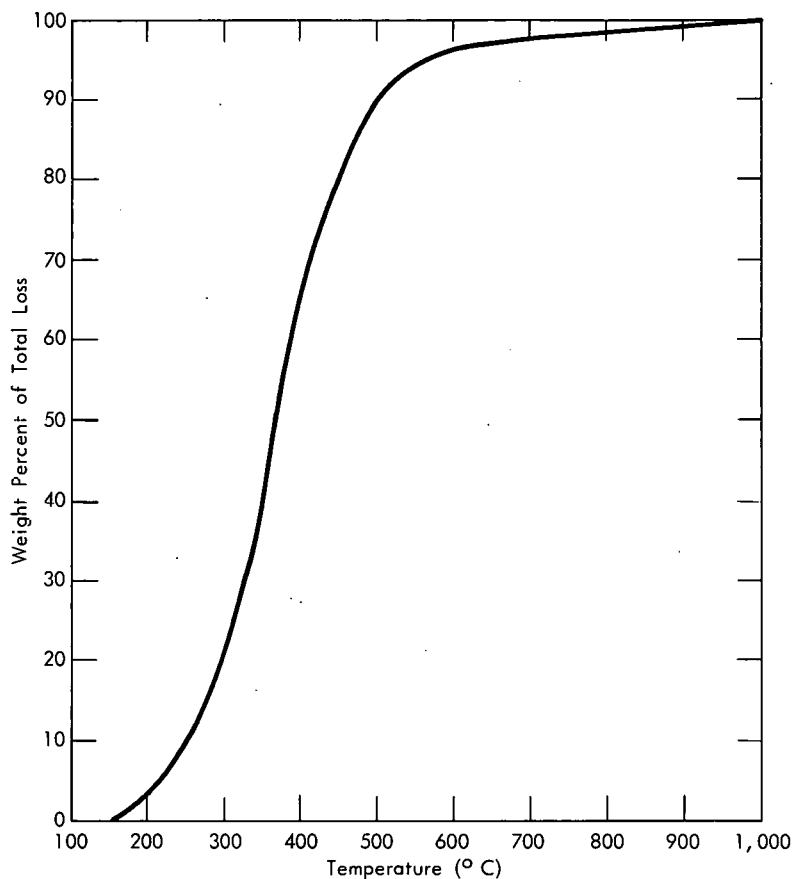
Figure 13. THERMOGRAVIMETRIC ANALYSIS (TGA) OF TYPE CP-227-15V PITCH.

It was found early in the development of the process that the pitch used in the early impregnation cycles must be diluted in order to preserve the integrity of the low-density fibrous structure during the subsequent pyrolysis cycles. Apparently, the low strength of the fibrous structure at this point in the process was not sufficient to contain the stresses generated by the decomposition of maximum amounts of pure pitch which were impregnated into the porous structure. Tests show that samples gained about 500 weight percent when initially impregnated with pure pitch and, after carbonization, exhibited numerous cracks and delaminations. Generally, an amount of pure pitch equal to the sample weight at any density successfully carbonized after it was impregnated into a structure.

This controlled impregnation rate was accomplished by impregnating the structures with benzene-diluted pitch, followed by a drying operation to no sample weight loss before carbonization to 1,000° C. Table 5 gives typical sample densification sequences when impregnated with diluted pitch. The table also shows the sample treatment and resultant carbonized densities for two typical samples. After a density of approximately 0.50 gm/cc was reached, the samples were considered strong enough for further

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Table 5

TYPICAL DENSIFICATION BY DILUTE PITCH IMPREGNATIONS

Sample Treatment	Carbonized Density (gm/cc)	
	Sample 1	Sample 2
Sprayed, Dried, and Carbonized to 1,000° C	0.2	0.2
Impregnated (25% pitch in benzene) and Carbonized to 1,000° C	0.29	0.29
Impregnated (25% pitch in benzene) and Carbonized to 1,000° C	0.36	0.34
Impregnated (50% pitch in benzene) and Carbonized to 1,000° C	0.42	0.46
Impregnated (50% pitch in benzene) and Carbonized to 1,000° C	0.52	0.54

impregnations using pure pitch until the desired sample density was achieved. Figure 14 shows a series of scanning electron microscope photographs of a spray-formed sample with seven-micron-diameter graphite fibers. The view is perpendicular to the spraying direction of the carbonized sample (not impregnated).

After densification by repeated pitch impregnation-carbonization cycles, the samples were tested or graphitized by heating in a suitable induction-type furnace to the desired temperature prior to testing. The typical heat cycle was to 1,000° C in two hours, then 200° C/hour to the desired temperature. The samples were usually buried in a natural-flake graphite to prevent surface oxidation.

Compacted (nonsprayed) Samples - Table 6 describes the process history for samples produced with a higher fiber content than that produced by spray forming alone. The table also shows the sample number, compaction process used, final process temperature, fiber diameter, initial binder and amounts, number of pitch impregnation-carbonization cycles, final fiber content of the sample, and its final density.

These samples were initially formed by vibrating the dry fibers into a suitable container followed by the addition of the listed amount of the appropriate resin diluted with a suitable solvent. The fibers were completely soaked with the diluted resin and allowed to dry in the container sufficiently for removal. The samples were then removed from the container and air dried at room temperature until all the resin diluent had been removed.

In Table 6, Samples IP-1A, IP-22G, IP-10A and B, and IP-9 were further processed by replacing the dried sample material in a 30-mil-thick stainless steel processing can with a high-pressure vent line attached to the lid. The outside edge of the lid was rolled to just slip inside the round can for welding. The cans containing the samples were welded and set up for compressing isostatically during the resin-thermosetting step. Samples IP-1A and IP-22E, C, and F were set up for compressing at

(a) ~ 50X   SM-1462

(b) ~ 100X   SM-1461
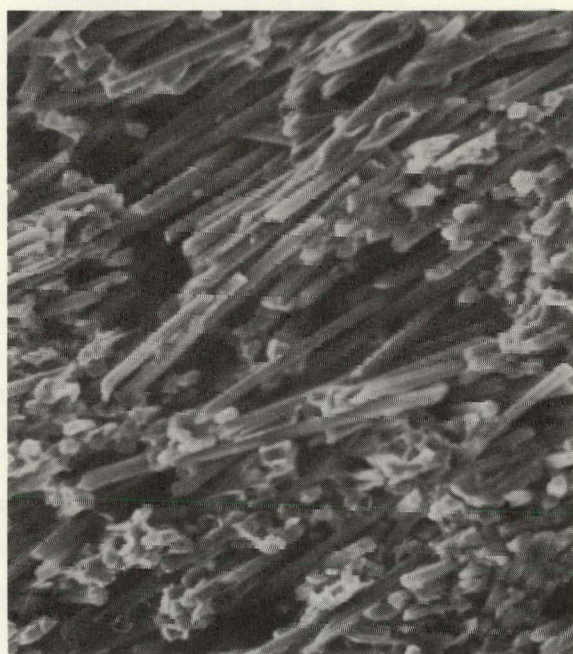
(c) ~ 150X   SM-1460
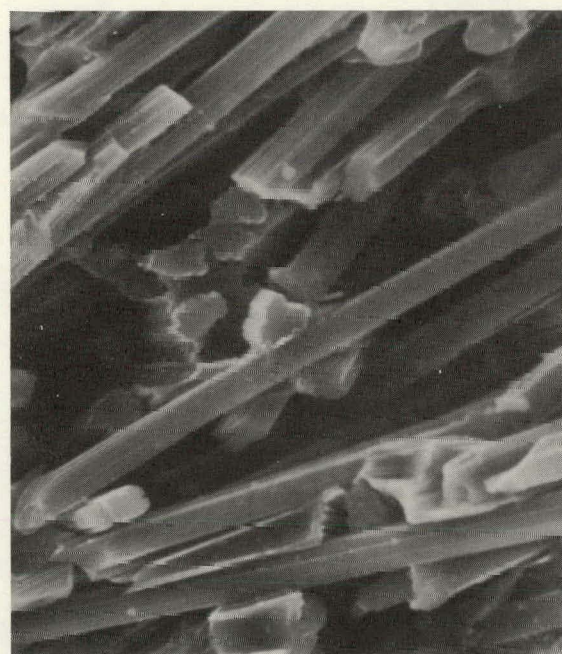
(d) ~ 500 X   SM-1459

Figure 14. SPRAY-FORMED SAMPLE FROM SEVEN-MICRON-DIAMETER GRAPHITE FIBERS. (View is Perpendicular to the Spraying Direction)

Table 6

DESCRIPTION OF MATERIALS AND PROCESSING FOR NONSPRAY-FORMED SAMPLES

Sample Number	Compacting Process	Final Temperature (°C)	Fiber Diameter (μ)	Initial Binder	Binder Content on a Weight Basis (parts binder/100 parts fiber)	Number of Pitch Impregnations[1]	Final Fiber Content (vol %)	Final Fiber Content (wt %)	Final Density (gms/cc)
IP-1A	Isostatically Pressure Thermoset and Carbonized	3,000	10	Phenolic[2]	65	9	53.0	44.0	1.69
IP-22G	Same as for Sample IP-1A Except Carbonized Unrestrained	1,000	2	Phenolic	90	11	37.0	32.0	1.62
IP-17	Pressure Carbonized	1,000	2, 7, & 10 in Equal Parts	Pitch[1]	100	8	59.3	52.5	1.58
IP-10A	Same as for Sample IP-1A Except Carbonized Unrestrained	1,000	7	Phenolic	90	10	28.4	28.4	1.80
IP-10B	Same as for Sample IP-1A Except Carbonized Unrestrained	3,000	7	Phenolic	90	10	36.6	29.6	1.73
IP-9	Same as for Sample IP-1A Except Carbonized Unrestrained	3,000	2	Phenolic	100	7	43.5	35.0	1.74
IP-22E	Same as for Sample IP-1A	(3)	2	Phenolic	90	10	41.6	36.4	1.60
IP-22C	Same as for Sample IP-1A	(3)	2	Phenolic	90	10	31.2	26.5	1.65
IP-22F	Same as for Sample IP-1A	(3)	2	Phenolic	90	10	35.7	29.6	1.69
SC-14A	Same as for Sample SC-14E	1,000	2	Phenolic	100	10	30.6	26.8	1.60
SC-14H	Same as for Sample SC-14E	1,000	2	Phenolic	100	10	30.6	26.8	1.60
SC-14E	Die Pressure Thermoset and Carbonized Unrestrained	1,000	2	Phenolic	100	0	33.6	32.4	1.45
SC-14B	Same as for Sample SC-14E	2,500	2	Phenolic	100	10	33.6	29.4	1.60

(1) All parts were impregnated with Allied Chemical Corporation's Type CP-227-15V pitch.
(2) Phenolic resin was obtained from the American Reinforced Plastics Company, 91-LD.
(3) Tested at various final process temperatures.

12,000 psi in a gas autoclave during the thermosetting and carbonization cycles, with the decomposition gases continually removed from the vent line. Samples IP-22G, IP-10A, and B, and IP-9 were thermoset at 30,000 psi in a completely closed can. The vent tube was closed off by welding while a vacuum was being applied to the sample can through the same tube. After thermosetting, the parts were removed from the cans and carbonized free standing. Figure 15 shows a detailed fabrication procedure for phenolic-resin-bound material, and Type IP-22 material in particular.

