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FABRICATION OF DISCONTINUOUS, HIGH-FIBER-
CONTENT, ISOTROPIC CARBON-
CARBON COMPOSITES

F. Lambdin
J. L. Cook

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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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OAK RIDGE Y-12 PLANT
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**FABRICATION OF DISCONTINUOUS, HIGH-FIBER-CONTENT,
ISOTROPIC CARBON-CARBON COMPOSITES**

F. Lambdin
J. L. Cook

Oak Ridge Y-12 Plant

P.O. Box Y, Oak Ridge, Tennessee 37830

operated for the U.S. ATOMIC ENERGY COMMISSION
by UNION CARBIDE CORPORATION-NUCLEAR DIVISION
under Contract W-7405-eng-26

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ABSTRACT

High-density, nearly isotropic, low-porosity carbon-carbon composites were produced by isostatically compacting previously prepared isotropic agglomerates of short carbon fibers and coal-tar pitch. The compacted composites were carbonized under high pressure for the high-fiber-content (37 - 50 vol %) materials or carbonized conventionally for the medium-fiber-content (20 - 35 vol %) materials. Spraying the fiber-pitch agglomerates in a dilute water slurry produced the lowest (15 vol %) fiber contents. Conventional pitch impregnation, or a unique combination of high-pressure pitch impregnation and carbonization, was used for composite densification.

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SUMMARY

A fabrication procedure was developed at the Oak Ridge Y-12 Plant^(a) for incorporating short, small-diameter carbon fibers into high-fiber-content (37 to 50 vol %), medium-fiber-content (20 to 35 vol %), and low-fiber-content (15 vol %) carbon-carbon composites. Producing high-fiber-content composites involved isostatically compacting loosely bound, carbon fiber-pitch binder agglomerates into billets for high-pressure carbonization compaction in a gas autoclave. Conventional carbonization of isostatically compacted, thin-walled shapes made from the agglomerates produced composites with a medium fiber content. Spraying the carbon fiber-pitch agglomerates in a dilute water slurry, followed by conventional carbonization, produced a low-fiber-content composite.

All composites were densified by either conventional liquid-pitch impregnation and carbonization, a combined high-pressure-pitch impregnation and carbonization in a gas autoclave, or a combination of these methods.

High-density, nearly isotropic, low-porosity carbon-carbon composites resulted with little or no residual stress due to shrinkage which occurred during processing.

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

INTRODUCTION

Interest in carbon-carbon^(b) composites continues to increase due to the unique and wide range of physical and mechanical characteristics displayed by carbon and graphite. Critical space, weight, and refractory applications exist in industrial, aerospace, and aircraft programs.⁽¹⁾ These composites have attractive properties (such as a high strength-to-weight ratio, toughness, shock and chemical resistance, and thermal stability) which make them very desirable for application in these problem areas.

A family of composites, of particular interest, were produced by the use of small-diameter, discontinuous carbon fibers in a fine-grain, low-porosity, well-graphitized matrix. A low-fiber-density type of this composite performed well in a six-atmosphere arc-jet test,⁽²⁾ while high-fiber-density compacted samples performed well at pressures up to 75 atmospheres.⁽³⁾ Many other composite types⁽⁴⁾ have been fabricated by varying the materials, processing, and fabrication techniques.⁽⁵⁾ This report discusses the development of the procedures and techniques used in producing a high-carbon-fiber density composite and to demonstrate the degree of product repeatability achieved. Particular emphasis was placed upon methods to attain composite isotropy and decreased processing time.

(b) In this report, carbon-carbon composites will be used to include all the composites which may have a carbon or graphite matrix that is reinforced with carbon fibers.

FABRICATION OF HIGH-FIBER-CONTENT COMPOSITES

THEORY AND OBJECTIVES

It is generally accepted that glassy-type⁽⁶⁾ carbon is a more ablation-resistant material than are the more graphitizable materials. Thus, it would appear that a composite to be used in an ablative environment should contain a large volume percent of the glassy-type carbon and yet have the desirable characteristics to minimize thermal stress; ie, high thermal conductivity, a low coefficient of thermal expansion, and high strain to failure. The material ideally should be isotropic with respect to these properties, and should possess a minimum of open porosity and a minimum percentage of large (> 100-micron) pores. The fabrication and densification process should be adaptable to both billet and shaped composites.

Earlier work⁽⁴⁾ had shown that nearly isotropic, solid billets could be produced with a high (~35 volume percent) discontinuous carbon fiber content, but that some improvement was desired to achieve a more random fiber orientation and to improve fiber distribution. The gas autoclave facility at the Oak Ridge Y-12 Plant was used as an effective tool in the initial compaction of the composites to achieve a high fiber density, but the conventional pitch impregnation-carbonization-densification cycles were excessively long for reaching a relatively high carbon density. Attempts to fabricate a high-fiber-density, thin-walled, shaped carbon-carbon composite by compacting a low-density, sprayed-carbon, fiber-pitch structure showed that more control over the fiber lay-up method would have to be exercised in order for the composite to be sufficiently isotropic to withstand the stresses generated by shrinkage during densification.

The following process improvements and objectives were the goal of this experimental fabrication and evaluation effort: To develop (1) a method of three-dimension composite fabrication with a high content of discontinuous fibers; (2) a uniform, flaw-free structure; (3) a composite with isotropic shrinkage as well as properties; (4) a reliable process for composite fabrication which could be scaled up for larger composites.

PROCESS DESCRIPTION

A fabrication procedure was planned and developed (shown in the process flow chart of Figure 1) in which a loosely bound, low-density, isotropic-carbon, fiber-pitch agglomerate was produced by grinding and used as a basic composite

Figure 1. FABRICATION PROCEDURE FOR HIGH-FIBER-CONTENT CARBON-CARBON COMPOSITES.

lay-up material. It was planned that the fibers would be held in a somewhat random orientation by the solidified pitch binder for subsequent forming and compaction under heat and pressure. The process flow diagram shows the general fabrication procedure developed for solid composite billets using a solvated pitch binder (dotted line) and a particulate pitch binder (solid line). The diagram also shows the process changes used for fabricating shaped composites (dashed line). It may be noted from the figure that in all processes the preheated composites were first canned and then isostatically compacted at 5,000 psi in oil prior to the initial carbonization of the pitch binder. In the case of the billet procedure, a 19-inch-diameter, high-pressure gas autoclave (Figure 2) was used for further isostatic, mechanical compaction of the composite during the initial carbonization to $\sim 700^{\circ}\text{C}$. (The working chamber of the autoclave is ~ 19 inches in diameter by ~ 50 inches long.) The procedure developed for shaped composites included a conventional inert-atmosphere carbonization after the isostatic compaction step. The billet process yielded a composite with approximately 37 volume percent fibers, while the shaped

