

FOUR ADVANCES IN CARBON-CARBON MATERIALS TECHNOLOGY

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ABSTRACT

Carbon-carbon composites are a specialty class of materials having many unique properties making these composites attractive for a variety of demanding engineering applications. Chief among these properties are exceptional retention of mechanical properties at temperatures as high as 4000°F, excellent creep resistance, and low density (1.6 - 1.8 g/cm³). Although carbon-carbon composites are currently in service in a variety of applications much development work remains to be accomplished before these materials can be considered to be fully mature, realizing their full potential. This paper describes four recent technology advances holding particular promise for overcoming current barriers to the wide-spread commercialization of carbon-carbon composites. These advances are: markedly improved interlaminar strengths (more than doubled) of 2-D composites achieved by whiskerization of the fabric reinforcing plies, simultaneously improved oxidation resistance and mechanical properties achieved by the incorporation of matrix-phase oxidation inhibitors based on carborane chemistry, improved oxidation resistance achieved by compositionally graded oxidation protective coatings, and markedly reduced processing times (hours as opposed to weeks or months) accomplished through a novel process of carbon infiltration and coatings deposition based on the use of liquid-phase precursor materials.

INTRODUCTION

Carbon-carbon (C-C) composites are a specialty class of materials having many unique properties making them attractive for a variety of demanding engineering applications. Similar to other high-performance composites, C-C composites consist of a continuous fiber reinforcement phase held within a matrix phase. Unlike other composites, however, both the reinforcement and matrix phases consist of essentially pure carbon. The unique properties of C-C composites derive from their all-carbon composition coupled with the unique properties of carbonaceous materials.

Desirable properties of C-C composites relate to their low density (1.6 - 1.8 g/cm³), high strength, and excellent retention of mechanical properties at very high temperatures. At typically encountered service pressures, carbon does not melt or soften, and it retains good strength and stiffness to temperatures as high as 4000°F [1-3]. Figure 1 illustrates the mechanical property advantages of C-C composites relative to other high-temperature materials [3,4]. Other useful engineering properties include good fatigue and shock resistance, low coefficient of thermal expansion, good frictional characteristics, zero moisture expansion, no outgassing, and insensitivity to natural space radiation. Carbon-carbon composite materials have also been demonstrated to have excellent biocompatibility and are of interest for dental and bone implant applications [5,6].

Because of these many desirable properties, C-C composite materials have found use in several applications and are under consideration for many more (fig. 2). Current applications include the thermal protection system for the wing leading edges and nose cap of the Space Shuttle, friction applications such as aircraft brake disks, and ablative applications such as missile nose tips and rocket nozzle throats. Selected additional potential applications are also illustrated in figure 2.

In spite of current successes, however, several technology issues are still in need of resolution to exploit fully the engineering potential of these materials. Among these technology issues are the susceptibility of C-C composites to oxidation, lower than desired interlaminar (IL) strengths of 2-directional (2-D) reinforcement constructions, long manufacturing times (and associated high cost), low strain to failure, and inadequate reproducibility in a production environment. Four recent advances holding particular promise for overcoming the first three of these technology barriers are described in the present paper. Specifically, these advances are whiskerization of the reinforcing fabric plies for improving IL properties, incorporation of molecular-level matrix-phase additives (carboranes) to improve both oxidation resistance and IL properties, compositionally graded oxidation-protective coatings, and markedly reduced processing times (hours as opposed to weeks or months) accomplished by a novel process of carbon infiltration and coatings deposition based on the use of liquid-phase precursor materials.

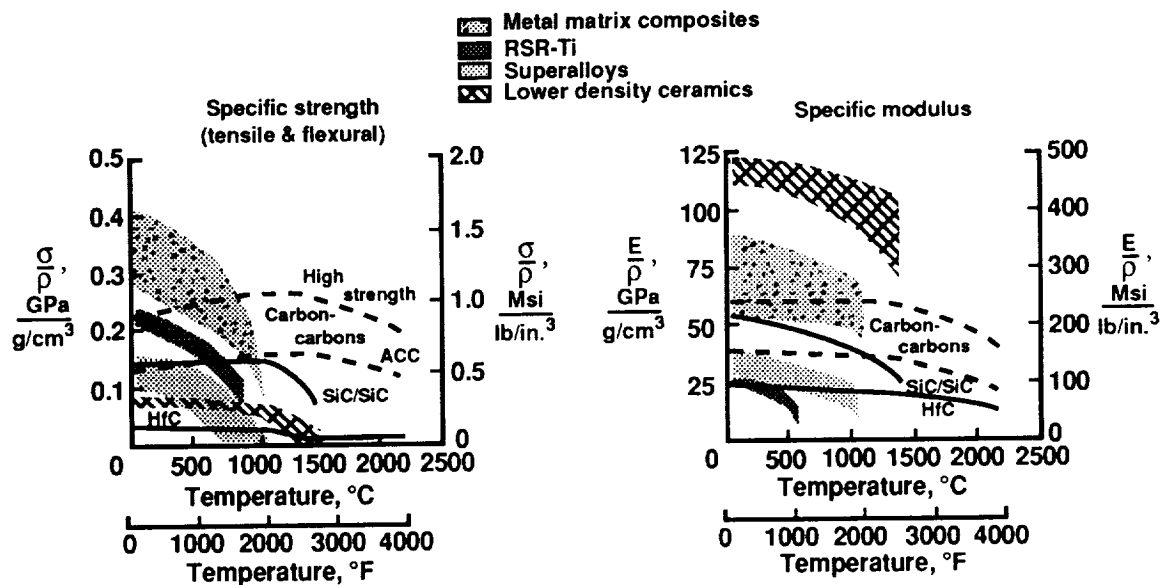


Figure 1. Specific strength and modulus for selected high-temperature materials [3,4].