Sample IP-17, using pitch as the initial binder, was pressure carbonized with continual removal of the pyrolysis gases. Figure 16 shows a detailed fabrication procedure for pitch-bound material, and Type IP-17 material in particular. Also included in the procedure are process alternatives for better process control and product uniformity. Figure 17 shows a section of this sample as carbonized (before impregnation). These samples were in the size range of eight inches in diameter by twelve inches high in the uncompacted state.
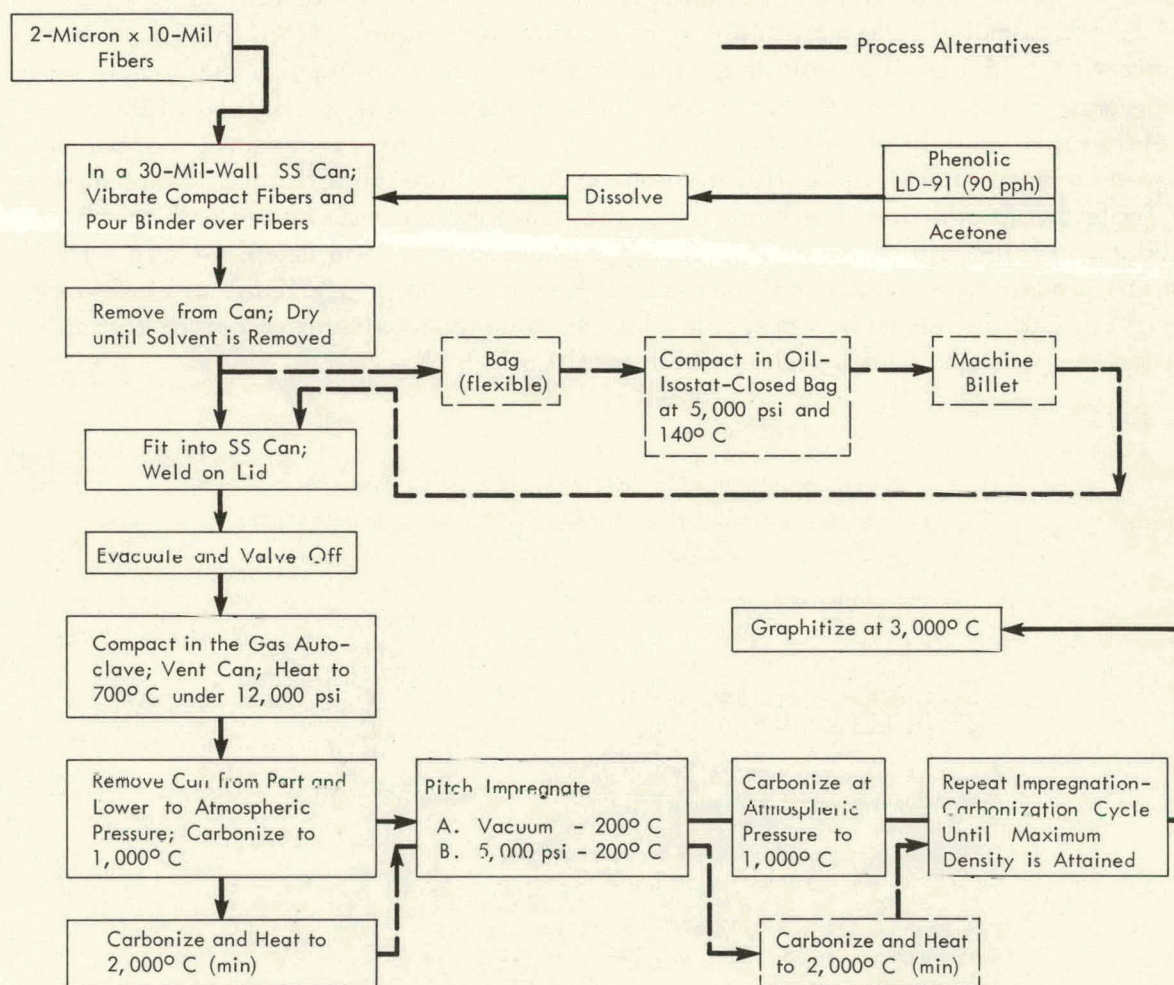
Figure 15. FABRICATION PROCEDURE FOR TYPE IP-22 MATERIAL. (Phenolic-Resin-Bound Material)

The high fiber content achieved (Table 6) in Sample IP-17 was probably due to the mixture of sizes of fibers, and the thermoplastic nature of the pitch allowed sample shrinkage to a higher temperature than with thermosetting resins.

Samples SC-14B and E were die-pressure thermoset after the diluent was evaporated. A pressure of 500 psi was applied to the cold sample, then the temperature was increased to approximately 300° C at a rate of 50° C per 30 minutes by the use of a graphite die in a hot platen press. The pressure-thermoset samples were then carbonized free standing to 1,000° C and impregnated to density, as described earlier. It can be seen from the calculated fiber contents of Table 6 that the fiber content of the samples die pressed at 500 psi were not generally lower than those isostatically thermoset at 30,000 psi. Sample IP-1A, which was also carbonized under 12,000 psi, did, however, show a considerable increase in fiber content.

Rapid Densification

Table 7 reports the results of an attempt to increase the density of low-density fiber-reinforced samples by a more rapid densification technique. After the initial carbonization and one dilute pitch impregnation-carbonization cycle, the sample was impregnated with pure pitch in the conventional manner and carbonized while completely submerged in pitch. The table shows that, with this procedure, the density increased more rapidly than with the conventional dilute densification cycle shown in Table 5. In addition, the integrity of the structure was maintained probably by a reduction of the stresses generated during carbonization. The complete cycle time for this procedure was reduced since the samples did not have to have the pitch diluent removed, and the submersion prevented loss of carbonaceous material before carbonization temperatures were reached which resulted in higher carbon yields.

Table 7

ACCELERATED DENSIFICATION BY SUBMERGED PITCH CARBONIZATION

Carbonization and Impregnation Method	Density (gms/cc)
Sprayed, Dried, and Carbonized at 1,000° C	0.2
Dilute Pitch Impregnated (25% pitch in benzene) and Carbonized at 1,000° C	0.3
Pure Pitch Impregnated (1,000 psi pressure) and Carbonized Submerged in Pitch to 1,000° C	0.93
Pure Pitch Impregnated (1,000-psi pressure) and Carbonized Submerged in Pitch to 1,000° C	1.23
Pure Pitch Impregnated (1,000-psi pressure) and Carbonized Submerged in Pitch to 1,000° C	1.43
Pure Pitch Impregnated (1,000-psi pressure) and Carbonized Submerged in Pitch to 1,000° C	1.52

———— Process Alternatives

```
┌─────────────────────┐
│ 2-Micron x 10-Mil   │
│ 7-Micron x 10-Mil   │
│ 10-Micron x 10-Mil  │
│ Fibers              │
└─────────────────────┘

┌ ─ ─ ─ ─ ─ ─ ─ ─ ─ ┐
  2-Micron x 10-Mil
│ Fibers            │
└ ─ ─ ─ ─ ─ ─ ─ ─ ─ ┘
```

| Compact by Vibrating Fibers into a 30-Mil-Wall SS Can; Warm Fibers; Pour Pitch over Fibers | ← | Heat Dissolve | ← | Pitch (90 pph) / Benzene |

Remove from Can; Dry → Bag (flexible) → Oil Isostat Closed at 5,000 psi and 150° C → Machine Billet

Can; Weld on Lid

Evacuate and Seal

| Autoclave (gas) vented; Operation at 700° C and 12,000 psi | Autoclave Unvented, Operation at 600 - 700° C and 5,000 - 15,000 psi |

Graphitize at 3,000° C

| Remove Can and Lower to Atmospheric Pressure; Carbonize to 1,000° C | Pitch Impregnate A. Vacuum - 200° C B. 5,000 psi - 200° C | Carbonize at Atmospheric Pressure and 1,000° C | Repeat Impregnation-Carbonization Cycles Until Maximum Density is Attained |

Remove Can and Carbonize to 2,000° C at Atmospheric Pressure

Carbonize at Atmospheric Pressure and 2,000° C

Figure 16. FABRICATION PROCEDURE FOR TYPE IP-17 MATERIAL. (Pitch-Bound Material)

Process Alternatives

Many alternate or additional steps and techniques are possible in the process both from a standpoint of material and procedure. Among those that have been attempted or investigated were:

1. Spray forming with noncarbonaceous binders. This operation has been performed with various glues, latex, and other materials which yield practically no carbon upon pyrolysis.

2. Spray-formed resin-bonded systems. Spray-formed samples of conventional fiber-reinforced resin systems have been fabricated.
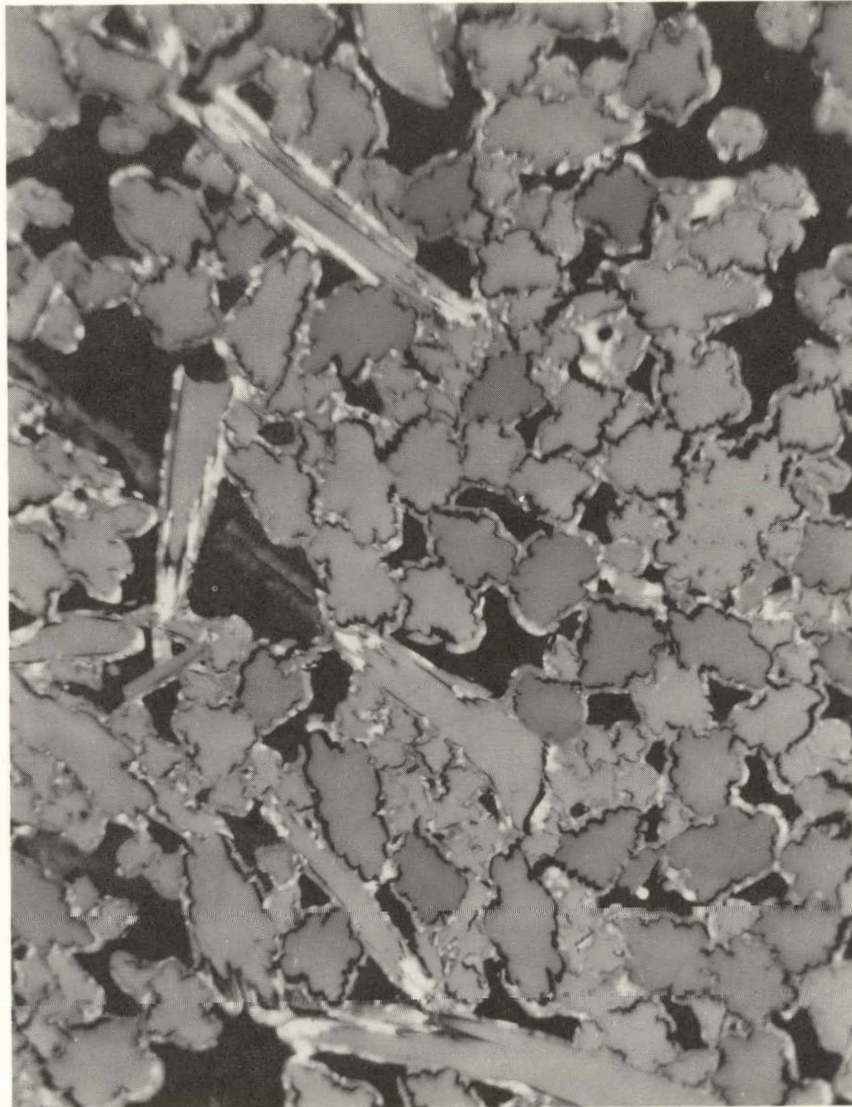
Figure 17. PITCH-BONDED, FIBER REINFORCED SAMPLE THAT WAS ISOSTATICALLY PRESSED AND CARBONIZED. (Sample IP-17; 1,000X; Bright Field Illumination; As Polished)

3. Pyrocarbon densification. Densification of these spray-formed and carbonized fibrous materials has been done by chemical vapor deposition (CVD) of pyrolytic carbon.