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Figure 2. GAS AUTOCLAVE FACILITY.

composite process yielded approximately 30 volume percent fibers. The lower fiber-volume value for the shaped composite process is attributed to a number of phenomena. In the billet process, additional fiber compaction was achieved during the binder carbonization, while in the shaped composite process some volume expansion or relaxation of the pressed composite was experienced during the conventional carbonization to 1,000° C. The increase in fiber volume due to compaction during the high-pressure carbonization step was limited somewhat since the carbon yield of the binder pitch carbonized under pressure was near theoretical, while a carbon yield of only 35 to 45 percent was achieved under conventional carbonization to 1,000° C. The higher yield of the pitch binder to carbon under pressure prevented the fibers from attaining a higher percent of the composite volume. Interestingly, a compacted billet with the higher pitch binder content was carbonized, with the high gas over-pressure but without the benefit of additional mechanical compaction, to a resulting 31.3 volume percent fibers. In both the billet and shaped composites, the carbonization was carried to a minimum of 2,000° C before densification was begun.

For both types of carbon-carbon composites, a rapid densification method was developed which combined the conventional vacuum-pressure pitch impregnation with a new pressure impregnation-carbonization process in the gas autoclave facility. In this way, a 15,000-psi pressure was exerted on the molten impregnating pitch causing continuous impregnation until carbonization (solidification) occurred. Carbonization to ~ 2,000° C between impregnating cycles subsequent to final graphitization completed the process for the composites.

CONSTITUENT MATERIALS

The carbon fibers were specially prepared by precision chopping 0.15-denier-per-filament Viscose rayon tow to lengths of 10 to 15 mils, followed by an inert-atmosphere carbonization to 2,100° C. The individual carbon-filament diameter was a nominal 2.0 microns and is shown on the left of Figure 3. Also shown for comparison are 7-micron and 10-micron-diameter commercial carbon filaments. The length of the carbon filaments was in the 8 to 10-mil range, and the figure also shows these chopped lengths of filaments. Tensile strengths of these filaments were in the 50,000-psi range.

The coal-tar pitch used in this work was a medium-melting point impregnating pitch (Type CP-277-15V). It was used as the binder in fabrication and as the impregnant in densifying the composites.

Figure 3. CARBON FIBERS USED IN COMPOSITES.

FABRICATION TECHNIQUES

Fiber and Pitch Preparation

Subsequent to carbonization to 2,100° C, the chopped carbon filaments were screened to decrease the fiber agglomeration. A rotating brush-type screener which did not allow the screened fraction to vibrate was found to be the most effective method for deagglomerating the fibers. The small dimensions of the fibers, however, caused serious reagglomeration problems after screening and before usage. A 40-mesh (420-micron) screen was found to be sufficient for deagglomeration without serious fiber breakage.

The benzene-solvated coal-tar-pitch binder solution was prepared by heated dissolution of appropriate amounts of pitch followed by decantation to eliminate insoluble material. Since the pitch used contained 12 to 16 weight percent benzene insolubles, the decanting process probably reduced this value by about half. A nominal 50 weight percent pitch solution was prepared and the concentration accurately determined by gravimetric analysis.

The particulate coal-tar-pitch binder was prepared by grinding chunks of pure pitch previously chilled in the liquid nitrogen. The grinding was accomplished in a high-energy shear-type mill shown in Figure 4. The ground pitch was screened to pass a 100-mesh (150-micron) screen before use. Storage of the screened pitch in a refrigerator prevented serious fusion of the particles.

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Figure 4. INTERIOR OF A HIGH-ENERGY, SHEAR-TYPE MILL.

Fiber-Pitch Agglomerate Preparation

In the solvated-pitch binder process (dotted line of Figure 1), the appropriate amount of pitch binder solution was diluted with benzene to equal the volume of screened carbon fibers which had been placed in a suitable container. The fibers were completely soaked with the diluted pitch binder solution and allowed to dry in the container until removal of the casting could be accomplished without the loss of liquid. After removal of the casting from the container, it was allowed to continue drying at room temperature until all

the solvent (benzene) was removed. The dried carbon fiber-pitch casting was broken into chunks, chilled in liquid nitrogen, and ground in the impact-type mill.

Although desirable fiber-pitch agglomerates were produced by the method just described, an easier, less-time-consuming method of particulate pitch binder dispersal in the fibers was developed. In this process (solid line of Figure 1), appropriate amounts of screened carbon fiber and screened particulate pitch were blended in a twin-cone blender for 45 minutes with the intensifier bar in operation. The blended material was dry cast into a flexible polyvinyl chloride (PVC) bag (~ 12 inches in diameter), sealed, and evacuated for 24 hours at 130°C . Figure 5 shows a bag containing particulate pitch binder and carbon fibers that were heat treated under vacuum. This treatment causes some volume shrinkage and also causes the particulate pitch to flow among the fibers. After chilling with liquid nitrogen, the casting was ground in the impact-type mill of Figure 4 to produce fiber-pitch agglomerates typical of those shown in Figure 6.

These agglomerates appear to have an isotropic fiber arrangement and a very low density. It can be observed in Figure 6(b) that the binder pitch was well distributed at fiber junctions and along the length of each fiber. The gross agglomerate size shown in Figure 6(a) was about 30 mils, but the distribution contained many smaller agglomerates. The bulk density of these agglomerates was $\sim 0.1\text{ gm/cc}$.

Compacting the Fiber-Pitch Agglomerates

To fabricate billets, the fiber-pitch agglomerates were vibrationally packed or tamped into 12-inch-diameter flexible PVC bags and evacuated while being held at $\sim 140^{\circ}\text{C}$ for 10 hours. The bag was sealed and isostatically pressed immediately in room-temperature oil at 5,000 psi with a 30-minute hold period. Experiments showed that the use of 140°C oil was not required for this operation. The thin-wall, shaped composites were likewise processed except that the fiber-pitch agglomerates were packed around a preshaped graphite mandrel of the desired contour. In addition, the flexible bag was sometimes contoured, depending upon the shape of the mandrel and the desired wall thickness of the composite. The commercial bulk graphite mandrel was covered with two layers of Grafoil tape prior to casting. The agglomerates were lightly tamped into the space between the mandrel and flexible bag. The mandrel covering acted as a mold release between the solid mandrel and compacted composite. Compacting was generally at 5,000 psi in room-temperature oil with a 30-minute hold at pressure.

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Figure 5. EVACUATED POLYVINYL CHLORIDE BAG CONTAINING HEAT-TREATED FIBER AND PARTICULATE PITCH.