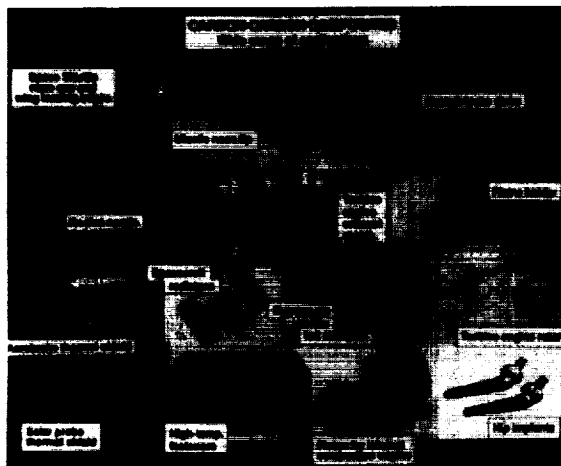


Figure 2. Current and projected applications for C-C composite materials.

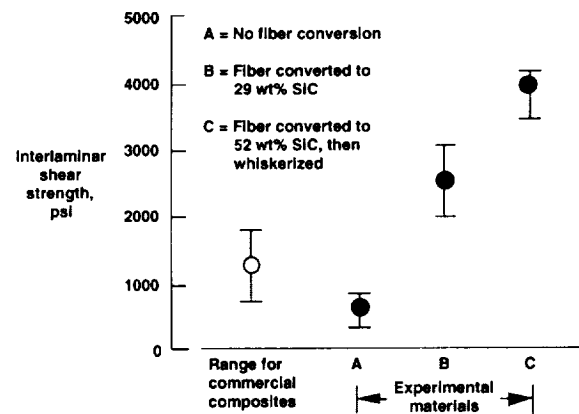


Figure 3. ILS strengths for composites with partially converted and whiskerized carbon fibers.

FABRIC PLY WHISKERIZATION

Thin structural C-C composites are typically reinforced with layers of woven fabric. This 2-D reinforcement construction affords good in-plane properties but IL properties are often lower than desired for many structural applications. Typically, interlaminar shear (ILS) strengths are on the order of 1.5 ksi and interlaminar tensile (ILT) strengths (cross-ply tension) less than 1 ksi. In some applications, the skillful structural designer can "design around" these low IL properties, but often they impose an undesirable design constraint.

Interlaminar properties in 2-D composites depend on the degree of fiber-matrix interaction, which, in turn, is controlled by various mechanical, chemical, and physical forces. Mechanical forces are influenced by fiber surface roughness, porosity, surface morphology and pore-filling capability of the carbon matrix. Chemical interactions depend on fiber surface activity and the nature of the functional groups on the carbon fiber surface. This chemical bonding can be increased to effect significant increases in the IL strengths of C-C composites, but too large an increase in bonding leads to brittle fracture and serious strength reductions [7-9]. Physical bonding is controlled by the wetting capabilities of the fiber and the Van der Waals interactions between the graphite crystallites on the fiber and matrix phases.

The use of through-the-thickness (3-directional, or 3-D) reinforcements is an obvious approach for increasing ILS strengths [10,11]. This 3-D reinforcement can be based on a variety of woven or braided constructions, or 2-D fabric plies stitched together. However, 3-D constructions are often boardy, difficult to densify, and have low fiber volume fractions (hence, low in-plane moduli). One attractive method being explored is to provide through-the-thickness reinforcement in just the right amount and at the micro-level by whiskers grown on the fibers in the reinforcing fabric plies of 2-D constructions. Although Fitzer [12] has shown that carbon whiskers grown on carbon fibers can significantly increase the ILS strengths in polymeric matrix composites, the application of whiskers in C-C composites is limited but encouraging [13]. In this section, initial results from a new whiskerization approach currently under development are described.



Figure 4. As-received T-300 fiber.



Figure 5. T-300 fibers partially converted to SiC; the carbon core has been oxidized away.

A chemical vapor reaction (CVR) process was developed to convert carbon fibers in a fabric ply either partially or completely to silicon carbide (SiC) as well as to grow strong, adherent SiC whiskers on the converted fibers. Figure 3 shows the very large (four-fold) increase in ILS strength achieved with this process. The range of ILS strengths for typical commercially available 2-D C-C composites is shown for comparison. (The relatively low value of 0.7 ksi for the experimental composite is due to the low density (1.39 g/cm^3) to which this composite was processed.) Figures 4-6 are scanning electron micrographs showing reinforcing fiber at the various stages in this whiskerization process. Figure 4 shows the as-received fibers (Amoco Performance Products T-300), and figure 5 the partially converted fiber (the carbon core has been oxidized away to enhance visualization). The increase in ILS strength observed for the partially converted but not whiskerized fiber is believed to be related, at least in



Figure 6. T-300 fibers partially converted and whiskerized.

part, to the significant increase in crenulation of the fiber surface following conversion. The fine network of whiskers produced by the CVR process is shown in figure 6; prospects for interlocking with adjacent plies is apparent. Certain advantages associated with this whiskerization include avoidance of brittle fracture because of too strong a fiber-matrix bond, controlled levels of whiskerization to provide optimum balance of properties, and flexibility to tailor the process for curved and complex shapes. An additional benefit is afforded by the SiC sheath, which sheath has been shown not to degrade fiber tensile properties but is expected to provide desirable oxidation resistance. Present research is exploring the range of processing conditions to optimize the CVR process and to establish the effect of ply whiskerization on a wide range of composite properties. Additional details on this process and property measurements are available in ref. [14].