4. Continuous fiber reinforcement. Samples have been prepared which incorporate a known amount of continuous high-strength, high-modulus graphite fiber in a preselected winding pattern. This system was fabricated by conventional filament winding by the spraying sequence.

5. Spray-formed high-modulus, high-strength fibers. High-modulus graphite yarn has been successfully chopped and spray formed into samples.

Table 8

APPROXIMATE ROOM-TEMPERATURE PROPERTIES OF VARIOUS GRAPHITIC MATERIALS

Property	Pyrolytic Graphite	Grade ZTA	Grade ATJ	Grade ATJS	Grade RVA	Grade PT-0178	Grade PT-0113	Grade PT-0181	Grade PT-0182	Spray Formed
Density (lbs/ft³)	137	120.6	108	113.6	115.2(113.5)[1]	93.8(86.7)[1]	73.5	89.8(78.5)[2]	81.1	100
(gms/cc)	2.19	1.93	1.73	1.82	1.85(1.81)[1]	1.50(1.39)[1]	1.18	1.60(1.26)[2]	1.3	1.6[3]
Flexural Strength (lbs/in²)										
With Grain	20,000	5,250	4,010	6,200	3,800	4,830	2,060	5,215	1,840	8,000
Across Grain	1,500	2,540	3,580	5,100	2,995	2,544	440	3,194	603	7,800
Tensile Strength (lbs/in²)										
With Grain	15,500	4,350	3.355	4,700	2,975	2,500	1,000	-	-	5,000
Across Grain	1,160	,625	2,935	3,800	2,115	-	220	-	-	-
Compressive Strength (lbs/in²)										
With Grain	15,000	3,320	8,270	11,800	9,960	6,950	2,970	-	-	12,000[4]
Across Grain	60,000	12,250	8,540	12,400	9,000	9,570	3,710	-	-	15,000
Initial Tensile Modulus (lbs/in²) x 10⁻⁶										
With Grain	5.00	2.525	1.45	1.75	1.84	1.68	1.23	-	-	3.0[5]
Across Grain	1.50	0.934	1.15	1.20	1.30	-	0.43	-	-	
Thermal Expansion Coefficient (in/in-°F) x 10⁶										
With Grain	0.1	0.5	1.22	-	0.916	0.4	0.734	-	-	1.61
Across Grain	13.1	3.82	1.90	-	1.54	-	-	-	-	3.10
Thermal Conductivity (Btu/ft-sec-°R)										
With Grain	8.1×10^{-2}	3.11×10^{-2}	1.89×10^{-2}	2.94×10^{-2}	1.76×10^{-2}	0.654×10^{-2}	3.92×10^{-4}	-	-	5.0×10^{-4}[6]
Across Grain	3.5×10^{-4}	1.67×10^{-2}	1.44×10^{-2}	2.44×10^{-2}	1.51×10^{-2}	0.448×10^{-2}	2.69×10^{-4}	-	-	2.6×10^{-4}[6]
Processing Technique	Vapor Deposition 2,100° C	Hot Forming Grade ATJ	Fine-Grained Molded Graphite	Fine-Grained Molded Graphite	Fine-Grained, Pressure-cured Graphite	Impregnated Fibrous Graphite	Low-Density Fibrous Graphite	Fibrous-Grade Impregnated Epoxy	Fibrous Grade Impregnated Pitch	Spray-Formed Impregnated Fibrous Graphite

(1) Purified version.
(2) Density after resin decomposition.
(3) Pitch impregnated - 1,000° C carbonized.
(4) Axis of the compression cylinder was paralled to the spraying direction.
(5) Density of 1.56 gms/cc, 1,000° C carbonized; 2.1 x 10⁶ at 2,500° C graphitized.
(6) 440° F and 1.40 gm/cc.

6. Spray forming fibers mixed with quantities of particulate graphite to increase uniformity, randomize fiber alignment, and increase carbonized density. It has been found that approximately 400 grams of fine particulate graphite particles per one hundred grams of fibers can be added during the spray forming without affecting the sprayed sample volume.

7. Spray forming with continuously evacuated mandrels. This technique has been used effectively to speed up the spraying process particularly with small samples, and has also been used with other binder systems such as soluble starch in an aqueous diluent to increase the uniformity of the fibrous reinforcement.

8. Densification of spray-formed fibrous samples has been accomplished by partial isothermal chemical vapor deposition followed by conventional pitch impregnation.

EVALUATION OF THE MECHANICAL AND PHYSICAL PROPERTIES

Mechanical and physical properties were determined for various types of fibrous graphite prepared by spray forming, by isostatic pressing, by die pressing, and by combinations of these techniques. Tables 4 and 6 describe the materials and the processing history.

Table 8 presents a general comparison of the various graphitic materials including spray-formed, impregnated-fiber-reinforced material. A discussion of the various properties is given in the sections that follow.

Porosity

Table 9 lists the results of mercury porosimetry measurements on spray-formed and densified samples, while Table 10 gives the results of similar measurements on compacted (nonsprayed) samples. Figure 18 presents typical pore distribution curves for spray-formed and compacted fibrous-graphite samples.

For the higher-density materials, the volume percentage of pores less than 10 microns is increased, and approximately 10 volume percent of the pore volume is less than 0.1 micron.

Sonic Modulus

Sonic-modulus determinations were made on specimens ranging in density from 0.3 to 1.57 gms/cc. The modulus increases gradually from 0.3×10^6 psi for the 0.3

Table 9

DENSITY AND POROSITY OF SPRAY-FORMED FIBROUS GRAPHITE

Material Batch Number	Bulk Density[1] (gms/cc)	Real Density[2] (gms/cc)	Porosity (vol %)	Porosity < 10 μ (%)
SC-12-1C	1.66	1.81	8.32	34.2
SC-12-1A	1.63	1.83	10.80	25.6
SC-12-1B	1.56	1.86	16.00	34.6
SC-12F	1.41	1.81	21.90	25.3
F-4	1.28	1.83	30.20	13.6
8-6	0.88	1.84	51.70	18.0

(1) Density obtained using the volume occupied after all pores larger than 100 microns in diameter were filled with mercury.

(2) Density obtained using the volume occupied after all pores larger than 0.0135 micron in diameter were filled with mercury.

gm/cc samples to 1.2×10^6 psi for the 1.1 gms/cc samples, as shown in Figure 19. Above this density, the modulus appears to increase more rapidly, and values of 3.0 $\times 10^6$ psi were obtained at a density of 1.5 gms/cc. Graphitization of the material reduces the modulus, as Figure 19 indicates.

In addition, two materials were tested in tension using strain gages, and the modulus was determined on each after carbonization and graphitization. For the spray-formed

Table 10

DENSITY AND POROSITY OF COMPACTED (NONSPRAYED) SAMPLES

Sample Number	Fiber Diameter (μ)	Final Processing Temperature (°C)	Bulk Density[1] (gms/cc)	Real Density[2] (gms/cc)	Porosity (vol %)	Porosity < 10 μ (%)	Average Pore Diameter (μ)	Calculated Surface Area (m²/gm)
IP-1A	10	3,000	1.70	1.91	10.95	99.6	0.57	9.1
IP-10	7	3,000	1.72	1.90	9.16	99.6	4.27	1.52
IP-9	2	3,000	1.74	1.97	11.61	99.7	0.29	8.11
IP-3	7	3,000	1.69	1.94	12.70	99.9	0.34	6.62
IP-17	2, 7, & 10 in Equal Parts	1,000	1.56	1.60	2.93	100.0	0.170	1.47
IP-22E	2	3,000	1.70	1.94	12.59	98.5	1.88	7.99

(1) Density obtained using the volume occupied after all pores larger than 100 microns in diameter were filled with mercury.

(2) Density obtained using the volume occupied after all pores larger than 0.0135 micron in diameter were filled with mercury.
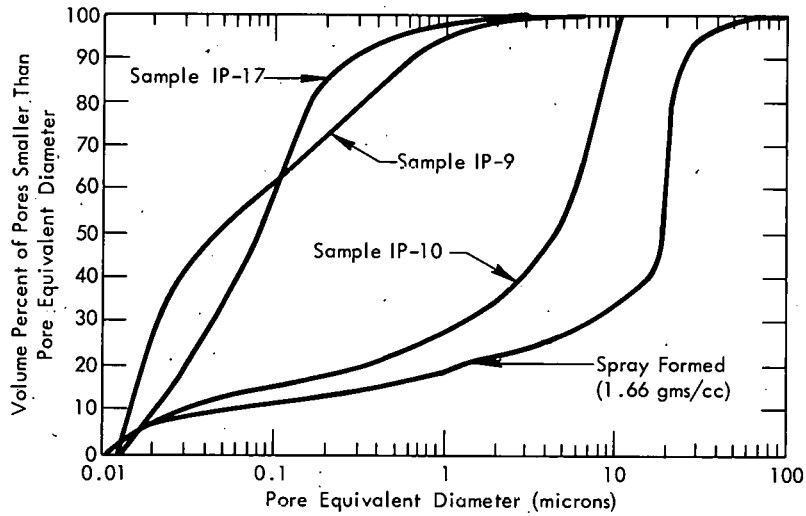
Figure 18. TYPICAL PORE-SIZE DISTRIBUTION CURVES FOR SPRAY-FORMED
AND COMPACTED FIBROUS GRAPHITE.

material with a density of 1.0 gm/cc, a modulus of 1.4×10^6 and 0.5×10^6 was
measured before and after graphitization to 2,500° C, respectively; an isostatically
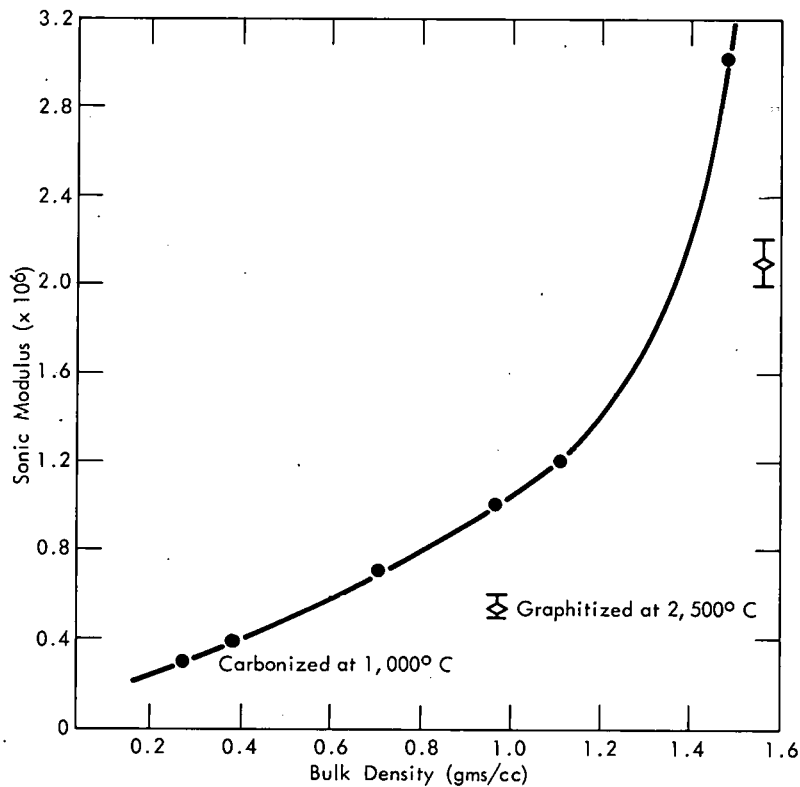

Figure 19. SONIC MODULUS AS A FUNCTION OF DENSITY FOR SPRAY-
FORMED FIBROUS GRAPHITE.

compacted sample having a density of 1.6 gms/cc exhibited a modulus of 4.1×10^6 and 1.4×10^6 before and after graphitization to $3,000°$ C, respectively.

