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FABRICATION OF CARBON-CARBON COMPOSITES
USING ELECTROSTATIC FIBER
DEPOSITION (FLOCKING)

F. Lambdin
J. L. Cook

MASTER

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ABSTRACT

Electrostatic deposition of fibers was investigated as a technique for producing discontinuous carbon-carbon composites and composites containing continuous graphite filaments. Parts were densified by either liquid or gas infiltration. Thermal expansion anisotropies were related to the fabrication parameters.

CONTENTS

SUMMARY	11
INTRODUCTION	12
CARBON-CARBON COMPOSITES	15
Fabrication of the Composites	15
Constituent Materials Description.	15
Combination of Filament Winding and Electrostatic Flocking	15
Electrostatic Fiber Flocking without Continuous Filaments	18
Data and Discussion of Results	20
Combination of Filament Winding and Electrostatic Flocking	20
Electrostatic Fiber Flocking without Continuous Filaments	27
Conclusions and Recommendations	36
REFERENCES	38
ACKNOWLEDGEMENTS	39

SUMMARY

Electrostatic deposition or "flocking" of short, small-diameter carbon fibers was evaluated as a fabrication method for producing carbon-carbon composites. The technique was used to place the fibers between spaced windings and layers of continuous, high-modulus graphite yarn in an alternate 0 and 90-degree pattern. Hollow cylinders, approximately 4 inches in diameter by 12 inches long, were fabricated to approximately a 0.5 inch wall thickness and densified by conventional impregnation-carbonization cycles with coal-tar pitch.

Most of the cylinders broke during densification due to the accumulation of anisotropic stresses which exceeded the strength of the material. The highly anisotropic character of the continuous yarns was apparently the cause of the composite anisotropy. Radial-to-length thermal expansivity ratios of the cylinders ranged from -27.2 to 23.1.

Composite plates, which did not contain continuous filaments, were prepared by inductively charging carbon fibers of different lengths and diameters. These flocked plates were densified with pyrolytic carbon by the chemical vapor deposition (CVD) method. Thermal expansivities were measured for directions parallel and normal to the plates, and the ratios of the thermal expansion coefficients for these two directions varied from 1.01 to 1.40, depending upon the type and size of the fibers used. Some considerations were given to a corona-type, singly-charged-wire, continuous flocking system for the fabrication of thicker parts and for eliminating the stepwise layering of fibers.

INTRODUCTION

The thermal behavior of composite materials and, in particular, those composed of fibers or fiber-like materials depends upon the characteristics of the individual components and the orientation of these materials in the final composites. This orientation is determined, in most cases, by the initial fabrication or layup technique. If secondary processes, such as compaction, are not used to alter the composite, orientation of the fibrous materials will remain as initially arranged.

A new technique for fiber orientation in carbon-carbon composites has been investigated at the Oak Ridge Y-12 Plant.^(a) By this technique (referred to as flocking), small-diameter, short carbon fibers are electrostatically deposited to form a preselected shape. Application of an electrostatic charge causes the fibers to move from a charged surface to the surface of a mandrel or pattern which is maintained at near ground potential. While in motion, the fibers are oriented so that their major axis is normal to the mandrel surface (ie, parallel to the force lines of the electric field). If a layer of adhesive is applied to the surface of the mandrel, the fibers will stick and remain oriented in that position. Repeated cycles of adhesive and fiber application add thickness to the composite. Primary flock layup and flocking, combined with the filament winding of continuous graphite yarn, were investigated.

In an idealized composite, which contains continuous filaments, the short, flocked fibers would fill the space between the continuous filament yarns and be oriented perpendicular to them. The continuous yarn layers would alternate orientation (0 and 90 degrees) between the layers of electrostatically flocked fibers. In a flocked fiber composite, without continuous filaments, electrostatic deposition would provide a primary fabrication technique for the uniform and, hopefully, controllable layup of a composite.

Ability to control the orientation of discontinuous fibers would provide fabricators with a means of adjusting the properties of a composite, and filament-winding or cloth layup procedures could be supplemented by adding fibers with orientations which would increase interlaminar strength, reduce porosity between filaments, or reduce expansion and shrinkage anisotropy.

The objectives of this work were to develop fabrication techniques for making carbon-carbon composites which contain small discontinuous fibers in conjunction

(a) Operated for the US Atomic Energy Commission by the Union Carbide Corporation's Nuclear Division.

with spaced continuous filament-winding patterns, to densify these composites by liquid impregnation-carbonization cycles with coal-tar pitch, and to evaluate the composite characteristics such as interlaminar strength and anisotropy as they relate to the fabrication. A secondary objective was to evaluate flocking as a primary fabrication technique for discontinuous carbon-carbon composites.