CARBORANE-BASED MATRIX ADDITIVES

The primary approach for protecting C-C composites from oxidation at high temperatures is to apply an oxidation-protective coating. However, conventional coatings typically develop microcracks and often suffer from other defects such as thin areas, pinholes, etc., making additional protection of the C-C substrate desirable. This additional protection can be afforded by adding inhibitor materials to the matrix phase of the substrate during its fabrication. Previous studies have shown that glasses based on boria perform well in this role [15,16]. Specifically, the borate glasses block the cracks in the exterior silicon-based coatings and coat the pores within the C-C substrate to reduce its oxidation. McCormick [17] estimated a four-order-of-magnitude decrease in the oxidation rate for C-C composites protected with SiC coatings when the coating cracks were filled with boria as compared to those with unfilled cracks. Boria affords such protection because it has a desirably low viscosity between 1300°F and 2200°F, which varies only modestly over this temperature range; it is chemically compatible with SiC and carbon at moderate temperatures; and, because of its low surface energies, it wets carbon well [18], a necessary property for effective oxidation protection.

The drawback to most boria-based inhibitors is that they rely on the use of boron or boron carbide powders to provide the source of boron. These powders are added to the composite at the prepreg stage. It is difficult to infiltrate the powders within the tow bundles of the fabric and, due to their hardness, they can physically damage the fibers during the molding operation. In addition, the powders cannot be added to the infiltration resins. This leaves the carbon matrix applied last during processing as being the most exposed to oxidation. One attractive approach to avoiding the effects of particulates is to use molecular inhibitors.

Carborane (dicarbododecaborane) and its derivatives provide an excellent source of molecular boron. The carboranes are soluble in phenolic resin and furfural alcohol and can be used to produce oxidation-resistant carbons [19,20]. They also have been used in conjunction with polyarylacetylene-derived matrix systems for carbon-carbon composites, in low levels, as a graphitization aid [21]. However, their use as oxidation inhibitors in C-C composites has not been previously reported.

In this study, the effects of carborane and several of its derivatives were first investigated in phenolic resin chars. After down-selecting to a single carborane (vinyl-o-carborane), a series of composites was produced to determine its effectiveness in carbon-carbon composites and its influence on mechanical properties. Composites were also fabricated containing boron carbide particles as a reference inhibitor. The composites produced included uninhibited, inhibited with vinyl-o-carborane, inhibited with boron carbide, and inhibited with mixtures of the two. In addition, one-half of each composite panel was densified using vinyl-o-carborane in the densification resin whereas the other half was densified only with neat phenolic resin. Processing information and other details can be found in ref. [22].

Composite Mechanical Properties

The subpanels were machined into compression, ILT, and oxidation specimens. The ILT strengths of the composites are shown in figure 7. (In the figures and the following text the composites are designated by a two part nomenclature: the first half gives the amount and type of inhibitor added during initial pre-pregging and molding operations and the second half the amount and type of inhibitor added to the infiltration resin for densification; quantities are in percent, with "V-C" designating vinyl-o-carborane.) The none/none composite average strength of 550 psi is low for a phenolic densified material. However, the materials were only processed through three densifications (1.54 g/cm^3) instead of the normal four or five (1.65 g/cm^3) and this would give a lower ILT strength. Note that the use of inhibitors increases the ILT strength of the composites up to 35 percent for the 20 V-C/none composite. Even larger increases were observed when the vinyl-o-carborane was used in the infiltration resin, with a 50-percent increase between none/none and none/10 V-C. The greatest overall strength was in the 20 B₄C/10 V-C composite; it is postulated that the increase in strength is primarily due to the increased matrix density of these composites.

The compression strengths of the composites show a trend similar to the ILT strength although the strength increase is not as large (fig. 8). The 20 V-C/none composite once again has the highest strength (29.5 ksi) of the composites infiltrated with just the neat resin. Clearly, the presence of vinyl-o-carborane in the infiltrants raises the strength of the composites. The none/10 V-C composite is 30-percent stronger than the none/none composite. The 10 B₄C + 10 V-C/10V-C composite has the highest strength (33 ksi), a 35 percent improvement over the none/none composite. Since compression strength is influenced strongly by the matrix strength, it is not surprising that the trends are similar to the ILT strength results.

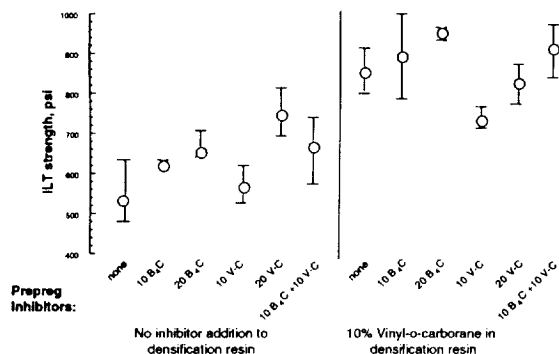


Figure 7. ILT strength of inhibited composites. Bars show total range of the data.