(a) At 100X

(b) At 300X

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Figure 6. SCANNING ELECTRON MICROGRAPHS OF FIBER-PITCH AGGLOMERATES AFTER GRINDING.

BILLET FABRICATION

Thirteen billets of carbon fibers and pitch binder were isostatically compacted. The compacting pressure, binder content, dispersion method, and mercury porosimetry data for these compacted composites are listed in Table 1. Also shown are the data for two experimental composites with different pitch binder contents which were compacted at 5,000 psi, sampled, and then recompactd at 30,000 psi and resampled. The composites were generally compacted in PVC bags similar to that shown in Figure 5, which were 15 inches in diameter by approximately 30 inches in length. After the composite was compacted (seen in Figure 7), the bag was removed (Figure 8), and the billets machined into solid cylinders, 10 inches in diameter by approximately 16 inches in length.

Table 1
POROSITY DATA ON ISOSTATICALLY COMPACTED FIBER AND PITCH BILLETS
PRIOR TO CARBONIZATION

Composite Number	Isostatic Compacting Pressure (psi)	Pitch Binder (parts per hundred fiber)	Pitch Binder Dispersion Method ⁽¹⁾	Bulk Density ⁽²⁾ (gms/cc)	Porosity (%)	Volume Average Equivalent Pore Diameter (microns)	Porosity less than 10 Microns in Diameter (%)
49	5,000	164	Liquid	1.242	8.85	5.09	89.17
50	5,000	140	Liquid	1.118	16.69	0.86	99.66
51	5,000	146	Liquid	0.948	30.27	8.00	90.74
52	5,000	127	Liquid	0.867	36.60	3.87	94.98
53	5,000	146	Liquid	0.861	36.03	2.60	96.85
54	5,000	157	Liquid	1.180	10.71	2.00	94.77
55	5,000	140	Solid	1.084	20.55	1.08	97.42
57	5,000	140	Solid	1.038	23.73	2.40	96.29
58	5,000	140	Solid	1.012	NS	NS	NS
59	5,000	140	Solid	0.911	NS	NS	NS
60	5,000	140	Solid	0.832	39.00	3.39	95.33
61	5,000	140	Solid	1.030	22.82	2.25	93.66
62	5,000	140	Solid	0.965	29.99	1.06	98.37
74	5,000	140	Solid	0.973	27.25	2.56	93.60
74	30,000	Recompactd above composite		1.048	20.63	1.56	97.50
75	5,000	90	Solid	0.904	35.24	4.10	94.20
75	30,000	Recompactd above composite		0.982	28.59	2.25	97.04

(1) "Liquid" refers to application of the pitch as a solution of pitch in benzene; "solid" refers to the use of particulates of pitch.

(2) Bulk density determined from the volume occupied at a mercury pressure of 1.8 psia which filled all open holes larger than 100 microns in diameter.

Each billet was then sealed in a 30-mil-wall-thickness stainless steel can while under vacuum, as shown in Figure 9. The canned composites were then carbonized to 700° C under an argon gas pressure of 15,000 psi in a gas autoclave

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Figure 7. ISOSTATICALLY COMPACTED COMPOSITE.

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Figure 8. ISOSTATICALLY COMPACTED COMPOSITE WITH FLEXIBLE BAG REMOVED.

131324

Figure 9. STAINLESS STEEL CAN CONTAINING A COMPOSITE.

using a heat cycle of eight hours. The technique for this operation is shown at the left of Figure 10. The method was developed with the objective of allowing only the hydrogen liberated by the pyrolysis of the pitch binder to diffuse through the thin stainless steel can. The hydrogen then is swept from the isolation liner by the bleeding of hydrogen-contaminated argon. This bleeding is also necessary to keep the pressure at 15,000 psi due to the gas expansion from room temperature to 700° C. The larger hydrocarbon molecules do not diffuse through the stainless steel at an appreciable rate, thus staying inside to decompose and form carbon and hydrogen. This action increases the carbon yield of the binder to near theoretical values while compacting the composite during the decomposition.

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Figure 10. TECHNIQUE FOR PRESSURE CARBONIZATION.

Figure 11 presents a view of a canned billet after a pressure carbonization-compaction cycle in the autoclave; a pressure carbonized-compacted billet

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Figure 11. CANNED BILLET AFTER A PRESSURE CARBONIZATION-COMPACTION CYCLE.

after removal of the stainless steel can can be seen in Figure 12. Note that the creases and folds in the billet are sharper and more pronounced than in the stainless steel can. This difference is due to the partial expansion of the can during the autoclave depressurization cycle.

Porosity data obtained by mercury intrusion of samples from the billets after completion of the isostatic pressure carbonization-compaction cycle in the sealed stainless steel cans are given in Table 2. It can be noted from the table that the average density after this step was ~ 1.15 gms/cc, excluding Composites 52 and 58. These two composites were lower in density due to the rupture of the thin stainless steel can before the carbonization and shrinkage was completed. The porosity of these two composites is also notably higher, as well as the average pore size, due to the absence of mechanical compaction.

Table 2
POROSITY DATA ON ISOSTATICALLY PRESSURE CARBONIZED BILLETS

Composite Number	Bulk Density ⁽²⁾ (gms/cc)	Porosity ⁽²⁾ (%)	Volume Average Equivalent Pore Diameter ⁽²⁾ (microns)	Porosity less than 10 Microns in Diameter ⁽²⁾ (%)	Calculated Values ⁽¹⁾		
					Fiber Content (vol %)	Pitch Coke Content (vol %)	Porosity (vol %)
49	1.153	27.46	2.76	99.29	33.26	44.07	22.67
50	1.145	27.84	3.66	97.74	36.19	41.33	22.48
51	1.101	31.39	2.73	99.28	33.99	39.34	26.67
52	0.901	43.00	7.05	93.38	30.03	25.55	44.42
53	1.144	26.39	2.81	98.61	35.31	41.87	22.82
54	1.130	28.30	4.26	97.30	33.45	42.09	24.46
55	Not Carbonized						
57	1.181	24.63	4.84	93.52	37.29	43.38	19.33
58	0.965	38.10	7.00	93.75	30.50	30.74	38.76
59	1.156	28.77	4.07	88.20	36.53	41.97	21.50
60	1.137	25.80	2.63	99.22	35.93	40.85	23.22
61	1.158	28.49	3.27	97.82	36.60	42.09	21.31
62	1.130	28.57	2.75	99.61	35.71	40.44	23.85
74	1.107	37.63	2.83	99.39	34.99	39.09	25.91
75	1.189	21.62	2.44	96.81	46.92	37.44	15.64

(1) Fiber density assumed to be 1.40 gms/cc, pitch carbon assumed to be 1.70 gms/cc, and carbon yield of the pitch binder after 2,000° C estimated to be 90%.