Compressive Strength

Compressive strengths for the spray-formed material at various densities are reported in Table 11. A graph of the data is presented in Figure 20. Low-voltage radiographs of several compressive specimens subsequent to testing revealed conical failures near the ends of the cylinders (diameter/length = 1/2) and an oblique fracture plane in the center portion of the specimen. This result is typical of brittle materials and graphite when properly tested. Table 12 presents the data for compacted samples of fiber-reinforced graphite.

Table 11

COMPRESSIVE STRENGTH OF SPRAY-FORMED FIBROUS GRAPHITE

Material Batch Number	Bulk Density (gms/cc)	Average Compressive Strength (psi)	Standard Deviation (psi)	Number of Samples	Average Compressive Modulus (psi x 10^{-5})	Standard Deviation (psi x 10^{-5})	Specimen Orientation to the Spray Direction
SC-12G	1.42	9,100	700	4	8.9	0.9	Normal
SC-12G	1.42	7,100	1,000	6	3.8	0.7	Parallel
SC-12-11C	0.35	330	40	16	0.1	0.04	Parallel
SC-12-11D	0.35	460	100	12	0.8	0.1	Normal
10-1	0.38	330	30	10	0.05	0.02	Parallel
10-2	0.52	570	50	5	0.06	0.01	Parallel
10-2	0.52	910	90	4	-	-	Normal
8-6	0.88	1,280	80	3	-	-	Parallel
10-3	0.97	2,060	60	5	-	-	Parallel
F-4	1.10	4,240	1,130	10	2.8	0.4	Parallel

Thermal Expansion

An understanding of the thermal-expansion characteristics of fibrous graphite as they relate to fabrication techniques is important to the development of parts with a minimum amount of residual stress. To effect such studies, a vertical, quartz dilatometer was assembled which would apply a minimum weight of 14 grams on the test specimen. Specimens from material with a density range from 0.5 to 1.6 gms/cc were carbonized at temperatures from 500 to $1,000°$ C and subsequently examined by dilatometry.
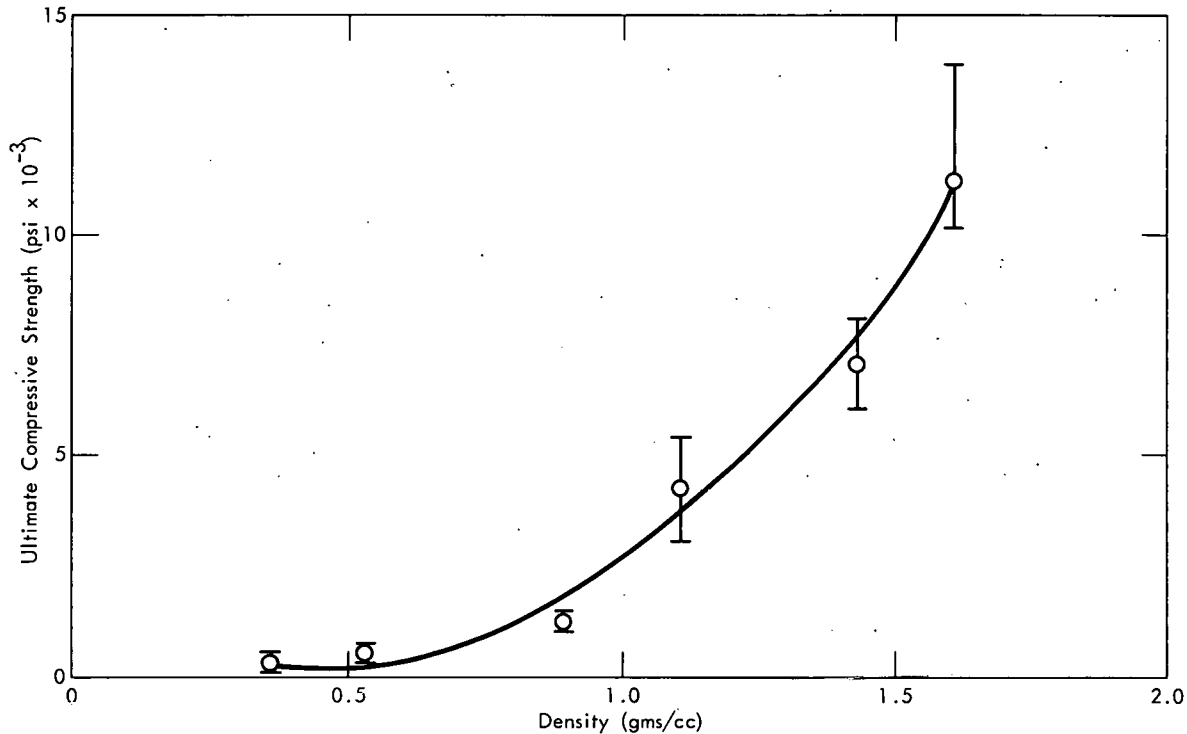
Figure 20. ULTIMATE COMPRESSIVE STRENGTH AS A FUNCTION OF DENSITY FOR SPRAY-FORMED FIBROUS GRAPHITE. (Parallel to the Spray Direction)

Initial results on a specimen having a density of 1.2 gms/cc indicated that reheating above an initial 900° C carbonization temperature to 1,000° C resulted in considerable permanent shrinkage of the specimen above 900° C. The quantity of this shrinkage and the rate appear to be dependent on the heating rate or the time at temperature.

Figure 21 shows the effect of carbonization to a temperature of 500° C on the shrinkage of a specimen with a density of 0.4 gm/cc. Two heating rates show that the instantaneous shrinkage response is different, but the total deformations are approxi-

Table 12

COMPRESSIVE STRENGTH OF COMPACTED FIBROUS GRAPHITE

Sample Number	Fiber Content (vol %)	Fiber Diameter (μ)	Final Pressing Temperature (° C)	Average Compressive Strength (psi)	Modulus of Elasticity (psi x 10⁻⁵)	Approximate Density (gms/cc)	Number of Samples
IP-10D	36.5	7	1,000	15,100	9.7	1.70	12
IP-10A	36.5	7	3,000	14,100	6.0	1.70	13
IP-1A	53.0	10	3,000	12,100	9.4	1.61	10
IP-9	42.5	2	3,000	9,150	7.7	1.60	1
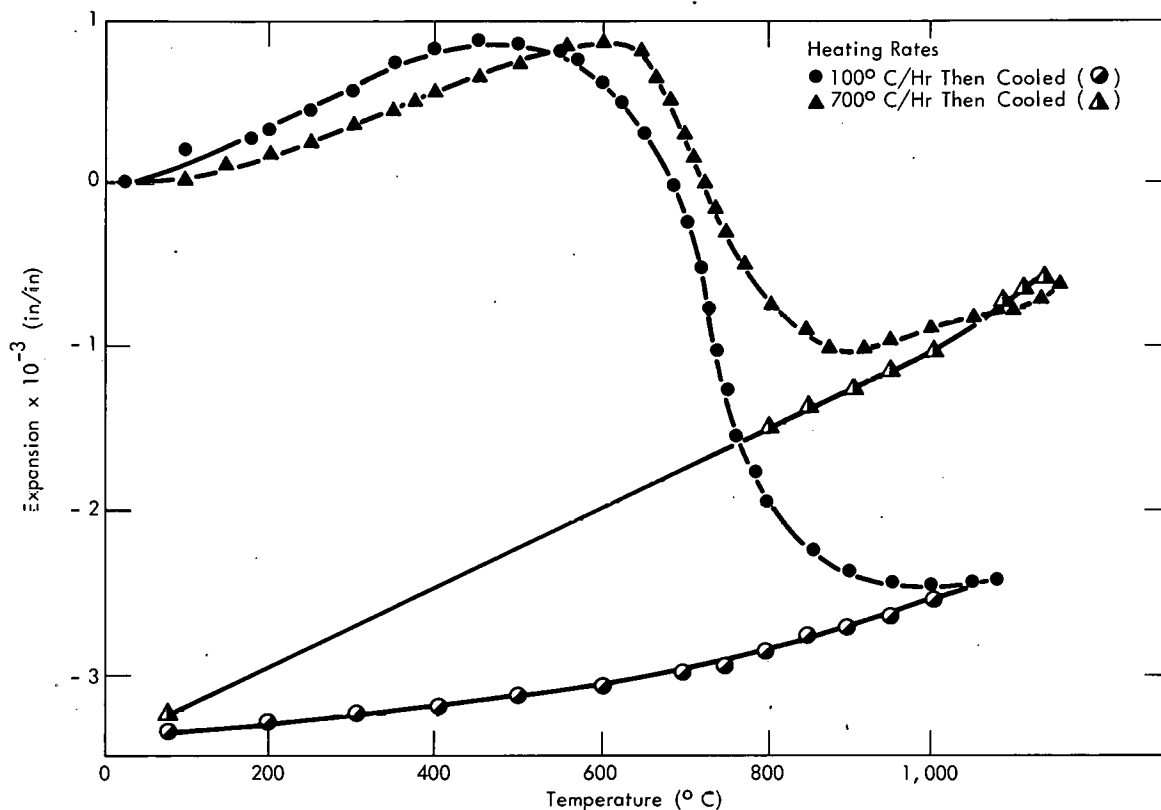
Figure 21. DILATION CURVES OF SPRAY-FORMED FIBROUS GRAPHITE AT TWO HEATING RATES. (Carbon Temperature, 500° C; Initial Density, 0.42 gm/cc; Specimen Length, 3 Inches)

mately equal. The shrinkage results in a permanent deformation of the material, and this will cause either failure or an increase in the internal stress for a closed-geometry part.

Figure 22 is a graph of typical dilation curves for material with a density of 0.28 gm/cc that was carbonized to 700 and 1,000° C. By comparison with Figure 21, it appears that the shrinkage is less for the lower-density materials and the higher carbonization temperatures. This relationship is further emphasized by the third curve in Figure 22 which represents material with a density of 1.45 gms/cc that was carbonized to about 1,000° C. The coefficient of expansion of this material is higher and the permanent shrinkage exceeds that of the lower-density (0.28 gm/cc) material. These preliminary results typify the dimensional changes that were experienced during processing to the final carbonization temperatures.

Linear coefficients of thermal expansion for the spray-formed material, prepared by the technique described previously, are listed in Table 13. Data for carbonization and graphitized specimens are compared.

The graphitization tends to reduce the coefficient of expansion in the plane perpendicular to the spraying direction for most of the materials shown. However, no appreciable change was noted for specimens tested parallel to the spray direction.