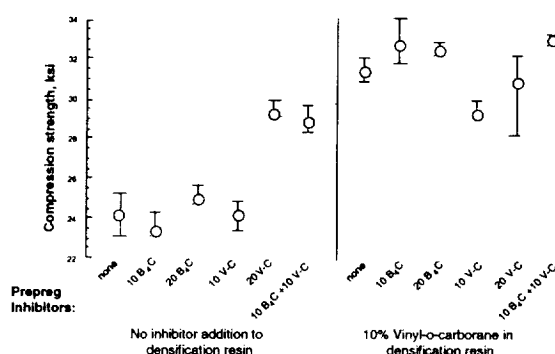


Figure 8. Compression strength of inhibited composites. Bars show total range of the data

Composite Oxidation Resistance

The oxidation performance of the composites was measured at 990°F and 1540°F at a pressure of 20 torr and a flow rate of 100 sccm in dry air, and the best two performing materials were also tested at 1271°F and 1820°F to enable a comparison with commercial materials over a range of temperatures. The oxidation results at 990°F are shown in figure 9. For the composites densified with neat phenolic resin, the 20 V-C/none composites had the best oxidation performance. The use of the vinyl-o-carborane in the densification resin gave improved results; even the none/10 V-C composite had the same oxidation performance as the 20 V-C /none composite. The use of prepreg inhibitors further decreased the oxidation rate, with the 20V-C/10 V-C composites (0.02 g/m²-min) showing one tenth the oxidation rate of the none/none composite. Comparison of the straight B₄C inhibited panels with the vinyl-o-carborane panels shows the advantages of the vinyl-o-carborane for oxidation protection.

The oxidation performance of the two best inhibited composites (20 V-C/10 V-C and 10 B₄C + 10 V-C/10 V-C) and the none/none composite was compared to commercially available inhibited C-C composites that were oxidized under identical conditions (fig. 10). At temperatures above 1700°F no advantage is gained by inhibitors since the rate of oxidation is controlled by diffusion rather than by chemical kinetics. As the temperature is lowered, the use of inhibitors becomes more important. The in-house composites perform comparably to the commercial systems down to temperatures of 1200°F, but below these temperatures the commercial systems have lower oxidation rates. The difference at low temperatures could be due to the overall higher loading of commercial inhibitors or the higher processing temperatures used in the commercial composites, since higher process temperatures tend to yield more oxidation resistant carbons, especially at lower temperatures [23].

The carborane systems reported here are at a very preliminary stage of development. Substantial work still needs to be done with respect to optimum loading and heat treatment. Based on the results to date, however, including the good mechanical properties achieved, this approach of using carboranes as molecular-level inhibitors is considered to have excellent potential for improving the oxidation resistance of structurally efficient C-C composites.

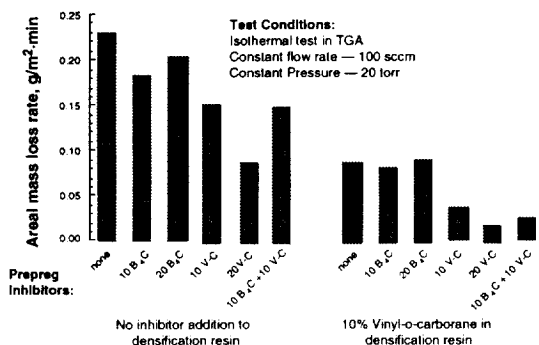


Figure 9. Oxidation rate of inhibited composites at 990°F.

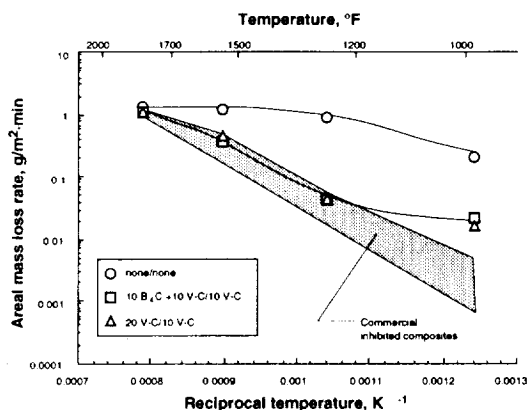


Figure 10. Comparison of oxidation rates for commercial and in-house inhibited composites.

FUNCTIONALLY GRADIENT COATINGS

As noted in the previous section, conventional oxidation-protective coatings typically develop microcracks, making substrate inhibitors desirable. Far preferable, however, would be totally crack-free coatings, but these are not easily produced because of the mismatch in coefficients of thermal expansion (CTE) of C-C substrates ($<1 \times 10^{-6}/^{\circ}\text{F}$) and typical coating materials, SiC ($2.8 \times 10^{-6}/^{\circ}\text{F}$), and silicon nitride ($1.7 \times 10^{-6}/^{\circ}\text{F}$). However, methods are presently emerging that hold particular hope for improving the situation and these methods are discussed in this section.

Two of the most widely used methods for coating C-C parts are chemical conversion of the outer layers of the part to SiC, and deposition of silicon-based coatings on the surface of the part by chemical vapor deposition (CVD). Both methods produce a relatively sharp substrate-coating interface and high thermal stresses develop at this interface. One way of minimizing these concentrated thermal stresses is to avoid formation of the sharp interface. This can be accomplished by effecting a gradual change in chemical composition and microstructure from the substrate to the coating. This deliberate grading of the coating to achieve a desired benefit falls within the rapidly growing technology area referred to as functionally gradient materials [24,25].