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CARBON-CARBON COMPOSITES

FABRICATION OF THE COMPOSITES

Constituent Materials Description

The fine-diameter carbon fibers used in the flocked and wound parts were prepared from 0.15-denier-per-filament Villwyte viscose rayon. The rayon tow was chopped to lengths of approximately 12 to 15 mils prior to carbonization to 1,000° C in a nitrogen atmosphere. The carbonized flock was heat treated to 2,100° C in a nitrogen atmosphere, using an induction-type graphite furnace. Final dimensions of these fibers were, nominally, 2 microns in diameter by 250 microns long. The continuous, high-modulus graphite yarn used for winding was WYG-130 1/2 (Thornel 50). The coal-tar pitch (Type CP-277-15V), used in the densification of these parts, had a low insoluble content and had a softening point in the 90 to 95° C range.

For the composites which contained only discontinuous fibers, rovings made from continuous WYB-115 1/2 (Thornel 25) yarn and the viscose rayon (as just described) were chopped. A medium carbon black was mixed with the flocking fibers to fabricate two cylinders. This solid particulate material was added in order to determine its effect on the fabrication and properties of the composite.

Cylindrical solid graphite mandrels were fitted with threaded steel center rods on the axis of the cylinder, and threaded securing nuts were countersunk into each end of the cylinders. The complete cylinders were then covered with 10-mil-thick Grafoil. The center rod of the covered mandrel was inserted into a 10-inch lathe chuck, rotated slowly, and sprayed with a 10 weight percent dispersion of uncured latex in water prior to the first application of fibers.

Combination of Filament Winding and Electrostatic Flocking

Short, small-diameter fibers and particles were electrostatically deposited onto a surface with a basically conventional system, shown schematically in Figure 1. In this work, the physical components of the system were changed so that a quantity of carbon fiber flock was placed on a flat metal surface underneath the horizontally rotating mandrel. The metal plate was positioned approximately two inches from the bottom of the mandrel and charged negatively to between 10,000 and 30,000 volts, as shown in the photograph of Figure 2. The fibers migrated to the electrically grounded graphite mandrel and stuck to it because of the adhesive (latex) coating. Orientation of the fibers tended to be normal to the surface of the mandrel; however, due to the small diameters of the fibers and their attraction

Figure 1. FLOCK LAYUP PROCESS.

to each other, some misalignment and randomness of orientation was experienced. In this inductive-type flocking field, the fibers were added in layers due to their ability to cover the glue and prevent further thickness buildup without glue additions. The glue physically prevented a layer of fibers from returning to the charged plate after losing their charge. An appropriately spaced graphite yarn was then applied, with tension, in a circumferential orientation to the flocked surface, as seen in Figure 3. The surface was again lightly sprayed with the latex emulsion and coated electrostatically with the carbon fibers. Average layer thicknesses for this type of system were about 10 to 15 mils. The part was then removed from the horizontal lathe and installed on a vertical lathe. A sphere winding apparatus (seen in Figure 4) was adapted to wind the mandrel from end to end. The winder was adjusted so that the payout eye was off center sufficiently to pass the mandrel center rod or turning lug. This arrangement caused the spaced yarns that spanned the length of the cylinder to be out of alignment with the axis of the cylinder by about 3 degrees. After completing the step of tension winding the yarn in this orientation, the part was repositioned in the horizontal lathe for further flocking and circumferential winding. In this manner, the desired

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Figure 2. ELECTROSTATIC FLOCKING ARRANGEMENT. (The Mandrel has been Wrapped in White Paper for the Picture)

wall thickness was obtained. The part was dried and carbonized to 1,000° C while still on the mandrel.

After carbonization, the parts were densified by combinations of diluted pitch impregnation, conventional undiluted pitch impregnation, and a newly developed technique of impregnation and carbonization under very high pressure. Dilute pitch impregnations required the evacuation of air from the pores of the composite while submerged in the appropriate solution of pitch dissolved in benzene. After evacuation, the system was pressurized to atmospheric pressure and the part was removed and dried to constant weight before carbonization to 1,000° C in nitrogen at atmospheric pressure. Impregnations, using undiluted pitch, were carried out by the vacuum-pressure method indicated by the drawing of Figure 5. The combined pressure impregnation-carbonization cycles were carried out in the hot zone (17 1/2" D x 50" L) of a gas autoclave⁽¹⁾ which was adapted for this technique (see Figure 6). These impregnation-carbonization runs were carried out at pressures of approximately 15,000 psi and attained a maximum temperature of 750° C. The system employed an isolation liner to prevent hydrogen contamination of the argon pressurizing gas, and the excess gas volume caused by heat expansion of the pressurizing gas continually purged the container.