Table 13
THERMAL EXPANSION OF FIBROUS GRAPHITE COMPOSITES

Material Batch Number	Material Description	Density (gms/cc)	Coefficient of Thermal Expansion[1] $(x\ 10^{-6})$		Specimen Orientation Relative to the Spraying Direction
			Carbonized[2]	Graphitized[3]	
10-1	Spray Formed with Pitch; Pitch Impregnated	0.38	1.8	1.6	Perpendicular
10-2	Spray Formed with Pitch; Pitch Impregnated	0.52	1.9	1.9	Perpendicular
8-6	Spray Formed with Pitch; Pitch Impregnated	0.88	1.9	1.8	Perpendicular
10-3	Spray Formed with Pitch; Pitch Impregnated	0.97	2.0	1.6	Perpendicular
SC-12-E1	Spray Formed with Pitch; Pitch Impregnated	1.36	2.8	2.4	Perpendicular
SC-12F	Spray Formed with Pitch; Pitch Impregnated	1.41	2.4	1.4	Perpendicular
SC-12F	Spray Formed with Pitch; Pitch Impregnated	1.41	3.8	4.2	Parallel
SC-12-1B	Spray Formed with Pitch; Pitch Impregnated	1.56	5.5	5.5	Parallel
SC-12-1B	Spray Formed with Pitch; Pitch Impregnated	1.56	2.7	–	Perpendicular
SC-12-1A	Spray Formed with Pitch; Pitch Impregnated	1.63	3.1	–	Perpendicular
SC-14E	Die Pressed with Phenolic Binder; Pitch Impregnated	1.45	2.5	–	Perpendicular
SC-14B	Die Pressed with Phenolic Binder; Pitch Impregnated	1.60	–	2.4	Perpendicular
IP-22G	Isostatic Pressed with Phenolic Binder; Pitch Impregnated	1.62	3.3	–	Length[4]
IP-10	Isostatic Pressed with Phenolic Binder; Pitch Impregnated	1.73	3.0	2.4 2.5	Length Length
IP-22E	Isostatic Pressed with Phenolic Binder; Pitch Impregnated	1.60	–	3.0 3.9	Diameter (0°) Diameter (90°)

(1) Room temperature to 900° C.
(2) Carbonization temperatures are at approximately 1,000° C.
(3) Graphitization for all specimens was at 2,500° C.
(4) Isostatic compaction – orientation reference is to billet dimensions.
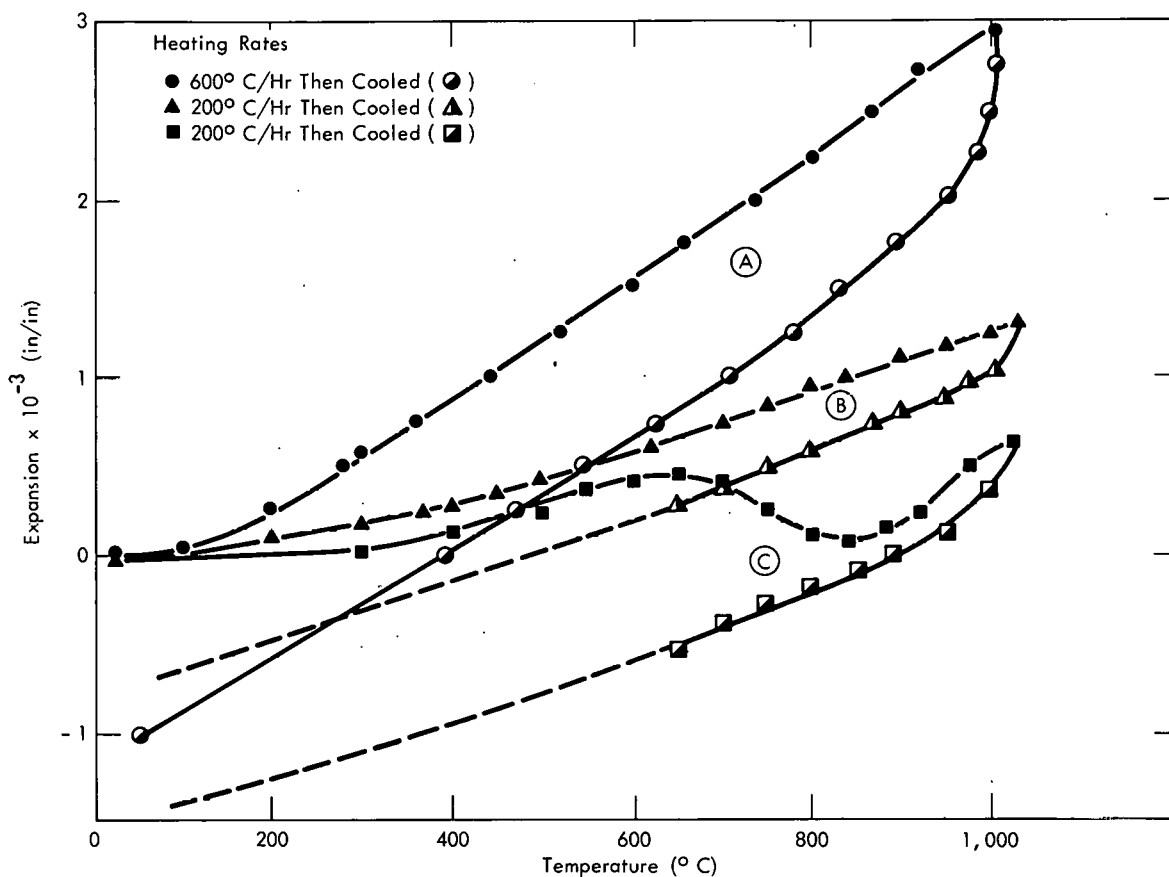
Figure 22. DILATION CURVES FOR SPRAY-FORMED FIBROUS GRAPHITE UNDER THREE SETS OF CONDITIONS. (A - Carbon Temperature, 1,000° C; Initial Density, 1.45 gms/cc; Specimen Length, 3 Inches—B - Carbon Temperature, 1,000° C; Initial Density, 0.28 gm/cc; Specimen Length, 3 Inches—C - Carbon Temperature, 700° C; Initial Density, 0.278 gm/cc; Specimen Length, 3 Inches)

Thermal Conductivity

Thermal conductivity for several densities of spray-formed and carbonized (1,000° C) material was determined up to 800° C using a commercial comparator technique. (m) The data are reported by the graph of Figure 23. The effect of bulk density and fiber alignment is apparent.

Several of these samples were graphitized to 2,500° C and the thermal conductivity measured. The results of these tests are compared with the previous data in Figure 24. Values obtained for the material having a density of 0.5 gm/cc in the direction parallel to spraying indicate that the conductivity of the graphitized material (heated to 2,500° C) is higher than the carbonized material by a factor of 10.0 at 100° C, but

(m) Developed by the Minnesota Milling and Mining (3-M) Company.
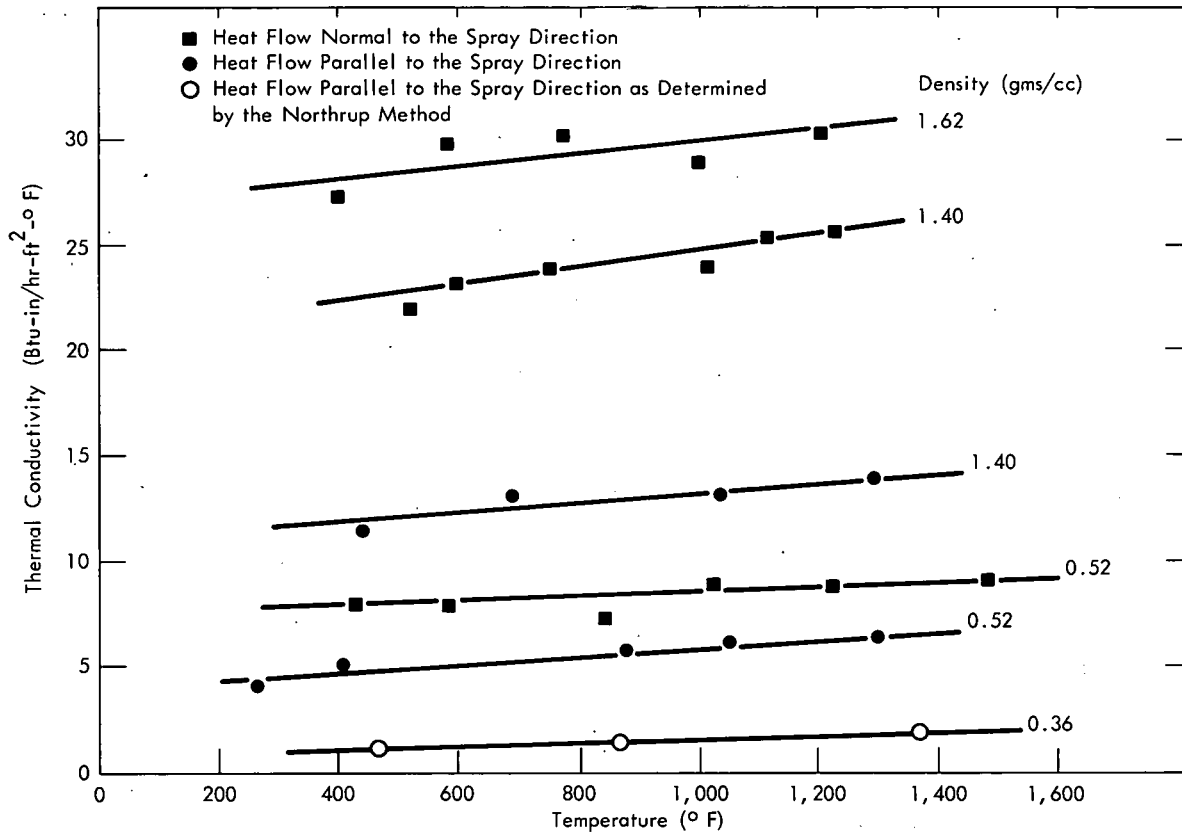
Figure 23. THERMAL CONDUCTIVITY OF SPRAY-FORMED SAMPLES AS DETERMINED USING THE COMMERCIAL COMPARATOR. (Samples Carbonized to 1,000° C)

decreases to a factor of 3.5 at 800° C. Perpendicular to the spray direction, the conductivities are greater by a factor of 12.5 at 100° C and 4.4 at 800° C. The decreasing conductivity of the graphitized material with increasing temperature, as shown in Figure 24, is responsible for the relationship just described since the carbonized material exhibits only a slight increase in conductivity with increasing temperature. Examination of material with a density of 1.0 gm/cc revealed a similar behavior but with a larger increase in thermal conductivity of the graphitized material.