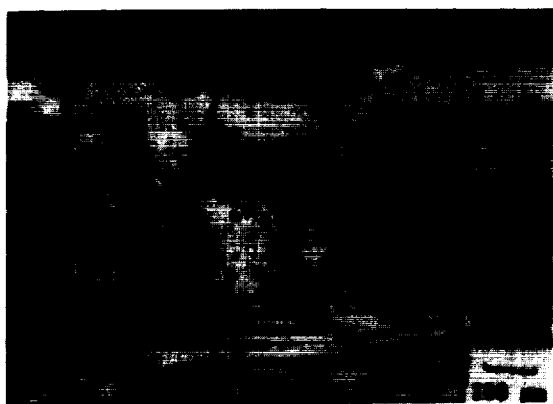


Figure 11. Two-layer CVD SiC, Si₃N₄ coating; after 20 oxidation cycles (see text).



Figure 12. Functionally gradient CVD C-SiC-Si₃N₄ coating; after 20 oxidation cycles (see text).

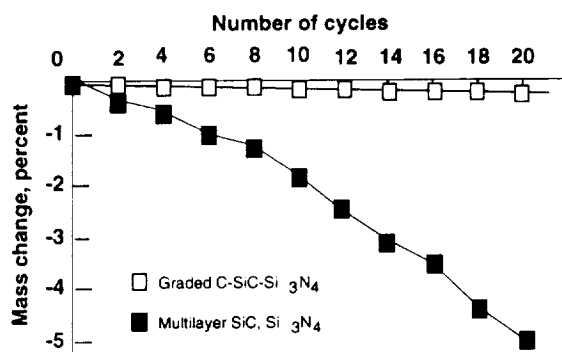


Figure 13. Oxidation results for coating systems in figs. 11 and 12.

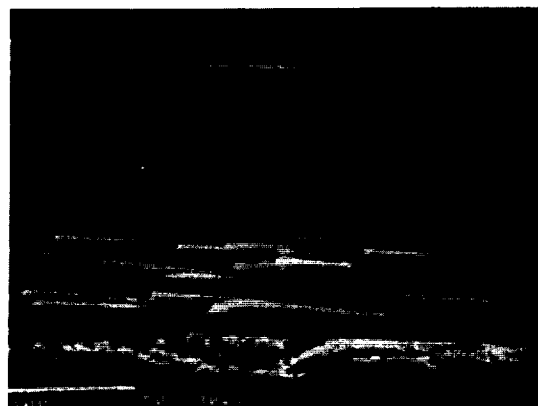


Figure 14. Functionally gradient CVR/CVD SiC-Si-Si₃N₄ coating.

Although the use of functionally gradient coatings on C-C composites is still very much in its infancy, these coatings are already showing high potential for reducing microcracks and achieving significant improvements in oxidation resistance. Figures 11 and 12 show sections of post-oxidized specimens illustrating the extent of improvements possible. Oxidation conditions consisted of 20 thermal cycles of: room temperature, rapid increase to 3000°F for 10 minutes, 1110°F for 20 minutes, and rapid decrease back to room temperature. This cycle, because of its high- and low-temperature holds and rapid temperature changes, constitutes a particularly severe test for coating

effectiveness. Figure 11 shows a section through a specimen protected with a state-of-the-art two-layer CVD-applied coating consisting of a SiC inner layer and silicon nitride (Si₃N₄) outer layer. Note the cracks in the coating and the large carbon loss within the substrate just below the coating. In contrast, figure 12 is for a similarly oxidatively exposed specimen (same substrate) protected with a functionally gradient CVD coating consisting of a layer of carbon-rich SiC adjacent to the substrate slowly graded to pure SiC and further graded to a pure Si₃N₄ outer layer. No cracks appear in the coating and no carbon loss occurred (the dark line in fig. 12 between the coating and the substrate is a polishing artifact and does not represent carbon loss or debonding). Mass change data for these materials as a function of the number of exposure cycles are shown in figure 13, clearly illustrating the much greater oxidation protection provided by the functionally gradient coating concept. Additional data and information concerning CVD functionally gradient coatings on C-C composites can be found in ref. [25].

Even more experimental are functionally gradient coatings produced by chemical conversion processes. A particularly convenient method here is the CVR process mentioned earlier. In this process, a reactive gas is brought into contact with the part to be coated, reacting with it and producing a layer of the new desired composition (e.g., SiC). The CVR process can be readily transitioned into a conventional CVD process by gradually changing the reactant gas composition and reactor conditions. This approach provides great flexibility for depositing coatings and grading compositions. Recently, C-C test materials have been successfully coated in the following manner: A thin outer layer of the C-C substrate was first converted to SiC by the CVR process; this SiC layer was then graded into a pure silicon (Si) overlayer using a combination of CVR and CVD. This was then followed by a controlled CVR conversion of the Si layer to Si₃N₄ giving a coating of the final composition: SiC graded to Si graded to Si₃N₄ (SiC-Si-Si₃N₄). Crack-free coatings have been successfully produced by this process (fig. 14) and preliminary oxidation tests are encouraging, but comparative oxidation data with conventional coatings are not yet available.