To use this technique, the cylinders are initially vacuum impregnated with molten pitch (Figure 5) and sealed under vacuum in a thin-wall (30-mil) stainless

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Figure 3. SPACED CIRCULAR WINDINGS. (The Mandrel has been Wrapped in White Paper for the Picture)

steel can with excess pitch on all sides, as Figure 6 indicates for a typical run involving a solid billet. The stainless steel acts as a semipermeable membrane, keeping the hydrocarbon molecules inside until decomposition to carbon and hydrogen is accomplished. The hydrogen then diffuses through the membrane, leaving essentially all the carbon. Pitch coking yields (on a weight basis) in such runs are normally 95 percent of the theoretical carbon content.

The mandrels are removed at this stage of the densification by cutting the continuous yarn covering from each end of the mandrel. This step was accomplished after sufficient density had been achieved for shape retention, usually 0.7 to 1.0 gm/cc. After each carbonization cycle, the cylinders are heated to 1,700° C prior to reimpregnation with undiluted pitch in an attempt to fully carbonize all of the organic material and stabilize the dimensions.

Electrostatic Fiber Flocking without Continuous Filaments

It was the initial intent to densify the composites which contained only flocked fibers by pitch impregnation and carbonization, but the low strength and density

135256

Figure 4. CONTINUOUS YARN WINDING APPARATUS. (The Mandrel has been Wrapped in White Paper for the Picture)

(< 0.1 gm/cc) of the as-flocked, unimpregnated, carbonized parts made it inadvisable. Instead, several flocked fiber parts were made and densified to ~ 1.4 gms/cc by infiltration with pyrolytic carbon, using the thermal gradient deposition process.^(2, 3) The infiltration with methane was at a nominal temperature of 1,150° C and one atmosphere pressure. These parts were fabricated as flat plates (8" x 8" x 0.75" T) and were produced by inductive up flocking. In this way, the fibers were spread on a metal tray under a flat-plate mandrel which had previously been sprayed with a small amount of the aqueous latex suspension. The fibers were charged, causing them to migrate to the surface of the grounded

Procedure

1. Evacuate Vessels 1 and 2
2. Heat Vessels 1 and 2
3. Transfer Pitch From Vessel 1 to 2
4. Pressurize Vessel 2
5. Remove Pressure and Transfer Pitch to Vessel 1
6. Remove Parts

Figure 5. METHOD USED TO VACUUM AND PRESSURE IMPREGNATE CARBON-CARBON COMPOSITES.

mandrel. Subsequent layers were added after successive glue applications. The parts were dried and carbonized to $1,150^{\circ}\text{C}$ prior to densification by infiltration with pyrolytic carbon.

DATA AND DISCUSSION OF RESULTS

Combination of Filament Winding and Electrostatic Flocking

Table 1 presents data on the cylinder sizes, yarn spacings, number of layers, and fiber types for the parts fabricated. In the table, a "layer" consists of one filament-wound layer in either direction, circumferential or longitudinal, and one flocked-fiber layer. The method used for densification of the individual cylinders, the final density achieved, and the results of densification are presented in Table 2. It can be noted that various densification plans were used in an attempt to achieve a high density, but all the methods resulted in highly stressed parts as evidenced by delaminations and two full-length radial cracks 180 degrees from each other. Cracks initiated at the cylinder inside wall and progressed to the

Figure 6. TECHNIQUE FOR PRESSURE IMPREGNATION AND CARBONIZATION.

outside circumference. These stresses were developed during carbonization of the pitch impregnant and appear to be caused by anisotropic shrinkage due to the filament orientation. This same type of cracking has been observed in moderately anisotropic-sprayed,⁽⁴⁾ carbon-fiber composites in which the ratios of the radial-to-axial expansion coefficients were in the range of 2.0. Figure 7 is a radiograph of the typical 180-degree radial failure cracks in a sprayed fibrous composite caused by anisotropic shrinkage during densification. Residual strain data on a similar part indicated that the inside wall surface was in tension and the outside wall surface was in compression by about the same magnitude. This condition would produce the type of crack shown in Figure 7 if the interlaminar strength was sufficient to prevent a delamination-type failure. Residual strain of this nature gives an overall effect of ring closure when a hoop is cut radially. Residual stresses which generate a compressive force on the inside surface and a tensile force in the outside surface combine to produce a ring opening