(2) Determined by mercury intrusion techniques.

Figure 13 points out the effect of mechanical compaction during pressure carbonization on pore-size distribution in the pressure-carbonized billets. Without mechanical compaction, the pore distribution favors the larger pores.

Also shown in Table 2 is the calculated fiber, pitch-coke, and porosity content. These values were calculated using the carbonized density and binder pitch

131609

Figure 12. PRESSURE CARBONIZED-COMPACTED BILLET.

Figure 13. EFFECT OF MECHANICAL COMPACTION DURING CARBONIZATION ON PORE-SIZE DISTRIBUTION.

content for each composite and assuming average values for fiber and pitch-coke density, and carbon yield of the binder pitch. It can also be noted from Table 2 that the calculated porosity values generally are in the range of the analytically determined values. In addition, Table 2 shows that the calculated fiber volume of the two composites pressure carbonized without mechanical compaction decreased by ~ 10 volume percent and the calculated porosity increased by ~ 18 volume percent.

The experimental composite with 90 pph pitch binder (Composite 75) is calculated to have a 10 volume percent increase in fiber content above that achieved in the other composites, but neither of the two experimental composites which were compacted at 30,000 psi (Table 1) showed a significantly different density from those compacted at 5,000 psi.

Figure 14 provides a view of a pressure carbonized-compacted billet which has been machined.

BILLET DENSIFICATION

After machining to a smooth cylindrical billet (~ 5 " D), the composites were heat treated to a temperature of $\sim 2,000^{\circ}\text{C}$ at $\sim 200^{\circ}\text{C}$ per hour. The billets were then vacuum and pressure impregnated in the conventional manner

131296

Figure 14. MACHINED PRESSURE-CARBONIZED BILLET.

with molten pitch (Type CP-277-15V) at a temperature of 200° C and a maximum pressure of 50 psi. The impregnated billets were recanned in excess pitch in another stainless steel can for a combined pressure impregnation-carbonization cycle to 700° C. Figure 15 shows a typical billet after removal from the stainless steel can after the combined pressure impregnation-carbonization step. Note that excess carbonized pitch completely surrounds the billet.

The billet densities after successive pressure impregnation-carbonization cycles are reported in Table 3. The billets were heat treated in the range of 1,750 to 2,000° C between carbonization cycles in order to open as much porosity and cause maximum shrinkage of the previously impregnated pitch

Table 3
DENSIFICATION OF BILLETS

Composite Number	Starting Carbonized Density (gms/cc)	Approximate Geometric Density After the Pressure Impregnation-Carbonization Cycle			Remarks
		Cycle			
		1 (gms/cc)	2 (gms/cc)	3 (gms/cc)	
49	1.15	1.47	1.65	1.77	internal cracking
50	1.14	1.47	1.69		
51	1.10	1.45	1.65		
52	0.90	1.36	1.53	1.77	internal cracking
53	1.14	1.45	1.58	1.84	internal cracking
54	1.13	1.34	1.62		
57	1.18	broke due to thermal shock during heat treatment			
58	0.96	1.34			not densified
59	1.16	1.51 ⁽¹⁾	1.74	1.87	
60	1.14	1.43	1.61		internal cracking
61	1.16	1.45	1.71		
62	1.13	1.44	1.65		internal cracking
74	1.11	1.35 ⁽²⁾	1.60 ⁽³⁾		
75	1.19				not densified

(1) Conventional pitch impregnation and carbonization in addition to a pressure impregnation-carbonization cycle to only 500° C.

(2) To this density by impregnation and carbonization of phenolic resin.

(3) To this density by impregnation and carbonization of pitch.

carbon. Some billets, as Table 3 reports, developed internal hairline cracks. Although this cracking was noted in the billets which had gone through three successive densification cycles, some showed these cracks on the second cycle. The cause of cracking has not been definitely isolated; and, since this densification method has not come into wide usage in the graphite industry, almost no previous experience or trouble has been reported. One problem could be lack of sufficient graphitization in the heat treatment between impregnation-carbonization cycles. Composite 49, which cracked extensively,

131775

Figure 15. BILLET AFTER A PRESSURE IMPREGNATION-CARBONIZATION CYCLE.

was heat treated in this manner to 2,000° C between each cycle. Composites 52 and 53 were heat treated in like manner, and the cracking was evident after the third impregnation-carbonization cycle.

Composite 59 was heat treated initially to 1,900° C, to 2,000° C after the first densification cycle, to 3,000° C after a conventional impregnation-carbonization cycle, and to 3,000° C after a second pressure impregnation-carbonization cycle. This composite was probably more graphitized by the heat treatment and attained a higher density than any other, and no cracking was observed. Composite 60 was initially heat treated to 1,800° C, then to 1,750° C after the first densification cycle. Cracks appeared during the second densification cycle. Composite 61, however, was heat treated in practically the same manner as Composite 60 without cracking. The maximum heat treatment between densification cycles for Composite 62 was 1,800° C, and cracking developed during the second densification cycle.

A further possible cause of the cracking may have been the sudden release of the pressurizing gas from the gas autoclave at the run termination. This circumstance could trap high-pressure gas in the porosity of the composite which would, in turn, place the part in tensile stresses sufficient for rupture.

THIN-WALLED COMPOSITE FABRICATION AND DENSIFICATION

It was noted during fabrication of the billet composites that the carbon fiber-pitch agglomerates were isotropic and produced a uniform, high-fiber-volume, isotropic composite by isostatically compacting the cast material in billet form. A previous attempt, mentioned earlier, to fabricate a thin-walled, high-fiber-density composite in which a sprayed, carbon fiber-pitch composite was isostatically compacted against a mandrel resulted in a highly anisotropic body, as indicated by the microstructures of Figure 16. The fiber-placement method (spraying) and subsequent compaction highly aligned the fibers in the composite so that anisotropic densification shrinkage produced stresses sufficient to break the composite. It may be noted in the figure that almost all fiber axes are oriented 90 degrees from the direction of spray and the direction of applied compacting pressure.

A series of experimental composites were fabricated in an attempt to extend the use of the isotropic fiber-pitch agglomerates and techniques to thin-walled, high-fiber-volume, shaped carbon-carbon composites. The experimental parts were fabricated by isostatically compacting the carbon fiber-pitch agglomerates subsequent to conventional carbonization in one atmosphere of flowing nitrogen. Experimental composites were fabricated by varying

136670

Figure 16. COMPACTED CARBON FIBER-PITCH SPRAYED COMPOSITE. (Top: View 90° from the Spray and Pressing Direction, Bottom: View Parallel to the Spray and Pressing Direction; 1000X)

the compacting pressure, the pitch binder content, and the particulate size. The results are summarized in Table 4.