RAPID PROCESSING AND REDUCED COST

Compared to the costs for other more conventional engineering materials, C-C composites are relatively expensive. Depending on such factors as production volume, part complexity, geometric tolerances, property requirements, whether oxidatively protected, etc., costs can range from approximately \$80/lb to as much as \$15,000/lb. Table 1 [3,26] shows a cost comparison. Because of their relatively high cost, C-C composites have been employed only in those applications where their unique properties are necessary to meet demanding service requirements. One notable exception to this statement, however, relates to aircraft brake disks, where the durability and performance afforded by C-C composites have lead to their supplanting steel brakes in transport aircraft for economic reasons.

Material	Cost, \$/lb
Aluminum alloys ^a	2-3
Titanium alloys ^a	20-60
Superalloys ^a	15-70
Refractory metals ^a	25-250
Organic matrix composites ^b	40-750
Carbon/carbon composites ^b :	
- Brakes	80-120
- Nozzles, exit cones, nose cones	600-1500
- Shuttle RCC	6000
- Advanced, oxidatively protected (in non-production environment)	2000-15,000

^a Approximate ranges for simple product forms
^b Approximate ranges for a mix of product shapes

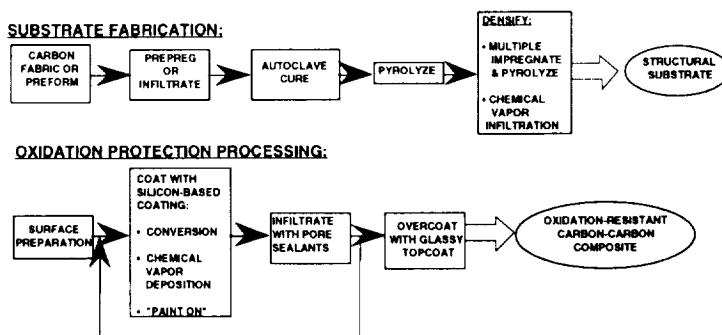


Table 1. Comparative costs of selected engineering materials [3,26].

Figure 15. Process diagram for C-C composites. After refs. [3,26].

For C-C composites to successfully compete with other engineering materials, their cost must be substantially reduced. These costs are strongly influenced by the lengthy processing times required by conventional fabrication methods, depicted schematically in figure 15. Although raw materials costs are generally relatively low (depending to a large extent on the particular fiber type selected), the large number of processing steps involved is responsible for long production times and, thus, high cost.

Referring to figure 15, one of the very time consuming steps in substrate fabrication is densification processing. Densification typically requires multiple cycles of resin or pitch impregnation, followed by cure, pyrolysis, and heat treatment. This cycle is repeated often four times and in some cases, many more. Another widely used densification method is that of chemical vapor infiltration (CVI), which is equally slow because of low mass transport rates in the

gas phase required to obtain full in-depth densification. To overcome these long processing times, a promising high-rate alternative densification process is being explored under a NASA contract with Lockheed Missiles and Space Company and their subcontractor Textron Specialty Materials [27]. This process is believed to offer the potential to reduce processing times from the order of weeks or months to only several hours.

The basic features of this high-rate densification process are described schematically in figure 16. An inductively heated porous carbon preform (the part to be densified) is immersed in a high-carbon-yield hydrocarbon liquid and the part is raised to a temperature sufficiently high so that the hydrocarbon liquid thermally cracks, depositing carbon within the porous part. By appropriate temperature control, the part can be densified from the interior to the surface, thus avoiding the development of a surface "skin," often encountered with gas-phase CVI. The heating also causes vigorous agitation of the liquid hydrocarbon, promoting excellent mass transport. By this process, thin-walled 1.5-in. dia. by 7-in. long tubes have been densified in as little as 4 hours (fig. 17). Densities and mechanical properties achieved are excellent: 1.75 g/cm^3 , with 28 ksi compression strength and 46 Msi compression modulus. In addition to tubes, other generic structural shapes including flat, curved, and stiffened structures are being investigated to explore the limits of the process. To date, flat panels having dimensions up to 6 in. by 12 in. have also been successfully densified.

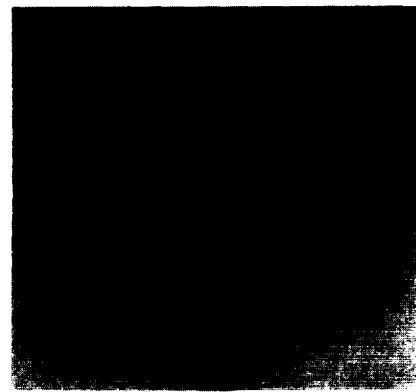
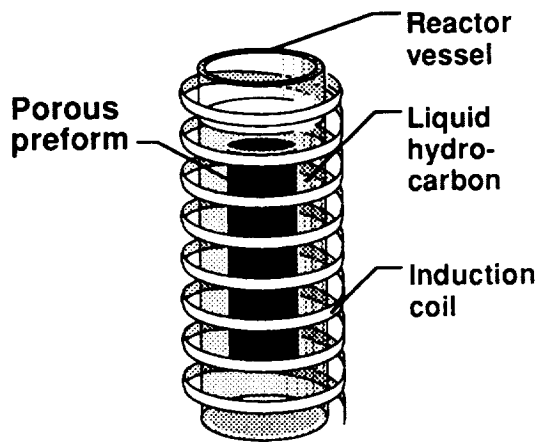


Figure 16. Schematic of rapid liquid-phase process for densification and applying coatings.

Figure 17. Carbon-carbon tubes densified in 4 hours.