Table 1
DESCRIPTION AND CONSTRUCTION OF FLOCKED AND WOUND CYLINDERS

Cylinder Number	Flocking Fiber(1)		Cylinder Inside Diameter (in)	Cylinder Outside Diameter (in)	Wall Thickness (in)	Yarn Spacing(2) (no/in)	Number of Layers	Average Layer Thickness (mils)
	Diameter (μ)	Length (μ)						
FF-4	2	250	5.20	6.51	0.654	19	80	8.1
FF-5	2	250	4.90	5.10	0.100	19	25	4.0
FF-6	2	250	5.27	6.37	0.551	19	56	9.8
FF-7	2	250	3.90	5.47	0.785	19	60	13.0
FF-8	2	250	2.77	4.13	0.681	19	59	11.5
FF-9	2	250	2.77	4.13	0.681	10	89	7.6
FF-10	2	250	5.20	6.37	0.586	10	71	8.2
FF-20	2	750	2.77	4.18	0.705	10	49	14.0
FF-21	2	750	5.20	6.65	0.710	20	54	13.0
FF-22	2	250	2.77	4.29	0.767	20	94	8.0(3)
FF-23	2	250	2.77	4.29	0.763	10	56	13.6(3)

(1) Prepared from a rayon precursor and heated to 2,100° C.

(2) All cylinders wound with Thornel 50 graphite yarn.

(3) Fibers contained 400 grams of thermal black carbon per 100 grams of fibers.

when a hoop is cut radially. In the sprayed, discontinuous-fiber composites, such stresses were evidenced in cracking after completion of the carbonization cycle to 1,000° C. In composites which contained continuous filaments, the cracking occurred during graphitization of the cylinder at higher temperatures (1,700 to 3,000° C). It was also noted that the cracking of the composites which were uniformly constructed of spaced filament windings did not begin until considerable density had been achieved, usually in excess of 1.4 gms/cc. This behavior can be attributed to the fact that the wound structures were stronger and could sustain the higher stress level due to the anisotropic shrinkage during carbonization better than the completely discontinuous fiber composites. It also seems that the differential thermal expansion at 1,000° C was not sufficient to overstress the wound and flocked cylinders, whereas the higher temperatures did result in stresses exceeding the breaking strengths. These anisotropic properties also result in stresses which cause delaminations in the thickness dimension, depending upon the value of the interlaminar strength at the time of the stress generation. A radiograph of Cylinder FF-4 after removing the mandrel (Figure 8) illustrates a typical failure. The density was 0.70 gm/cc, and the part had received only dilute pitch impregnations. The cylinder broke radially after the second undiluted pitch impregnation at a density of 1.25 gms/cc. A comparison of the coefficients of thermal expansion (CTE) in two orthogonal directions for each of four cylinders is given in Table 3. The values indicate that this type of composite is very anisotropic. The radially oriented CTE is through the wall thickness of the cylinders and is influenced, primarily, by the diametral characteristics of the high-modulus yarn. The axial CTE orientation is along the

Table 2
DENSIFICATION METHOD FOR FLOCKED AND WOUND CYLINDERS

Cylinder Number	Number of Diluted Pitch Impregnations Followed by Carbonization at 1,000° C Without Pitch								Number of Conventional Undiluted Pitch Impregnations Followed by Carbonization at 1,000° C				Number of Combined Pressure Impregnation-Pressure Carbonizations in the Autoclave (700° C—15,000 psi)		Final Density (gms/cc)	Remarks
	25	25	25	25	25	50	50	50	1	2	3	4	1	2		
FF-4	X	X	X	X	X				X	X	X	X	X		~ 1.8	ID crack on second undiluted pitch carbonization.
FF-5	X	X				X									~ 1.0	Circular wound only; not uniformly constructed.
FF-6	X	X	X			X	X	X	X	X					1.43	Badly delaminated.
FF-7	X					X			X	X	X	X	X		1.78	Badly wrinkled and delaminated.
FF-8	X	X				X			X	X	X	X	X ⁽¹⁾	X ⁽²⁾	1.80 ⁽¹⁾ 1.95 ⁽²⁾	ID cracks.
FF-9	X	X				X			X	X	X	X	X ⁽¹⁾	X ⁽²⁾	1.80 ⁽¹⁾ 1.99 ⁽²⁾	Delaminated; ID crack.
FF-10	X					X			X	X	X	X	X		~ 1.72	Delaminated.
FF-20									X	X	X					Not well constructed; badly wrinkled; delaminated.
FF-21	X	X				X			X				X		~ 1.48	Delaminated.
FF-22	X	X				X			X	X					1.67	Delaminated; ID crack.
FF-23	X	X				X			X				X	X	1.73	Delaminated; ID crack.