Tensile Strength

Tensile strengths of the fibrous-graphite structures were determined using a slightly modified and minaturized version of the ASTM graphite specimen (C565-65T). The cylindrical specimen has a smooth radius between the grip sections, and failures due to notches and undercuts which are usually a problem with graphite were minimized. As a check on the validity of the strength values obtained with this specimen, ATJS-type graphite was tested. An average ultimate tensile strength of 5,100 psi with a standard deviation of 110 psi was observed, which is within the range reported by the
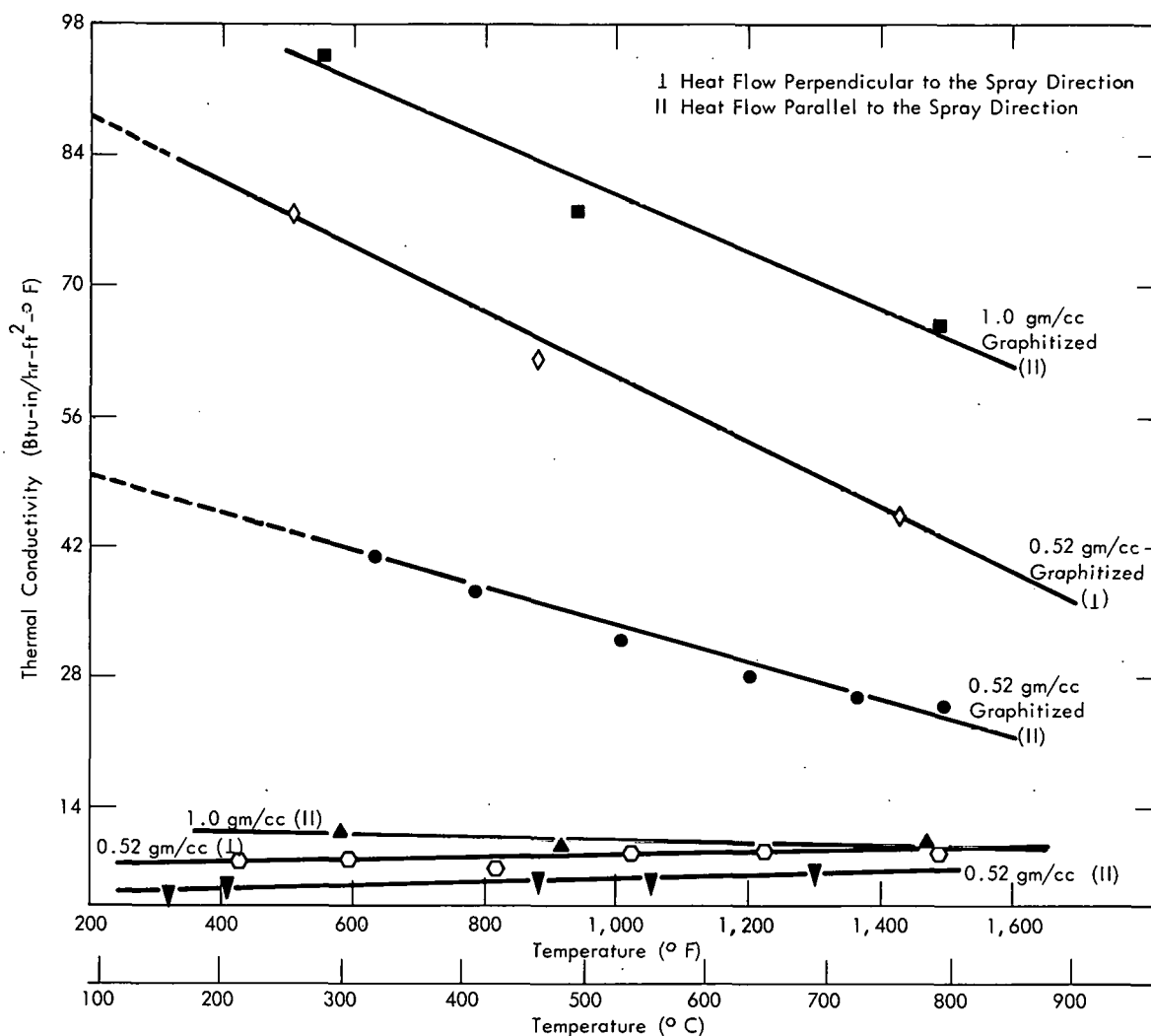
Figure 24. THERMAL CONDUCTIVITIES OF SPRAY-FORMED FIBROUS COMPOSITES AS CARBONIZED AND AFTER GRAPHITIZATION TO 2,500° C.

manufacturer.[n] Tensile strengths for several densities of spray-formed material are presented in Figure 25. The density variations were obtained through repeated impregnations with coal tar pitch[o] and carbonization cycles. Values for the fibrous-graphite structures prepared by either isostatic or die-pressure carbonization are given in Table 14. Also included in Figure 25 and Table 14 are data for material graphitized to temperatures of 2,500° C and above.

From the data shown in Figure 25, it appears that graphitization to 2,500° C did not affect the tensile strength of the spray-formed material. In Table 14, where the fiber

(n) Union Carbide Corporation – Carbon Products Division.
(o) Allied Chemical Corporation's CP-227-15V.
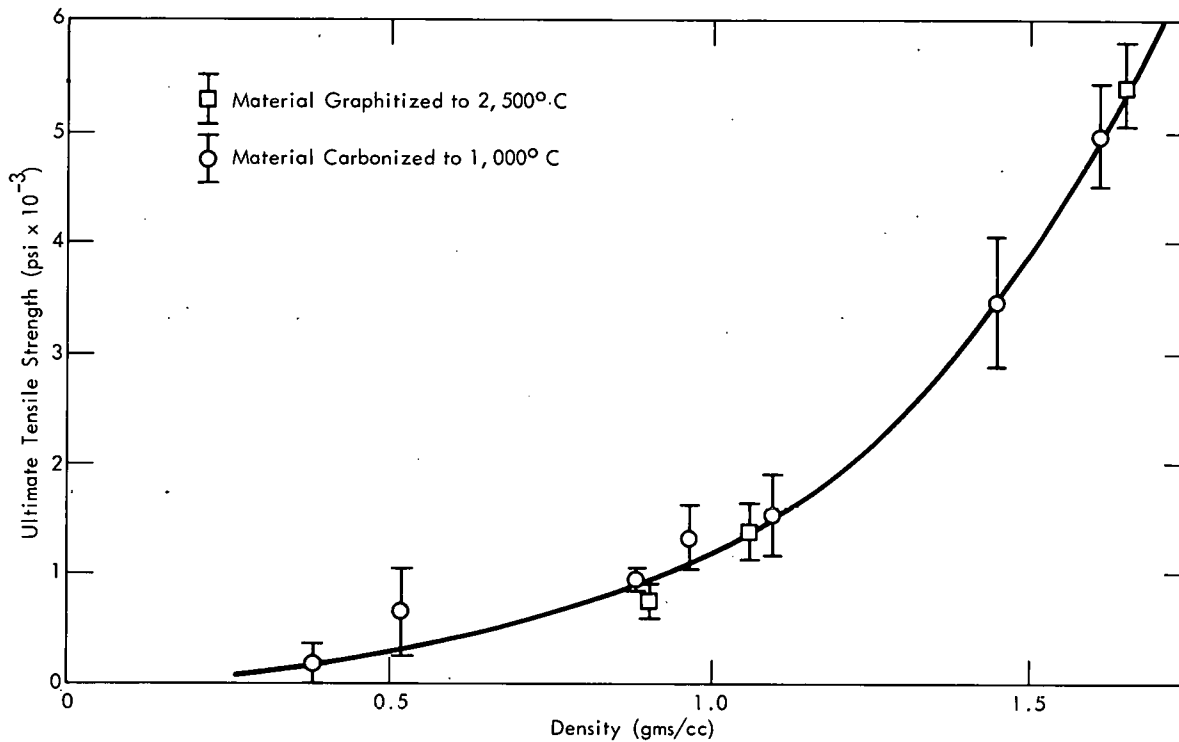
Figure 25. ULTIMATE TENSILE STRENGTH AS A FUNCTION OF THE DENSITY FOR SPRAY-FORMED FIBROUS GRAPHITE. (Perpendicular to the Spray Direction)

content of the compacted samples was much higher than spray-formed samples, any effect is probably obscured by fiber orientation in the samples. In the isostatically

Table 14

ULTIMATE TENSILE STRENGTH FOR COMPACTED COMPOSITES OF FIBROUS GRAPHITE
TESTED PERPENDICULAR TO THE MOLDING DIRECTION

Material Batch Number	Fiber Content (vol %)	Fabrication Method	Bulk Density (gms/cc)	Final Process Temperature (° C)	Average Ultimate Tensile Strength (psi)	Standard Deviation (psi)	Number of Specimens Tested
IP-1A	53.0	Isostatic Pressed[1]	1.69	3,000	2,950	210	4
IP-22G	34.0	Isostatic Pressed[1]	1.62	1,000	3,300	470	7
SC-14B	33.6	Die Pressed	1.60	2,500	3,340	130	4
SC-14E	33.6	Die Pressed	1.45	1,000	5,060	270	3

(1) Tested with the tensile bar length along the length of a 4-inch-diameter by 8-inch-long billet.

prepared samples (IP-1A and IP-22G), the fiber orientation was probably more random than the spray-formed samples; thus, decreasing the measured tensile strength. In the material that was die pressed at 1,000° C (SC-14E), the tensile strength was 5,060 psi at a density of 1.45 gm/cc.

Flexural Strength

Figure 26 presents the flexural strength data available from spray-formed samples. The samples were tested by four-point loadings. It is apparent that the fibers are randomly distributed in the spraying plane since the flexural strengths were equal when the load was applied both in the spray direction and transverse (perpendicular) to the spray direction.

Specific Heat

Specific heat was determined for the spray-formed material at 50 and 150° C for densities ranging from 0.4 to 1.45 gms/cc. A value of 0.20 cal/gm/°C ± 10 percent
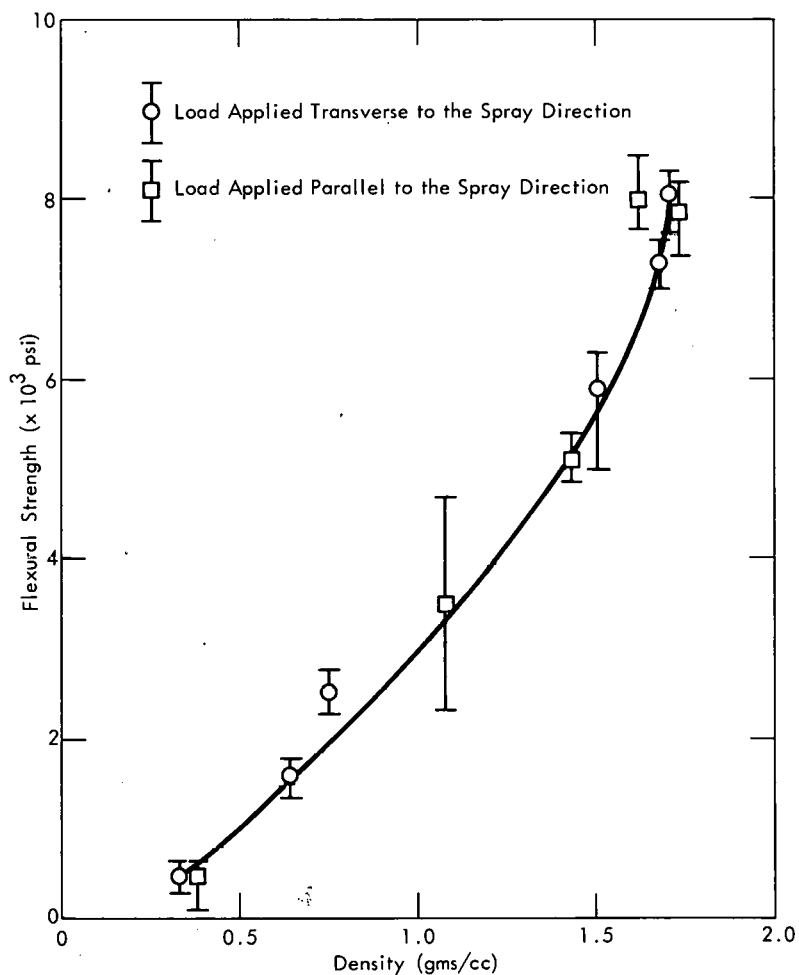
Figure 26. FLEXURAL STRENGTH AS A FUNCTION OF THE DENSITY FOR SPRAY-FORMED FIBROUS GRAPHITE.

was obtained for all densities at 50° C, and 0.23 cal/gm/°C ± 10 percent for the material at 150° C. This range is about equal to commercial graphite.[p]

Diametral Compression

Table 15 gives the results of diametral compression tests[1] on compressed composites of fibrous graphite. The samples were generally 0.375 inch in diameter and 0.3785 inch in length. Included in the table are data obtained in the same manner from testing ATJS-type graphite. Since material modulus affects the results of this test, no conclusions can be drawn except in a comparative way. It will be noted in the table that the isostatically compacted sample (IP-22G) showed superior strength in both orientations while the die-pressure-thermoset samples (SC-14A, B, and H) were somewhat weaker in the interlaminar-oriented tests.