The first series of composites shown in Table 4 were fabricated as four-inch-diameter billets using compacting pressures from 1,000 to 5,000 psi and pitch binder levels of 90 and 140 pph. Mercury porosity data and composite fiber contents for the compacted composites are tabulated and compared with the same data taken after the free-standing carbonization cycle. The fiber content of the composites prepared with 140 pph pitch binder did not increase with increasing compacting pressure, while the fiber content for those containing 90 pph pitch increased significantly with the compacting pressure. The compacted and carbonized densities of these composites are

plotted with the compacting pressure in Figure 17. The curves show that by using 140 pph particulate pitch binder, no significant increases were attained in the carbonized density. Since the composites were carbonized in a free-standing, unrestrained mode, they were free to expand during the process to satisfy any compacting stresses. The fiber content of the carbonized composite compared to the fiber content of the compacted composite is a direct

Figure 17. COMPOSITE DENSITY VARIATIONS WITH COMPACTING PRESSURE AT TWO BINDER CONCENTRATIONS.

measure of this composite volume expansion. This comparison of fiber contents for the composites is also shown in Table 4. Using the compacted fiber volume of each composite as 100 percent of theoretical (no expansion), the carbonized fiber volume is expressed as a percent of theoretical. The composites with 140 pph binder were significantly lower in the percent of theoretical fiber content than the composites with 90 pph binder, which indicates more expansion for the higher binder content.

Table 4
DATA FOR ISOSTATIC-COMPACTED, CONVENTIONALLY CARBONIZED COMPOSITES

Composite Number	Isostatic Compacting Pressure (psi)	Particulate Binder Pitch Content Size		Compacted					Carbonized ⁽¹⁾					Compacted Fiber Volume ⁽⁴⁾ (%)	Remarks
		(pph) ⁽²⁾	(mesh)	Bulk Density (gms/cc)	Porosity (%)	Volume Average Pore Diameter (microns)	Porosity less than 10 microns in Diameter (%)	Fiber Volume (vol %)	Bulk Density (gm/cc)	Porosity (%)	Volume Average Pore Diameter (microns)	Porosity less than 10 microns in Diameter (%)	Fiber Volume ⁽³⁾ (vol %)		
66	1,000	140	- 80	0.99	27.6	2.80	98.69	29.5	0.542	66.82	12.93	18.34	22.8	77.3	4" diameter billet
67	1,000	90	- 80	0.82	39.6	6.20	94.44	30.8	0.435	72.76	12.93	17.05	21.4	69.5	4" diameter billet
68	2,000	140	- 80	0.98	27.4	1.60	96.56	29.2	0.595	63.47	12.46	21.03	25.0	85.6	4" diameter billet
69	2,000	90	- 80	0.75	46.1	6.10	94.81	28.2	0.552	65.35	12.11	29.27	27.2	90.5	4" diameter billet
70	3,000	140	- 80	0.94	29.3	1.40	97.99	28.0	0.574	65.04	12.90	18.11	24.1	86.1	4" diameter billet
71	3,000	90	- 80	0.87	37.3	5.10	97.52	32.7	0.618	61.32	8.68	84.91	30.5	93.3	4" diameter billet
72	4,000	140	- 80	0.99	26.1	1.80	96.75	29.5	0.557	65.77	12.46	17.64	23.4	79.3	4" diameter billet
73	4,000	90	- 80	0.87	37.1	3.20	97.32	32.7	0.607	61.78	8.60	79.21	29.9	91.4	4" diameter billet
74	5,000	140	- 80	0.97	27.3	2.56	93.60	28.9	Not conventionally carbonized						4" diameter billet
75	5,000	90	- 80	0.90	32.2	4.10	94.20	33.8	Not conventionally carbonized						4" diameter billet
120	5,000	90	- 80	0.926	NS ⁽⁵⁾	NS	NS	34.8	0.658	58.45	7.53	92.50	25.9	74.4	3" ID x 0.75" wall x 12" long cylinder
121	5,000	80	- 80	0.970	NS	NS	NS	39.7	0.616	60.43	7.67	92.33	31.4	79.1	3" ID x 0.75" wall x 12" long cylinder
122	5,000	70	- 80	0.903	NS	NS	NS	37.9	0.577	63.30	7.64	91.68	30.5	80.5	3" ID x 0.75" wall x 12" long cylinder
123	5,000	60	- 80	0.853	NS	NS	NS	38.0	0.559	63.75	7.65	90.95	30.7	80.8	3" ID x 0.75" wall x 12" long cylinder
131	5,000	50	- 80	0.909	NS	NS	NS	43.3	0.601	62.47	5.90	95.97	34.3	79.2	3" ID x 0.75" wall x 12" long cylinder
130	5,000	40	- 80	0.834	NS	NS	NS	42.5	0.561	64.93	6.63	94.32	33.4	78.6	3" ID x 0.75" wall x 12" long cylinder
126	5,000	90	- 60 + 70	1.078	NS	NS	NS	40.5	0.585	62.46	7.46	92.12	28.8	71.1	3" ID x 0.75" wall x 12" long cylinder
127	5,000	90	- 80 + 100	1.156	NS	NS	NS	43.4	0.586	61.97	8.60	82.32	28.9	69.7	3" ID x 0.75" wall x 12" long cylinder
128	5,000	90	- 100	1.134	NS	NS	NS	42.9	0.607	61.02	7.97	89.98	29.9	69.7	3" ID x 0.75" wall x 12" long cylinder
133	5,000	90	- 100	1.016	NS	NS	NS	38.2	0.581	NS	NS	NS	28.6	74.9	3" ID x 0.75" wall x 12" long cylinder
134	5,000	90	- 100	1.012	NS	NS	NS	38.0	NS	NS	NS	NS	--	--	3" ID x 0.75" wall x 12" long cylinder
135	5,000	90	- 100	1.035	NS	NS	NS	38.9	NS	NS	NS	NS	--	--	3" ID x 0.75" wall x 12" long cylinder
104A	5,000	90	- 80	NS	NS	NS	NS	--	0.653	59.18	7.45	92.83	32.2	--	18" high conical frusta
104AB	5,000	90	- 80	NS	NS	NS	NS	--	0.660	60.88	9.58	60.88	32.5	--	18" high conical frusta
104	5,000	90	- 80	NS	NS	NS	NS	--	0.729	54.05	8.26	86.50	35.9	--	18" high conical frusta
105C	5,000	90	- 80	NS	NS	NS	NS	--	0.629	59.69	8.20	87.32	31.0	--	18" high conical frusta
105G	5,000	90	- 80	NS	NS	NS	NS	--	0.600	63.08	10.23	54.54	29.6	--	18" high conical frusta
Billets ⁽⁶⁾	5,000	140	- 80	0.996	24.8	2.5	--	--	1.15	28.0	3.5	--	35.7	--	

(1) Conventional 1.0 atm, 1,000° C.
(2) Parts pitch per 100 parts fiber by weight.
(3) Binder pitch coke yield of 50 weight percent.
(4) Carbonized fiber volume x 100 divided by compacted fiber volume.
(5) Not sampled.
(6) Typical of values obtained for pressure compacted-carbonized billets.