(1) Whole cylinder.
(2) Partial cylinder.

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Figure 7. RADIOGRAPH OF A SPRAYED CYLINDER WHICH FAILED DUE TO ANISOTROPIC SHRINKAGE.

length of a cylinder and is influenced, primarily, by the axial characteristics of the yarn. A quartz tube-type dilatometer was used for the CTE measurements and was calibrated with two graphite standards.^(b) The values in Table 3 may be viewed as reasonable since the available data on high-modulus graphite yarn fibers exhibit a high degree of thermal expansion anisotropy. Measurements⁽⁵⁾ show that for Thornel 40, in the direction of the filament axis, the coefficient of thermal expansion is negative ($\sim -0.99 \times 10^{-6}$ in/in/ $^{\circ}$ C), while in the transverse (across diameter) it is about 16.7×10^{-6} in/in/ $^{\circ}$ C. Thornel 50 probably would exhibit even more anisotropy than Thornel 40. From Table 3 it would be expected that the 19 yarns/inch of Cylinder FF-8 would influence the CTE more than the 10 yarns/inch of Cylinder FF-9. However, Table 1 shows that Cylinder FF-9 contained about 50 percent more layers in the same thickness, thus the amount of continuous Thornel 50 yarn is approximately the same in each composites.

(b) Types AXM-9Q and ATJS graphite were supplied by the Los Alamos Scientific Laboratory, subsequent to certifying the expansion on a 30-inch length of material.

135206

Figure 8. RADIOGRAPH OF CYLINDER FF-4 AFTER REMOVAL FROM THE MANDREL. ($\rho = 0.7$ gm/cc)

In comparing the next two composites listed in Table 3 (Cylinders FF-22 and FF-23), Cylinder FF-22 is constructed with continuous yarn spaced at 20 filaments per inch and has thinner layers than Cylinder FF-23. The coefficients of thermal expansion for these two composites show that the composite with the most yarn (FF-22) has a higher radial coefficient and that the radial-to-length coefficient ratio is approximately 47 percent higher than for Cylinder FF-23. It can be noted in Table 1 that these two composites contained 400 grams of

Table 3

EXPANSIVITY COMPARED WITH THE FABRICATION PARAMETERS OF FLOCKED AND WOUND COMPOSITES

Cylinder Number	Coefficient of Thermal Expansion ⁽¹⁾ ($\times 10^{-6}/\text{in}/\text{in}/^{\circ}\text{C}$)			Density ⁽²⁾ (gms/cc)	Porosity (%)	Yarn Spacing (no/in)	Average Thickness (mils)
	Radial	Axial	Radial-to-Axial Ratio				
FF-8	5.09	0.22	23.1	1.80	14.6	19	11.5
FF-9	4.34	- 0.16	- 27.2	1.80	17.6	10	7.6
FF-22	7.71	1.36	5.7	~ 1.67	NA	20	8.0
FF-23	6.72	1.74	3.9	~ 1.73	NA	10	13.6
FF-10	6.58	1.21	5.4	1.72	NA	10	8.2
FF-21	4.10	0.76	5.4	1.48	NA	20	13.0

(1) Mean CTE between 25 and 1,000° C.

(2) Bulk density determined by mercury porosimetry at a pressure of 1.8 psia, which fills open pores larger than 100 microns in diameter.

carbon black per 100 grams of fiber. This particulate material was blended with the fibers prior to the electrostatic deposition.

Composites FF-10 and FF-21 (Table 3) show the same trend as Composites FF-8 and FF-9. FF-21 has the closest yarn spacing, but each layer is thicker than for FF-10. The coefficient-of-expansion ratios are about equal. The actual coefficients for Cylinder FF-21 are somewhat lower than for Cylinder FF-10, but this is probably due to the lower density. Table 1 shows that Cylinder FF-21 contains 30-mil-long fibers rather than 10 mils. This difference apparently had little or no effect on the expansion isotropy of the wound and flocked composites. This conclusion is brought out more conclusively for the entirely flocked composites using the two fiber lengths.