Table 15

DIAMETRAL COMPRESSION TESTS ON FIBROUS GRAPHITE COMPOSITES

Sample Number	Sample Orientation	Number of Samples	Density (gms/cc)	Average Tensile Stress (psi)	Standard Deviation	Maximum Process Temperature (° C)
IP-22G	Length[1]	21	1.62	4,115	759	1,000
IP-22G	Width	13	1.62	4,056	647	1,000
SC-14A	Interlaminar	4	1.60	2,658	557	1,000
SC-14A	Noninterlaminar	4	1.60	3,579	713	1,000
SC-14A	Noninterlaminar	3	1.60	3,305	650	1,000
SC-14A	Interlaminar	4	1.60	2,272	792	1,000
SC-14A	Noninterlaminar[2]	5	1.60	4,358	645	1,000
SC-14B	Interlaminar	6	1.60	1,608	170	2,500
SC-14B	Noninterlaminar[2]	4	1.60	2,521	459	2,500
SC-14H	Noninterlaminar	20	1.60	4,091	839	1,000
SC-14H	Interlaminar	13	1.60	3,850	530	1,000
ATJS[3]	Against Grain[1]	23	–	2,804	135	–

(1) Major axis of the sample along the length of the billet.
(2) Samples taken through the thickness of the die-pressed plate.
(3) Product of Union Carbide Corporation.

(p) National Carbon Company's Grade ATJ is 0.19 and 0.22 cal/gm/°C at 50 and 150° C, respectively.

Ablation

The ablation performance of several isostatically compacted samples was investigated[2] in the five-megawatt arc heater test unit of the Propulsion Wind Tunnel Facility (PWT) at the Arnold Engineering Development Center in cooperation with the Sandia Corporation. The test unit is a continuous-flow, arc-heated facility using air, and is equipped for ablation tests over a wide range of conditions.[3]

The ablation model configuration was a hemisphere cylinder. The hemisphere nose radius was 0.20 inch; the cylinder had a 0.40 inch diameter. Figure 27 shows a side view of the samples in the test position in the facility.

Figure 28 shows a typical surface brightness temperature history and the pyrometer position for the measurement. Table 16 shows the ablation runs and the maximum temperature observed in testing the individual ablation sample models. After the model ablated past the indicated pyrometer alignment point, the pyrometer output decreased sharply; therefore, the maximum temperature recorded is the most valid value.

Table 17 reports the arc heater data recorded in each of the ablation runs, while Table 18 gives the final process temperature, fiber content, carbon content from the initial binder resin, carbon content resulting from the impregnant (pitch), and approximate geometric density of the ablation model. Table 19 lists the ablation run and the weight and length data for each model before and after ablative testing. Samples of ATJS-type graphite were included in the tests, and the models shown in this table are generally of a higher density than the isostatically compacted models.

Table 20 summarizes the results obtained from the ablation exposure as well as a few of the important conditions of testing. In this table, the mass-loss rate data are probably more indicative of ablation resistance than the recession rate data, since many of the samples were pitted and eroded nonuniformly. At 35 and 45-atmosphere stagnation pressures (S-8 and S-13 respectively), the loss rates for all models were approximately the same. At a 55-atmosphere (S-9 and S-10A) stagnation pressure, the mass loss rates for the IP-17, IP-22E, and IP-22F models were significantly less than the rates for the ATJS and IP-22C models.

All surfaces of the IP-22E and two of the IP-17 models were smooth, but one IP-17, the ATJS, and the IP-22C models were rough. A small piece of carbon broke from one corner of the IP-22F model. At a 75-atmosphere stagnation pressure (S-11 and S-12A) the mass loss rate of Model IP-22E-67-4 was low and the ablative surface was smooth. All other models tested at this pressure showed greater mass loss rates and rougher surfaces, indicating severe erosion.

Ablative performance of various carbon-carbon composites and graphites have been comparatively screened at the Giannini Scientific Corporation in cooperation with Sandia.[4] The test configuration is illustrated in Figure 29. All samples were flat plates mounted 45 degrees in the six-atmosphere pressure jet. Figure 30 shows the
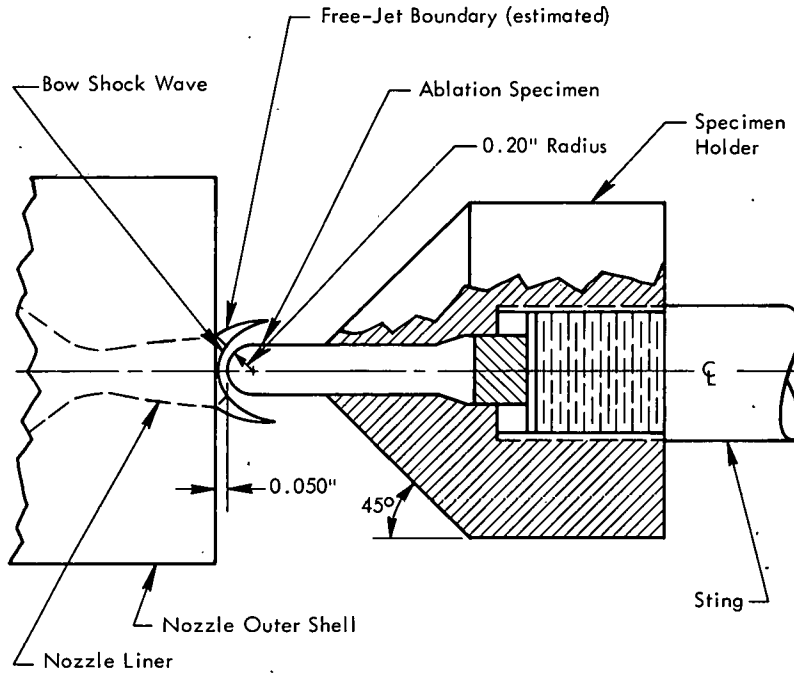
Figure 27. SIDE VIEW OF THE MODEL IN THE TEST POSITION. (Not to Scale)
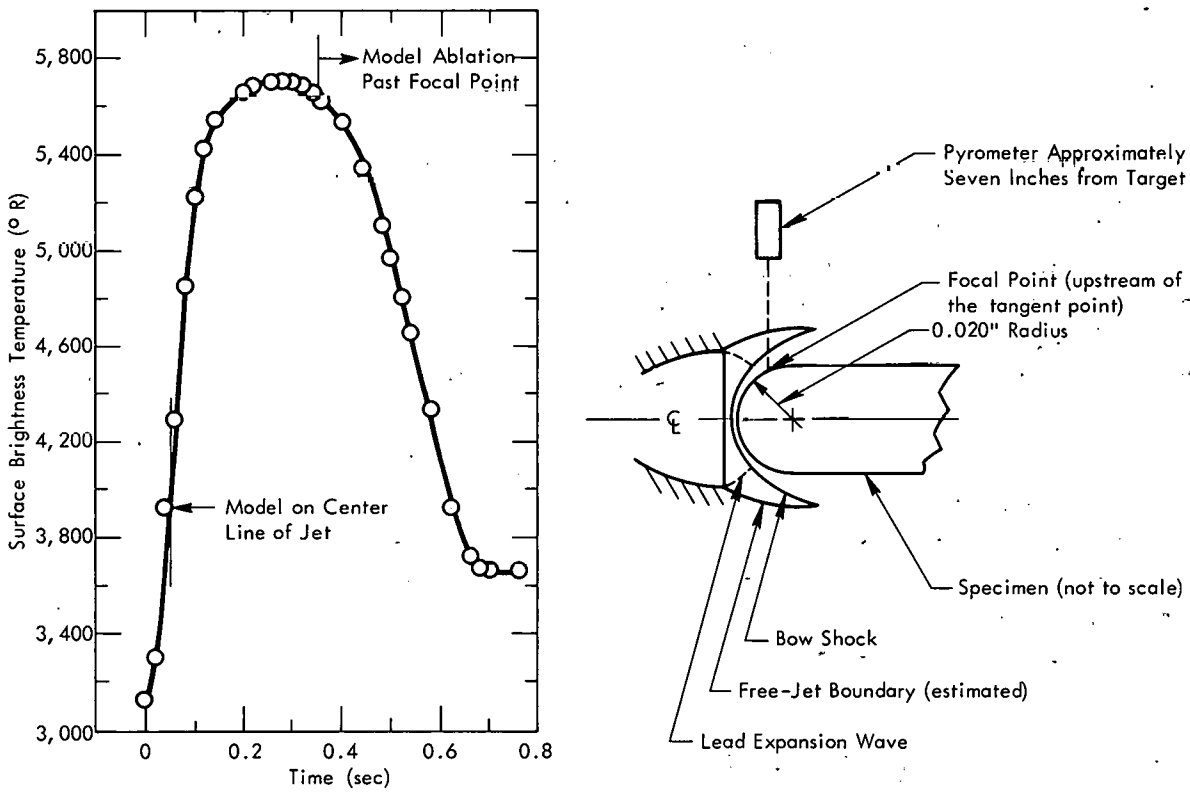
Figure 28. TYPICAL SURFACE BRIGHTNESS TEMPERATURE HISTORY.

Table 16

PYROMETER DATA

Run Number	Model Number	Maximum Temperature Observed During Test ($^{\circ}$R)
S-8	ATJ-S1	5,625
	ATJ-S2	5,600
	IP-22E-67-2	5,600
	IP-22E-68-2	5,600
	IP-22C-71-2	5,600
S-9	ATJ-S3	5,150
	ATJ-S4	5,200
	IP-17-26-1	5,050
	IP-17-27-1	4,975
	IP-17-66-1	4,975
S-10A	IP-22E-67-1	5,285
	IP-22E-68-1	5,325
	IP-22F-69-1	5,175
	IP-22C-70-1	5,500
	IP-22C-71-1	5,425
S-11	ATJ-S5	5,650
	IP-22E-67-3	5,525
	IP-22E-68-2F	5,635
S-12A	ATJ-S6	5,625
	IF-22E-67-4	5,550
	IF-22F-69-2	5,575
	IF-22F-69-3	5,650
S-13	ATJ-S7	5,425
	ATJ-S8	5,450
	IP-22F-69-4	5,425
	IP-22C-70-3	5,325
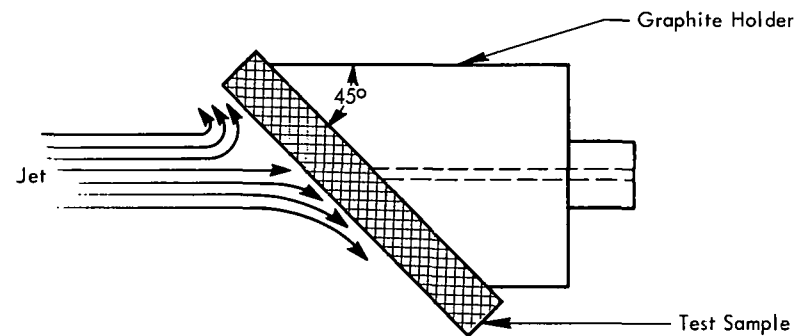
Figure 29. FLAT-PLATE SAMPLE CONFIGURATION. (Test Sample Dimensions: 2 1/2" x 4" x 1/2")