The next series of composites shown in Table 4 (Composite 120 through 130) were thin-walled cylinders fabricated by compacting fiber-pitch agglomerates produced with varying amounts of pitch binder. The binder content ranged from 40 to 90 pph and all composites were compacted at 5,000 psi. The carbonized fiber content increased slightly as the pitch binder content was decreased, while the percent of the theoretical fiber content remained almost constant. This trend indicates that the volume expansion during carbonization was about the same for each composite. The carbonized composite density is plotted in Figure 18 as a function of the pitch-binder contents. Although the curve shows a decrease in the carbonized density with a decrease in the pitch-binder content, the fiber content actually increased slightly, as reported in Table 4.

Figure 18. CARBONIZED DENSITY VARIATIONS WITH PITCH BINDER CONTENT.

For three composites listed in Table 4 (Composites 126, 127, and 128), the particle size of the pitch binder was varied. Relatively high compacted densities and fiber volumes were achieved in these composites, but the carbonized density and fiber volumes were generally lower than those experienced in the previous composite series. In addition, expansion during carbonization was considerably more than previously experienced, as indicated by the percentages of theoretical fiber volume.

Table 5 lists the dimensional measurements taken on the last two series of cylindrical composites just described from Table 4. Measurements taken

Table 5
ISOSTATICALLY COMPACTED CYLINDER DATA

Composite Number	Particulate Pitch Binder	Outside Diameter			Inside Diameter			Length			Weight			Geometric Density			Carbonized Bulk Density by Mercury Intrusion ⁽²⁾ (gms/cc)
	Screen Fraction Fiber Content ⁽¹⁾	Compacted (in)	Carbonized (in)	Change (%)	Compacted (in)	Carbonized (in)	Change (%)	Compacted (in)	Carbonized (in)	Change (%)	Compacted (gms)	Carbonized (gms)	Change (%)	Compacted (gms/cc)	Carbonized (gms/cc)	Change (%)	
126	- 60 + 70 mesh 90 pph	3.648	3.887	+ 6.6	2.748	2.400	- 12.7	10.894	11.258	+ 3.3	870	668	- 23.2	1.078	0.493	- 54.27	0.59
127	- 80 + 100 mesh 90 pph	3.592	3.880	+ 8.0	2.746	2.388	- 13.0	10.617	11.108	+ 4.6	847	646	- 23.7	1.156	0.483	- 58.22	0.59
128	- 100 mesh 90 pph	3.692	3.913	+ 6.0	2.745	2.424	- 11.7	10.026	10.399	+ 3.7	883	678	- 23.2	1.340	0.537	- 59.93	0.61
120	- 80 mesh 90 pph	3.709	3.761	+ 1.4	2.744	2.428	- 11.5	10.675	10.619	- 0.5	792	592	- 25.3	0.926	0.525	- 43.30	0.66
121	- 80 mesh 80 pph	3.583	3.670	+ 2.4	2.780	2.478	- 10.9	10.520	10.569	+ 0.5	671	504	- 24.9	0.970	0.506	- 47.84	0.62
122	- 80 mesh 70 pph	3.626	3.731	+ 2.9	2.751	2.454	- 10.8	10.508	10.619	+ 1.1	681	535	- 21.4	0.903	0.496	- 45.07	0.58
123	- 80 mesh 60 pph	3.488	3.594	+ 3.0	2.768	2.444	- 11.7	9.490	9.597	+ 1.1	469	377	- 19.6	0.853	0.440	- 48.42	0.56
131 ⁽³⁾	- 80 mesh 50 pph	3.730	3.960	+ 6.2	2.850	2.850	0	13.445	13.935	+ 3.6	911	909	- 0.2	0.909	0.671	- 26.18	0.60
130 ⁽³⁾	- 80 mesh 40 pph	3.800	4.035	+ 6.2	2.850	2.860	+ 0.3	13.445	13.915	+ 3.5	912	910	- 0.3	0.834	0.627	- 24.82	0.56

(1) Content of the particulate pitch binder is given in parts per hundred parts of fiber (pph).

(2) Bulk density determined from the volume occupied at a mercury pressure of 1.8 psia, which filled all open holes larger than 100 microns in diameter.

(3) All data for these composites is after holding for 24 hours at 95° C only, except density by mercury intrusion (last column) which is after carbonization.

from the compacted and machined composites are compared with measurements taken after carbonization. The large decrease in density of the three composites with varying binder particulate sizes is shown. It may be noted from Table 5 that the carbonized density by mercury intrusion is higher by ~ 0.1 gm/cc than the density computed from geometric dimensions. The measurements shown in Table 5 for the last two composites were taken after a 24-hour heat treatment at 95° C. It can be noted that some composite expansion was experienced in this low-temperature heat treatment. Of particular interest is the fact that the inside diameters remained about the same as in the compacted composites, with the shrinkage in this dimension taking place during the carbonization cycle.

The last series of composites in Table 4 (Composites 104 and 105) were compacted as conical frustums on graphite mandrels which varied from 2 to 8 inches in diameter and were approximately 18 inches in length. The fiber volume in the carbonized composites varied from 29.6 to 35.9 volume percent. This range of values compares to an average fiber volume of 35.7 percent for all the pressure-compacted, carbonized billets with 140 pph pitch binder, described previously.

Densification of these thin-walled composites was done by conventional liquid-pitch impregnation and carbonization, a pressure impregnation-carbonization cycle in the gas autoclave, and by isothermal and gradient^(7,8) methods of pyrolytic carbon deposition, as well as combinations of these techniques. Several of these composites were densified to 1.8 gms/cc, and others were densified to 1.5 gms/cc without a single composite failure due to composite anisotropy.

Two composite cylinders were fabricated by the vacuum-assisted spraying technique⁽⁵⁾ using the carbon fiber-pitch agglomerates with 25 pph particulate starch binder in a water slurry. After inert atmosphere carbonization, the composite density of each cylinder was 0.30 gm/cc.