Mercury porosimetry data on Cylinder FF-8 after each of two pressure impregnation-carbonization cycles are listed in Table 4. The data show that after the first cycle a large percentage of the porosity was in the form of large-size pores which remained after the second cycle, although the bulk density increased by a large amount (ie, the total porosity decreased). This condition is shown in the polished section of Composite FF-8, Figure 9. Large pores which have their inside surface partially coated with pitch carbon from the impregnation-carbonization process still exhibit a large void volume. A circularly wound yarn which has been flattened due to the winding tension in the fabrication stage is seen in Figure 9. Some flocked, short fibers are seen between the circumferential yarn ends and the longitudinal yarn.

Views of an undensified section of a flocked and wound substrate are given in Figure 10 and show quite clearly the random orientation of the flocked fibers.

Table 4
DENSIFICATION OF CYLINDER FF-8

Property	After First Pressure Impregnation-Carbonization Cycle	After Second Pressure Impregnation-Carbonization Cycle
Bulk Density ⁽¹⁾ (gms/cc)	1.80	1.95
Porosity (%)	14.6	4.5
Real Density (gms/cc)	2.10	2.04
Porosity < 10 Microns (%)	76.6	87.7
Surface Area ⁽²⁾ (m ² /gm)	2.7	0.9
Volume Average Equivalent Pore Diameter (microns)	6.6	4.9

(1) Bulk density was determined by mercury porosimetry at a pressure of 1.8 psia, which fills open pores larger than 100 microns.

(2) Calculated from mercury porosity data.

The extent to which the fiber bundles were impregnated with pitch carbon was also studied (Figure 11). The carbon from the impregnant is shown as light circular areas around the darker filaments. This well-impregnated bundle is probably a result of the high-pressure (15,000-psi) impregnation-carbonization technique. Cracks appearing in the fiber bundle were caused by the differential in expansion between the fibers and graphite matrix and the anisotropic thermal coefficients of the filaments. Figure 12 is a scanning electron micrograph of a fractured section of Cylinder FF-8 and shows the random orientation of the small carbon-flocked fibers relative to the continuous filaments, and emphasizes the degree of impregnation of the highly orientated filament bundles.

Product uniformity was a direct result of operator experience and training in the fabrication stage for these flocked and wound cylinders. Cylinder FF-20 was fabricated by several operators, each with a minimum of experience. The result was a cylinder which was badly wrinkled, delaminated, and uneven after the initial carbonization. This cylinder was one of two constructed with 30-mil-long fibers.

Electrostatic Fiber Flocking without Continuous Filaments

Flat plates were fabricated by the induction charging method using each of the fiber types described previously. Data on the number of layers in each plate sample, the average layer thickness, and the dimensions of several specimens are summarized in Table 5. After carbonization and densification with pyrolytic carbon by the chemical vapor infiltration process, the coefficients of thermal expansion of the plates were measured in two orthogonal directions, listed in

F948

Figure 9. SECTION OF CYLINDER FF-8. ($\rho = 1.80$ gms/cc; 100X)

Table 6. In the flocking process used for these samples, a large diameter, discrete, untangled fiber would be preferentially oriented with its axis normal to the plane or surface of the part. The preferential fiber orientation of the spraying and flocking processes are represented schematically in Figure 13, and the CTE measurement directions of Table 6 are defined. The coefficients and ratios on the flocked samples indicate that the type and length of fibers used had a great influence on the ability of the electrostatic field to orient the fibers. Generally, the fibers with the larger diameter ($7\ \mu$) and greater length (30 mils) gave parts with a higher degree of fiber alignment. The coefficients with the grain are increased in these samples due to both preferential fiber orientation

(a) At 55X.

(b) At 60X.

Figure 10. FILAMENT-WOUND YARN BUNDLES SEPARATED BY FLOCKED FIBERS.

G94-2

Figure 11. SECTION OF CYLINDER FF-8. ($\rho = 1.80$ gms/cc; 250X)

and higher C-axis expansion of the pyrolytic carbon. The parts fabricated from the two-micron-diameter by 10-mil-long graphite fibers exhibited more nearly isotropic thermal expansions, as indicated in Table 6. A typical sample prepared by the spray layup process with the simple orientation, as previously defined (Figure 13), is compared in Table 6. It may be noted by a careful study of the data (Table 6) and the graphic representation of the fiber orientation (Figure 13) that a true random orientation of fibers will give a thermally isotropic composite with the highly oriented pyrolytic carbon matrix. If, however, preferential fiber orientation exists for any composite direction then the pyrolytic carbon matrix deposited on the fibers is also preferentially oriented. Since the individual fiber isotropy (crystal orientation) varies with the type fiber, a wide variation in expansivity can be obtained in a discontinuous fiber-pyrolytic carbon system. The high expansivity in the diametral dimension of an anisotropic fiber (16.7×10^{-6} in/in/ $^{\circ}$ C for Thornel 40) is comparable in size and direction to the high thermal expansivity of the C-axis of a pyrolytic

(a) At 3,000X.