Referring once again to figure 15, another step contributing significantly to overall part fabrication time is coating application, generally for oxidation protection. Two coating methods discussed previously are chemical conversion of the outer layers of the C-C part to SiC, and CVD of various silicon-based coatings and other interlayer materials. Yet a third method involves ceramic-based slurries which are painted on and fired in multiple steps. All these coating approaches are complex and time consuming. A modification of the rapid liquid-phase densification process described above holds significant promise for applying coatings at a much increased rate. This modification depends on the availability of suitable metal-organic liquid precursors which, when thermally decomposed, deposit a coating of the desired composition, whether it be SiC, hafnium carbide, or other desired chemistry. In addition to the high rates at which coatings can be applied, an additional advantage of this approach is that, at least conceptually, the hydrocarbon liquid employed for densification processing can gradually be replaced with the metal-organic liquid precursor for coating deposition. This approach enables processing to be accomplished in the same reactor without having to remove or handle the part, and also enables the coating to be graded in composition, thus eliminating sharp interfaces and reducing thermal stresses. To date, several organochlorosilane compounds have been identified and experiments run successfully demonstrating that SiC coatings can be deposited with compositions ranging from silicon-rich to stoichiometric to carbon-rich. Coating deposition rates approaching 1 mil/hr have been shown to be possible. Detailed technical discussions of the process are available in refs. [27,28].

Although process feasibility has been demonstrated both for densifying C-C components and for depositing coatings, considerable development work remains before the process can be considered economically viable and ready for factory production. One key technology issue needing resolution is improving uniformity of density. Scale-up and reproducibility issues must also be addressed, and the feasibility for continuous processing, especially for tubes, is worth pursuing. Studies are also planned to explore the feasibility of depositing coatings other than SiC—in particular, hafnium carbide and silicon. Nevertheless, no matter how technically viable the process, the ultimate measure of success will be cost savings relative to traditional methods. Once the process moves out of the

experimental stage and process parameters are better established, an economic analysis of the process will be conducted to establish its cost benefits relative to traditional current processes.

SUMMARIZING REMARKS

Current primary applications for carbon-carbon composites are aircraft brakes, missile nose tips, rocket nozzles and exit cones, and the nose cap and wing leading edge of the Space Shuttle Orbiter. Numerous additional engineering applications are envisioned for this material, however, provided important technology issues relating to improved oxidation resistance, increased interlaminar strengths, cost effective manufacturing, and production reproducibility are properly addressed. The authors are confident that many of these barriers will be overcome, and that this unique material will be exploited to an increasing extent in the future.

The present paper has described four recent technology advances that contribute to overcoming some of these barriers. These include fabric ply whiskerization for increased interlaminar properties, carborane-based molecular level inhibitors providing both improved oxidation resistance and interlaminar properties, functionally gradient coatings to minimize coating cracks and improve oxidation resistance, and a novel liquid-phase process for carbon infiltration and coatings deposition holding considerable promise for reducing fabrication costs. Clearly, extensive research and development remains yet to be accomplished in these areas, and others as well. However, these advances afford the optimism that continued improvements can and will be made in those key technology areas that advance the maturity of this class of materials and provide a sound basis for design engineers to include them more frequently in their range of materials options.

REFERENCES

1. Fitzer, E.; and Heym, M.: High-Temperature Mechanical Properties of Carbon and Graphite—A Review. *High Temperature-High Pressure*, Vol. 10, 1978, pp. 29-66.
2. Fitzer, E.: Carbon-Based Composites. *J. Chim. Phys.-Chim. Biol.*, Vol. 81, 1984, pp. 717-733.
3. Maahs, Howard G.: Carbon-Carbon Composites. Chapter 16 in *Ceramics and Ceramic Matrix Composites*, S. R. Levine, ed., in *Flight-Vehicle Materials, Structures and Dynamics—Assessment and Future Directions*, Vol. 3, A. K. Noor and S. L. Venneri, eds., American Society of Mechanical Engineers, New York, 1992, pp. 307-332.
4. Stein, B. A.; Maahs, H. G.; and Brewer, W. D.: Airframe Materials for Hypersonic Vehicles. *Metal Matrix, Carbon, and Ceramic Composites 1987*, J. D. Buckley, ed.; NASA CP-2482, 1987, pp. 1-24.
5. Louis, Jean-Paul: Immediate Complete Prostheses With Fibrous Carbon Artificial Roots. *Am. J. Dentistry.*, Vol. 3, No. 3, 1990, pp. 125-132.
6. Adams, D.; and Williams, D. F.: The Response of Bone to Carbon-Carbon Composites. *Biomaterials*, Vol. 5, 1984, pp. 59-64.
7. Kowbel, W.; and Shan, S. H.: The Mechanism of Fiber-Matrix Interactions in C-C Composites. *Carbon*, Vol. 28, 1990, pp. 287-299.
8. Maahs, H. G.; and Yamaki, Y. R.: Effects of Fiber Surface Treatment and Sizing on Fiber-Matrix Interactions in Carbon-Carbon Composites. 16th Conference on Metal Matrix, Carbon, and Ceramic Matrix Composites. NASA CP-3175, 1992, pp. 305-318.
9. Ransone, P. O.; and Spivack, B. D.: Effect of Fabric Thickness, Fiber Type, and Densification Process on Mechanical Properties of Thin 2-D Carbon-Carbon Composites. Presented at the 17th Annual Conference on Composites, Materials, and Structures. United States Advanced Ceramics Association, Cocoa Beach, FL, Jan. 10-15, 1993. (To appear in NASA CP)
10. Ransone, P. O.; Spivack, Bruce D.; and Maahs, H. G.: Mechanical Properties of Thin 3-D Reinforced Carbon-Carbon Composites Densified with Different Matrices. The 16th Annual Conference on Composites, Materials, and Structures. NASA CP-3175, 1992, pp. 347-366.
11. Yamaki, Y. R.; Ransone, P. O.; and Maahs, H. G.: Investigation of Stitching as a Method of Interlaminar Reinforcement in Thin Carbon-Carbon Composites. The 16th Conference on Metal Matrix, Carbon, and Ceramic Matrix Composites. NASA CP-3175, 1992, pp. 367-386.
12. Fitzer, E.: R-F Sputtered SiC Coatings on Carbon Fibers. *Thin Solid Films*, Vol. 170, 1987, pp. 93-108.
13. Munoz, C.; Ngai, T. T.; and Shyne, J. J.: Shear Property Enhancement of 2D Carbon-Carbon (C/C) Composites. Presented at the 15th Annual Conference on Composite Materials and Structures. United States Advanced Ceramics Association, Cocoa Beach, FL, January 16-18, 1991. (Unpublished)