The cylinders were three inches at the inside diameter by 10 inches in length and had a wall thickness of ~ 0.75 inch. The sprayed structure showed no evidence of layering, and the CTE ratio (radial to length) was 1.0 for each cylinder. The fiber volume was calculated to be 15 volume percent.

MATERIAL PROPERTY AND PROCESS EVALUATION

Billets

This report covers primarily the fabrication history and processing procedures for discontinuous carbon fiber composites; however, some limited

composite evaluation was necessary. Generally, the evaluations were during the process for improvement rather than a complete material characterization. Further material characterization has been done⁽⁹⁾ and mechanical properties determined from room temperature to 4,500°F. A future report may be issued⁽¹⁰⁾ showing further characterization data.

Five of the densified billet composites were examined for homogeneity by X-ray attenuation scanning.^(c) Each billet (~ 5.0 " D x 12" L) was examined using a 0.78-inch-diameter X-ray beam with 216 longitudinal scans per 180 degrees around the billet. This technique provided an approximately 0.043-inch circumferential overlap for each scan.

Three of the billets were above 1.65 gms/cc when examined. The maximum deviation from the mean density-thickness product was 3.2 percent and the average deviation was less than 2.0 percent.

One billet was scanned at a density of 1.5 gms/cc and again after densification to 1.77 gms/cc. The maximum deviation from the mean of the density-thickness product was reduced from 3.9 to 1.7 percent by the additional densification. For reference, variations from the mean of about 3 to 5 percent is the detectable limit for conventional film radiography. Thus, it appears that even the low-density material is relatively homogeneous.

Table 6 presents a tabulation of the average room-temperature properties of the densified billet composite material. The properties are given at the composite density shown in the table, which represents samples from four billets.

Figure 19 shows the microstructure of a billet (Composite 60) after the pressure carbonization-compaction processing. Somewhat more random and uniform fiber orientation can be observed in this microstructure when compared to that of Figure 16 of a sprayed and pressed carbon-fiber composite.

Table 7 provides the mercury porosimetry data needed to determine the homogeneity of a billet (Composite 59) after densification. The "core" sample shown in the table was removed from the center of a five-inch-diameter billet; the "edge" sample was removed from the outside of the billet. The bulk density of the core is shown to decrease by approximately 2.25 percent and the porosity to increase by about 2.3 volume percent. A graph of the

(c) Work performed by the Metals and Ceramics Division of the Oak Ridge National Laboratory.

(a) Axial

S-69-2896-5

(b) Radial

S-69-2896-6

Figure 19. COMPOSITE 60 (BILLET) AT A DENSITY OF 1.137 GMS/CC.

Table 6
AVERAGE ROOM-TEMPERATURE PROPERTIES OF FIBROUS CARBON-CARBON COMPOSITES

Property	Value	Material Density (gms/cc)
Compressive Strength (psi)	~ 12,000	1.77
Tensile Strength (psi)	~ 4,600	1.77
Flexural Strength (psi)	4,640 (14) ⁽¹⁾	1.74
Flexural Modulus (psi)	1.09×10^6 (14)	1.74
Strain to Failure, Flexural (%)	0.7 to 0.8 (14)	1.74
Sonic Modulus (psi)	2.5×10^6 (2)	1.74
Coefficient of Thermal Expansion, Axial and Radial (RT - 1,000° C)	$2.6 \times 10^{-6} \text{ } ^\circ \text{C}^{-1}$ (1)	1.74
Open Porosity (%)	15.9 10.7	1.74 1.87
Thermal Diffusivity (cm ² /sec)	1.1 to 1.6 (6)	1.74
Thermal Conductivity at 150° F (Btu/ft-sec-° F)	2.42×10^{-2} (1)	1.71

(1) Number of samples tested.

Table 7
HOMOGENEITY OF A DENSIFIED BILLET
(Composite 59)

	Core	Edge
Bulk Density (gms/cc)	1.74	1.78
Porosity (%)	15.9	13.6
Real Density (gms/cc)	2.07	2.06
Porosity Less Than 10 Microns in Diameter (%)	100.00	100.00
Surface Area (m ² /gm)	3.3	4.1
Volume-Average Equivalent Diameter (microns)	0.45	0.46

pore-size distribution of the two samples from the the billet is presented in Figure 20.

Typical pore-size distribution curves are seen in Figure 21 after various steps in the fabrication cycle. Shown are the distribution curves after the isostatic compaction of the pitch-fiber agglomerates, the pressure compaction-carbonization cycle, and two densification cycles. One-inch-thick discs of material from Composites 58 and 61 were densified by four pressure

Figure 20. PORE-SIZE DISTRIBUTION OF SAMPLES FROM THE CORE AND EDGE OF A BILLET. (Composite 59)

impregnation-carbonization cycles in the gas autoclave facility. The mercury porosimetry data after each cycle is summarized in Table 8, along with similar data for Composite 49 and an eight-inch-diameter by four-inch-long billet of ATJS graphite. The table also shows data for Composite Cylinder CY-77 which was fabricated by vibrating the fiber-pitch agglomerates into a cylindrical graphite mold and conventionally carbonized freestanding without pressure.

Figure 21. TYPICAL POROSITY DISTRIBUTION DURING A FABRICATION CYCLE.

Table 8
EFFECT OF PRESSURE IMPREGNATION-CARBONIZATION CYCLES ON POROSITY

After Cycle	Bulk Density (gms/cc)					Porosity (%)					Real Density (gms/cc)					Description of Composite
	0(1)	1	2	3	4	0	1	2	3	4	0	1	2	3	4	
Composite Number																
58	0.97	1.39	1.69	1.77	1.82	38.10	9.89	6.17	5.59	1.40	1.56	1.55	1.80	1.87	1.85	1-inch-thick disc
61	1.16	1.48	1.69	1.75	1.77	28.29	5.84	4.47	3.31	1.64	1.62	1.57	1.77	1.81	1.80	1-inch-thick disc
49	1.15	NS ⁽²⁾	NS	1.77	--	27.46	NS	NS	7.72	--	1.59	NS	NS	1.92	--	5-inch-diameter by 12-inch-long billet
CY-77	0.77 ⁽³⁾	NS	1.75	--	--	NS	NS	17.86	--	--	NS	NS	2.13	--	--	dry-cast fibrous cylinder, not compacted during conventional carbonization
ATJS	1.82 ⁽⁴⁾	NS	1.94	--	--	14.75	NS	8.13	--	--	2.13	NS	2.12	--	--	8-inch-diameter billet

(1) Starting material.