SM-10932

(b) At 1,000X.

SM-10933

(c) At 300X.

SM-10934

(d) At 100X.

SM-10935

Figure 12. SCANNING ELECTRON MICROGRAPHS OF A FRACTURED SECTION OF DENSIFIED COMPOSITE FF-8.

Table 5
PARTS FABRICATED USING ONLY FIBER FLOCKING
(Flat Samples, 6" x 8")

Plate Number	Type and Size of Fiber Used	Number of Layers ⁽¹⁾	Average Layer Thickness (mils)	Total Thickness (in)
BF-12	Thornel 25 Chopped to 0.010-Inch Long	50	1.9	0.95
BF-11	2- μ -Diameter by 0.010-Inch-Long Graphite ⁽²⁾	77	1.5	1.16
BF-9	2- μ -Diameter by 0.010-Inch-Long Graphite ⁽²⁾	30	3.0	0.90
BF-6	2- μ -Diameter by 0.030-Inch-Long Graphite ⁽²⁾	48	1.8	0.54
BF-4	7- μ -Diameter by 0.010-Inch-Long Graphite ⁽²⁾	19	4.7	0.89

(1) A layer is defined as one application of adhesive and one flocking of the fibers.

(2) Carbon fibers heated to 2,100° C.

graphite ($\sim 22 \times 10^{-6}$ in/in/° C).⁽⁶⁾ The low axial fiber expansivity (-0.99×10^{-6} in/in/° C for Thornel 40) would be comparable to the low a-b plane expansivity of pyrolytic graphite ($\sim 1.3 \times 10^{-6}$ in/in/° C).⁽⁶⁾ Others⁽⁷⁾ have pyrolytic carbon-infiltrated, all-warp weaves of high-preferred orientation yarn (Thornel 40) and low-preferred orientation carbon yarn. Expansivity data on

Table 6
COEFFICIENTS OF THERMAL EXPANSION OF FLOCKED SAMPLES
THAT WERE DENSIFIED BY PYROLYTIC GRAPHITE INFILTRATION

Plate Number	Fiber Properties			Coefficient of Thermal Expansion ⁽¹⁾ ($\times 10^{-6} \text{ }^{\circ} \text{C}^{-1}$)		WG-to-AG Ratio
	Type	Size		WG(2)	AG	
		Diameter (μ)	Length (mils)			
BF-12	Thornel 25	7	10	4.89	3.52	1.40
BF-11	Y-12 ⁽³⁾	2	10	4.95	4.83	1.03
BF-9	Y-12	2	10	4.82	4.77	1.01
BF-6	Y-12	2	30	4.45	4.18	1.06
BF-4	Y-12	7	10	4.41	4.15	1.06
SC30-19 ⁽⁴⁾	Y-12	2	10	3.70 3.33 ⁽⁶⁾	6.01 ⁽⁵⁾	0.58

(1) From room temperature to 1,000° C.

(2) If all fibers were aligned perpendicular to a plane being flocked, the WG-direction CTE would be influenced primarily by the C-axis expansion of the pyrolytic graphite crystal (largest). This dimension is perpendicular to the flocking direction.

(3) Rayon-derived material, heated to 2,100° C.

(4) Typical sprayed sample densified by pitch impregnation to 1.6 gms/cc, 1,000° C carbonized.

(5) Parallel to the spray direction.

(6) Perpendicular to the spray direction—90 degrees from the other WG value.

Figure 13. THEORETICAL FIBER ORIENTATION IN THE SPRAYING AND FLOCKING PROCESSES.

composites where measurements were taken primarily across the filament diameters showed only slightly higher values where Thornel 40 was used instead of carbon filaments. However, measurements of the expansivity of the composites in a direction parallel to or at a slight angle to the filament axis showed that the carbon-yarn composites gave much higher values while the Thornel 40 yarn composites shrank during the initial part of the measurement temperature cycle. Unidirectional composites of Thornel 40 graphite yarn and a pyrolytic carbon matrix⁽⁷⁾ or an epoxy resin matrix⁽⁵⁾ show anisotropic thermal coefficients of expansion.