Table 17

ARC HEATER DATA

Run Number	Mach Number	Arc Heater Voltage, V (volts)	Arc Heater Current, I (amps)	Air Mass Flow Rate, ṁ (lbs/sec)	Total Reservoir Pressure, p_t (atmos)	Total Enthalpy, h_t (Btus/lb)	Arc Heater Efficiency, η (%)	Estimated Model Stagnation Pressure, p_s (atmos)
S-8	2.0	4,370	735	0.406	51.1	3,430	44.3	35
S-9	2.3	7,500	670	0.866	99.3	2,440	42.7	56
S-10A	2.3	7,510	670	0.897	99.9	2,455	44.2	56
S-11	1.6	6,735	670	0.848	89.9	2,315	44.0	76
S-12A	1.6	7,375	670	0.818	90.4	2,495	41.8	76
S-13	1.6	4,785	725	0.461	53.0	3,435	46.8	45

Table 18

ABLATION MODEL PROCESS HISTORIES

Run Number	Sample Number	Model Number	Final Process Temperature (° C)	Fiber Content (wt %)	Carbon Content		Geometric Density (gms/cc)
					From Binder (wt %)	From Impregnant (wt %)	
S-8	IP-22E	67-2	3,000	36.4	13.6	50.0	1.612
	IP-22E	68-2	2,500	36.4	13.6	50.0	1.583
	IP-22C	71-2	2,500	26.5	8.4	65.1	1.658
S-9	IP-17	26-1	2,500	52.5	13.1	34.4	1.573
	IP-17	27-1	2,700	52.5	13.1	34.4	1.673
	IP-17	66-1	3,000	52.5	13.1	34.4	1.642
S-10A	IP-22E	67-1	3,000	36.4	13.6	50.0	1.600
	IP-22E	68-1	2,500	36.4	13.6	50.0	1.635
	IP-22F	69-1	3,000	29.6	11.1	59.3	1.686
	IP-22C	70-1	3,000	26.5	8.4	65.1	1.648
	IP-22C	71-1	2,500	26.5	8.4	65.1	1.662
S-11	IP-22E	67-3	3,000	36.4	13.6	50.0	1.652
	IP-22E	68-2F	2,500	36.4	13.6	50.0	1.583
S-12A	IP-22E	67-4	3,000	36.4	13.6	50.0	1.619
	IP-22F	69-2	3,000	29.6	11.1	59.3	1.689
	IP-22F	69-3	3,000	29.6	11.1	59.3	1.677
S-13	IP-22F	69-4	3,000	29.6	11.1	59.3	1.713
	IP-22C	70-3	3,000	26.5	8.4	65.1	1.694

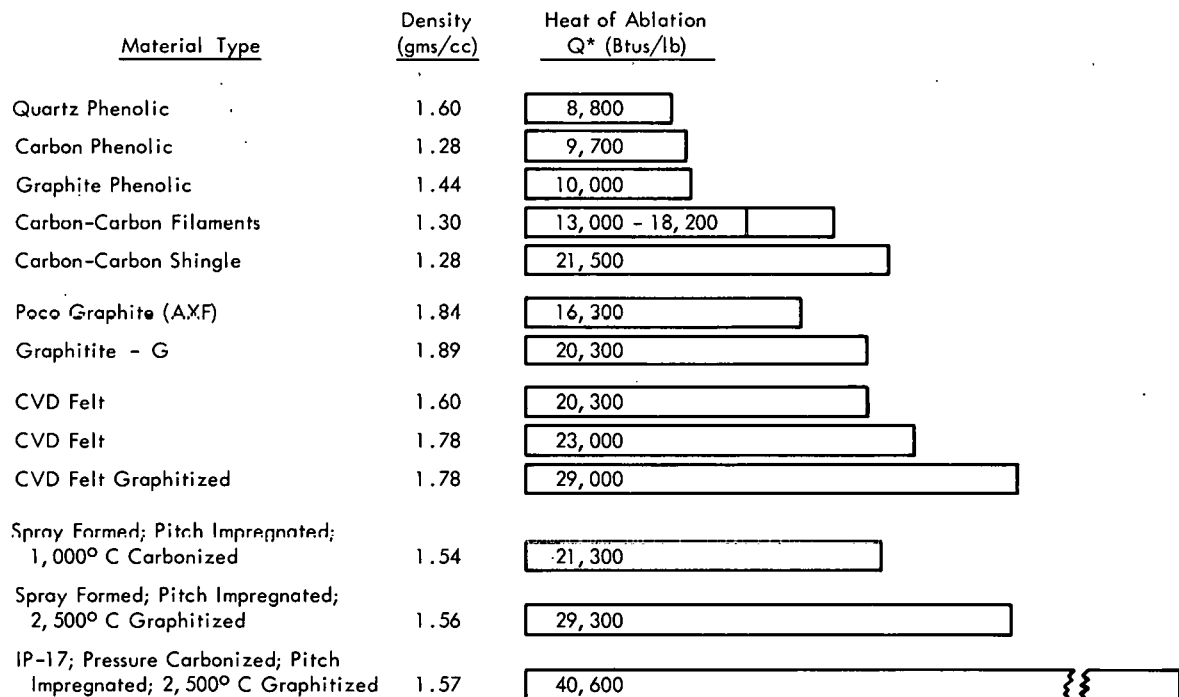| Material Type	Density (gms/cc)	Heat of Ablation Q* (Btus/lb)
Quartz Phenolic	1.60	8,800
Carbon Phenolic	1.28	9,700
Graphite Phenolic	1.44	10,000
Carbon-Carbon Filaments	1.30	13,000 - 18,200
Carbon-Carbon Shingle	1.28	21,500
Poco Graphite (AXF)	1.84	16,300
Graphitite - G	1.89	20,300
CVD Felt	1.60	20,300
CVD Felt	1.78	23,000
CVD Felt Graphitized	1.78	29,000
Spray Formed; Pitch Impregnated; 1,000° C Carbonized	1.54	21,300
Spray Formed; Pitch Impregnated; 2,500° C Graphitized	1.56	29,300
IP-17; Pressure Carbonized; Pitch Impregnated; 2,500° C Graphitized	1.57	40,600

Figure 30. COMPARISON OF VARIOUS ABLATOR MATERIALS. (Test Conditions: Heat Flux, $\dot{q}$ - 1,350 Btus/ft²-sec; Pressure - 6 Atoms; Test Duration - 15 sec)

Table 19

SPECIMEN WEIGHTS AND MEASUREMENTS BEFORE AND AFTER TEST

Run Number	Model Number	Preweight (gms)	Prelength (in)	Postweight (gms)	Postweight (in)
S-8	ATJ-S1	6.2270	1.6093	5.5950	1.3905
	ATJ-S2	6.2182	1.6070	5.5972	1.3898
	IP-22E-67-2	5.4996	1.6060	4.8624	1.3627
	IP-22E-68-2	5.5322	1.6062	4.9276	1.3845
	IP-22C-71-2	5.4219	1.6062	4.7837	1.3658
S-9	ATJ-S3	6.1987	1.6060	5.3006	1.3880
	ATJ-S4	6.2142	1.6075	5.4274	1.4523
	IP-17-26-1	5.3522	1.6049	4.9528	1.4547
	IP-17-27-1	5.5844	1.6059	5.0546	1.4528
	IP-17-66-1	5.5417	1.6015	5.1419	1.4635
S-10A	IP-22E-67-1	5.4213	1.6057	5.0849	1.4950
	IP-22E-68-1	5.3923	1.6045	5.0696	1.4935
	IP-22F-69-1	5.8850	1.6037	5.4986	1.5031
	IP-22C-70-1	5.6679	1.6077	4.8167	1.3962
	IP-22C-71-1	5.5250	1.6078	4.6654	1.3762
S-11	ATJ-S5	6.2328	1.6085	5.3987	1.3761
	IP-22E-67-3	5.3939	1.6057	4.6699	1.3852
	IP-22E-68-2F	5.3660	1.6058	4.6171	1.3723
S-12A	ATJ-S6	6.2137	1.6085	5.0641	1.4393
	IP-22E-67-4	5.4637	1.6060	5.0830	1.4521
	IP-22F-69-2	5.9168	1.6055	5.2397	1.4380
	IP-22F-69-3	5.8745	1.6036	5.2333	1.4676
S-13	ATJ-S7	6.2209	1.6092	5.4866	1.3912
	ATJ-S8	6.2338	1.6067	5.4915	1.3756
	IP-22F-69-4	5.9555	1.6060	5.2185	1.3816
	IP-22C-70-3	5.5695	1.6066	4.8112	1.3523

comparative performance of some of the materials and the testing conditions. It appears that the low porosity of the IP-17-type material may subdue the high-temperature erosion rate since the dominant mass-loss mechanism is the sublimation of solid carbon.

Table 20

SPECIMEN RECESSION AND MASS LOSS

Run Number	Model Run	Exposure Time, Δt_m (sec)	Mass Change, Δm (gm)	Length Change, ΔL (in)	Loss Rate, $\Delta m/\Delta t_m$ (gm/sec)	Recession Rate, $\Delta L/\Delta t_m$ (in/sec)	Total Enthalpy (Btus/lb)	Stagnation Pressure (atmos)
S-8	ATJ-S1	2.59	0.6320	0.2188	0.2440	0.0845		
	ATJ-S2	2.58	0.6210	0.2172	0.2407	0.0842		
	IP-22E-67-2	2.59	0.6372	0.2433	0.2460	0.0939	3,430	35
	IP-22E-68-2	2.57	0.6046	0.2217	0.2352	0.0863		
	IP-22C-71-2	2.63	0.6382	0.2404	0.2426	0.0914		
S-9	ATJ-S3	2.13	0.8981	0.2180	0.4216	0.1023		
	ATJ-S4	2.05	0.7868	0.1552	0.3838	0.0757		
	IP-17-26-1	2.04	0.3994	0.1502	0.1958	0.0736	2,440	56
	IP-17-27-1	2.14	0.5298	0.1531	0.2476	0.0715		
	IP-17-66-1	2.15	0.3998	0.1380	0.1859	0.0642		
S-10A	IP-22E-67-1	2.07	0.3364	0.1107	0.1625	0.0535		
	IP-22E-68-1	2.08	0.3227	0.1110	0.1551	0.0534		
	IP-22F-69-1	2.14	0.3864	0.1006	0.1805	0.0470	2,450	56
	IP-22C-70-1	2.07	0.8512	0.2115	0.4112	0.1022		
	IP-22C-71-1	2.13	0.8596	0.2316	0.4035	0.1087		
S-11	ATJ-S5	1.62	0.8341	0.2324	0.5149	0.1434		
	IP-22E-67-3	1.68	0.7240	0.2205	0.4309	0.1312	2,315	76
	IP-22E-68-2F	1.62	0.7489	0.2335	0.4622	0.1441		
S-12A	ATJ-S6	1.59	1.1496	0.1692	0.7230	0.1064		
	IP-22E-67-4	1.62	0.3807	0.1539	0.2350	0.0950	2,495	76
	IP-22F-69-2	1.66	0.6771	0.1675	0.4079	0.1009		
	IP-22F-69-3	1.63	0.6412	0.1360	0.3934	0.0834		
S-13	ATJ-S7	2.06	0.7343	0.2180	0.3564	0.1058		
	ATJ-S8	2.06	0.7423	0.2311	0.3603	0.1122		
	IP-22F-69-4	2.08	0.7370	0.2244	0.3543	0.1079	3,435	45
	IP-22C-70-3	2.11	0.7583	0.2543	0.3594	0.1205		

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