(2) No sample.

(3) Geometric density of conventionally densified composite.

(4) As purchased.

The data show that, although the disc from Composite 58 had a lower starting bulk density due to the lack of mechanical compaction, after two impregnation cycles the bulk density was the same as that achieved in the disc from Composite 61. The same is true with Composite CY-77 with a starting density of only 0.77 gm/cc; however, the amount of porosity in this composite is considerably larger after the two densification cycles. The large amount of open porosity in this composite is probably due to the large percentage of rather large diameter pores since the composite had no compaction at any stage in fabrication. A similar composite had 9.57 percent porosity after densification to a bulk density of 1.91 gms/cc. The ATJS billet is shown to contain 8.13 percent porosity at a density of 1.94 gms/cc after two pressure impregnation-carbonization cycles. Porosity distribution curves for each of the impregnations for the disc of Composite 58 can be seen in Figure 22. As might be predicted, the curve slope increases with increasing impregnation. Cracking occurred in all the one-inch-thick discs similar to that experienced in some five-inch-diameter billets, but it was not observed until after the fourth impregnation cycle. The maximum heat-treatment temperature of the discs between densification cycles was 1,500° C.

Figure 22. POROSITY DISTRIBUTION DURING IMPREGNATION-CARBONIZATION CYCLES OF COMPOSITE 58.

Thin-Walled Composites

A microstructure is shown in Figure 23 of a typical composite produced by isostatically pressing the fiber-pitch agglomerates. This structure, at a density of 0.70 gm/cc, was produced by a conventional carbonization cycle.

Figure 23. MICROSTRUCTURE OF A THIN-WALL COMPOSITE AFTER ISOSTATIC COMPACTION AND ATMOSPHERIC PRESSURE CARBONIZATION. (Density = 0.70 gm/cc; 100X)

The top photograph in Figure 23 is an axial view of the cylinder; in the bottom photograph, the cylinder is oriented radially or in the direction of the compacting pressure. A small amount of preferential fiber orientation is observed.

Table 9 lists the thermal expansion coefficients of four composites fabricated as thin-wall shells. The table shows the coefficients in the three orthogonal directions of the composite and the radial-to-axial ratio. Composites with the number "104" were tested after carbonization and before any densification. (The composite densities are listed in Table 4.) Composite 105C was densified to 1.10 gms/cc by conventional isothermal chemical vapor deposition

Table 9
THERMAL EXPANSION COEFFICIENTS OF THIN-WALL COMPOSITES

Composite Number ⁽¹⁾	Density (gms/cc)	CTE $\times 10^{-6}$ in/in/ $^{\circ}$ C			Ratio:Radial/Axial
		Radial	Circumferential	Axial	
104A (top)	0.653	2.50	2.30	2.17	1.15
104A (bottom)	0.660	2.76	2.22	2.47	1.12
104	0.729	2.12	1.98	1.89	1.12
105C	1.55	4.29	-	3.15	1.36

(1) All samples were carbonized at 1,000 $^{\circ}$ C.

of pyrolytic carbon from a carbonized density of 0.63 gm/cc. The composite was given a pressure impregnation-carbonization cycle to a density of 1.55 gms/cc, graphitized to 2,800 $^{\circ}$ C, and tested for expansivity. Data shows that the composites are nearly thermally isotropic. Continuous rings cut from Cylinder 105C after densification were tested for residual strain by cutting the ring. Slight opening of the ring was observed with the inside surface in low compression and the outside surface in low tension. This behavior is exactly opposite that experienced in the more anisotropic, sprayed carbon fiber composites^(4,5) where ring closure was experienced, with the inside surface in tension. The high incidence of composite failure during densification of the sprayed carbon-fiber composites was attributed to anisotropic shrinkage stresses due to preferential fiber orientation. These failures were always in the form of delaminations or radial cracks starting from the inside wall. Usually two cracks appeared 180 degrees from each other. The shape of the cracks indicated that the inside diameter was under tension stresses. Thermal expansivity coefficients were found to be a reliable measure of fiber orientation and a means of predicting if a composite would survive the densification process without delaminating or developing shrinkage stress cracks.

Thin-wall composites made by the isotropic agglomerate technique are near thermally isotropic and no composite has been broken by uneven shrinkage stresses in the densification cycle.

CONCLUSIONS AND RECOMMENDATIONS

The carbon fibers used in this work were highly anisotropic in shape and crystal orientation. Other fiber physical characteristics such as expansivity, conductivity, resistivity, and strength vary with the fiber axes as a result of this preferential crystal orientation. After consideration of these fiber characteristics, the known fibrous lay-up techniques and the certainty of composite shrinkage in the liquid resin densification procedure, it became apparent that a more random fiber composite would be desirable to reduce the residual stresses of fabrication. After successfully producing and densifying the high-fiber-content billets and shaped composites by the isotropic agglomerate process, it appears that residual stresses in these types of composites can be controlled if not eliminated. Because carbon-carbon composites of this nature serve in applications where high thermal shock resistance is needed, composite isotropy is desirable beyond that necessary to insure survival through the processing steps. Variations in the orthogonal values of the composite parameters⁽¹¹⁾ which determine the thermal shock factor would increase the probability of early mechanical failure of the composite. Preliminary data⁽⁹⁾ on the billets show the material to be increasingly shock resistant with increased temperature.

Experience with the billet fabrication technique has shown that the process is repeatable and should serve as a basis for improved carbon-carbon composites where uniformity of product, high fiber volume, and smaller unit grain size is desirable. Other than the cracking problem, no serious problems were encountered in the process or with the composites. The experimental billet composite showed that composites could be fabricated by these techniques with higher fiber contents (~ 47 vol %) should this characteristic be desirable. Thin-wall, shaped composites with uniform texture and low porosity were produced with medium fiber contents (30 vol %) and sufficient isotropicity to withstand the fast densification process.

Actually, the isotropic agglomerate fabrication approach lends itself to low as well as medium and high fiber contents by the use of hand-held spray equipment. The carbon fiber agglomerates were sprayed using a water slurry with 25 pph particulate starch^(5, 12) as binder. The resulting carbonized composite was isotropic, had a 0.31 gm/cc density, and contained 15 vol % fibers.

The rapid densification process using combined pressure impregnation-carbonization cycles was developed in the course of densification of these composites and represents a faster densification method than conventional procedures. This pressure technique also permits higher densities to be achieved and more uniform impregnation of a thick body. The method could also be used with other carbonizing resins and pitches.

Other types of carbon fibers could be used in the general fabrication process to produce composites with the enhancement of particular properties. Desirable additives could also be incorporated into the fabrication process for special product properties.

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