Flocking the first layer of fibers presented no problems from the standpoint of adhesion to the covered mandrel. Any adhesive that presented a sticky surface to the fibers was apparently adequate. However, the proper type and amount of adhesive which was applied for the second and subsequent layers is critical. Adhesives sprayed on the flocked fiber ends of the previous layer caused the new fibers to orient radially around the slightly longer fibers already in place on the surface. This action disrupted the orientation of the fibers in the layer and caused large lumps on the surface. Fiber-length measurements show a range of fiber lengths from 90 to 270 microns.⁽⁸⁾ The problem was resolved by selecting a water-based latex emulsion which presented a minimum adhesion to the new fibers but dried to hold the fibers of the previous layer in place. In fact, it was determined that almost no adhesive was necessary to fabricate the parts except for handling purposes. It was also apparent that the amount of

adhesive should be held to a minimum since even the smallest amount of adhesive would prevent the fibers from interlocking from layer to layer and produce an area which would cause voids in the carbonized part. A typical structure produced by two-micron-diameter by 250-micron-long fibers is seen in Figure 14. The part has been carbonized to 1,000° C, but not densified. A definite density variation can be seen because the structure was fabricated stepwise. These variations in density make it nearly impossible to achieve uniform densification, a result that was especially true in the case of densification with pyrolytic carbon where each fiber serves as a plating substrate. In this process, the low-fiber-density areas remain as low-density areas, as noted in Figures 15 and 16. These low-density areas between layers produce low-strength parts. Note that fiber ends are primarily visible, and it appears that the fiber orientation in the low-density areas is more aligned than in the high-density areas. The broken section exposes the small fibers as white or dark dots in the circle centers, while the coated fiber ends appear as unblemished circles.

Cylinders of the sizes described earlier were fabricated by this method but were not densified due to the problem with the low-density area between separate applications of fibers. However, preliminary work was done on a continuous flocking method which showed some promise. In this corona-type flocking

Figure 14. FLOCKED FIBER DENSITY VARIATION. (BF-11; Not Densified)

(a) At 50X.

(b) At 150X.

Figure 15. DENSITY VARIATION AFTER DENSIFICATION.

approach, a negatively charged wire was placed approximately one inch above a horizontally rotating graphite mandrel and oriented with the major axis along the major axis of the mandrel. The short graphite fibers which had previously been blended with 10 weight percent of a coating grade of particulate epoxy powder was vibrated into the area between the wire and mandrel. The low (5-kv) potential applied to the wire charged the fibers and fine epoxy particulates and deposited them onto the rotating mandrel, but was not sufficient to reattract the material from the deposit. After an initial adhesive application to the mandrel, a thick fiber deposit could be produced continuously without further adhesive.

Figure 16. LOW-DENSITY VARIATION IN A FLOCKED SAMPLE.

The deposited fiber mat was very fragile during the fabrication, but strength was improved by heat treating the epoxy-fiber composite. Fiber density was no higher (~ 0.1 gm/cc) than that achieved with the induction charging system, but the substrate was uniform and showed no layering effects. The fibrous substrate was observed to be random in fiber orientation. The deposition rate was somewhat slower than with the induction system. No samples produced by this method were densified.

CONCLUSIONS AND RECOMMENDATIONS

The more important findings and recommendations of the investigation are:

1. Isotropy was not achieved by the combination of flocking short, low-modulus carbon fibers between 0 and 90-degree-oriented, spaced, continuous high-modulus graphite yarns.
2. A possible solution to the anisotropy in the flocked and wound system would seem to be the use of a more discrete, individual, anisotropic fiber for flocking so that the effect of the continuous yarn would be normalized.
3. Isotropy is probably the most important factor to be controlled in a fibrous composite of this type where densification shrinkages are encountered as with pitch impregnation and carbonization.

4. Thermal expansion isotropy is directly related to the orientation, type, and amount of fiber used in a composite.
5. The continuous-filament component of the flocked and wound system appears to aid the liquid impregnation since the long voids in the fiber bundle probably facilitate reaching more open porosity with a given pressure.
6. Control of isotropy by fiber orientation was demonstrated in composites which contained only short fibers with different characteristics.
7. Layering or stepwise construction in the flocked composite is a problem especially if densified with pyrolytic carbon.
8. Pressure impregnation and carbonization with pitch is a fast, effective way to densify carbon-carbon composites; especially above a density of approximately 1.5 gms/cc.
9. Increased interlaminar strength probably was not achieved (although not measured) in the flocked and wound composites since shrinkage stresses caused delaminations. This failure was probably due to the inability of the fabrication method to orient and maintain the small carbon fibers in the composite radial direction. Low-fiber-density areas between layers in the pure flocked composites caused the interlaminar strength to be low.

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