14. Withers, J. C.: The Optimization of an Advanced Carbon-Carbon Composite with Improved Interlaminar and Flexure Properties and Oxidation Resistance. Materials and Electrochemical Research (MER) Corporation. Final report for NASA Contract NAS1-19528, Oct. 1992.
15. McKee, D. W.: Oxidation Behavior and Protection of Carbon/Carbon Composites. *Carbon*, Vol. 25, No. 4, 1987, pp. 551-557.
16. Ehrburger, P.; Baranne, P.; and Lahaye, J.: Inhibition of the Oxidation of Carbon-Carbon Composites by Boron Oxide. *Carbon*, Vol. 24, No. 4, 1986, pp. 495-499.
17. McCormick, E. Scott: Factors Influencing the Oxidation Performance of Carbon-Carbon Composites. Proceedings—Air Force Workshop on Oxidation-Resistant Carbon-Carbon Composites, AFWAL-TR-88-4071, U.S. Air Force, Mar. 1988, pp. 113-129.
18. Gray, Paul E.; and Sheehan, James E.: Oxidation Protected Carbon-Carbon Composite Development. Metal Matrix, Carbon, and Ceramic Matrix Composites 1986, Proceedings of a Joint NASA/DOD Conference, Cocoa Beach, FL, Jan. 21-24, 1986, NASA CP-2445, 1986, pp. 197-209.
19. Baicher, L. A.; Valetskil, P. M.; Vinogradova, S. V.; Zlatkis, A. M.; and Korshak, V. V.: Influence of Carborane-Containing Compounds on the Oxidative Stability of Products of Pyrolysis of Network Polymers. *Polymer Science U.S.S.R.*, Vol. 23, No. 10, 1981, pp. 2453-2459. Originally appeared in *Vysokomol. Soedin., Ser A.*, 23(10), 2257-62, 1981.
20. Chen, Philip S. H.; and Stevens, Ward C.: Novel Molecular Sources for Dispersing Boron in Carbon-Carbon Composites. AFSOR Report FQ8671-9101273, December, 1991.
21. Zaldivar, R. J.; Kobayashi, R. W.; and Rellick, G. S.: Carborane-Catalyzed Graphitization in Polyarylacetylene-Derived Carbon-Carbon Composites. *Carbon*, Vol. 29, No. 8, 1991, pp. 1145-1153.
22. Vaughn, Wallace. L.; and Petty, John T.: Carborane Based Inhibitors for Carbon-Carbon Composites. Proceedings of the 17th Annual Conference on Composites, Materials, and Structures (Restricted Sessions), NASA/DOD Conference, Cocoa Beach, FL, Jan. 10-15, 1993, Paper No. 84, to be published as NASA CP.
23. Ragan, S.; and Emmerson, G. T.: The Effect of Heat-treatment Temperature Upon the Properties of Matrix-Inhibited Carbon-Carbon Composites. *Carbon*, Vol. 30, No. 3, 1992, pp. 339-344.
24. Hirai, T.: Design of SiC-C Functionally Gradient Material and Its Preparation by Chemical Vapor Deposition. Proceedings of Japan Ceramic Soc. in Tohoku-Hokkaido Branch, 1987, p.37-48.
25. Kowbel, W.: The Mechanism of Oxidation of Oxidation Protection of C-C Composites Coated With Graded Codeposited Carbides and Nitrides. *Ceramic Transactions*, Vol. 34, 1993, pp. 237-244.
26. National Center for Advanced Technologies (NCAT): Carbon-Carbon Composites, in National Advanced Composites Strategic Plan, Symposium Draft. National Center for Advanced Technologies (NCAT), 1250 Eye Street, N.W., Washington DC, December 1990, pp. 253-301.
27. Finley, J. W.; Klavins, A.; Baker, D. F.; Carroll, T.; Thurston, G.; and O'Connor, T.: Efficient Processing of Carbon-Carbon Composites. Lockheed Missiles & Space Company Report LMSC/F109055, for the period March-Dec. 1992. To appear as NASA Contractor Report.
28. Thurston, G. S.; Carroll, T. J.; and Rawal, S. P.: Advanced Understanding of the Rapid Densification RDTM Process. Final Report to Office of Naval Research for the Period July 1991 to Sept. 1992, contract #N00014-91-C-0285, Dec. 1992.