Fabrication Routes for Continuous Fiber–Reinforced Ceramic Composites (CFCC)

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November 1998

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ABSTRACT

The primary approaches used for fabrication of continuous fiber-reinforced ceramic composite (CFCC) components have been reviewed. The CFCC fabrication issues related to fiber, interface, and matrix have been analyzed. The capabilities, advantages and limitations of the five matrix-infiltration routes have been compared and discussed. Today, the best fabrication route for the CFCC end-user is not clear and compromises need to be made depending on the details of the CFCC application. However, with time, this problem should be reduced as research continues to develop advanced CFCC constituents and fabrication routes.

I. INTRODUCTION

The microstructure of a ceramic matrix composite (CMC) consists of distinct ceramic phases imbedded within a host ceramic matrix material. The advantage of forming such a multiphase system is that by the judicious selection of the ceramic constituent compositions, sizes, geometric forms, and volume fractions, the CMC can display technically desirable properties which are better than those of competing state-of-the-art materials. For instance, one area of current high interest for CMC is that of structural application in hot-section components of advanced propulsion and power systems. Here CMC have the capability for operating at higher temperatures than metallic alloys and thus can provide significant system payoff in terms of efficiency and performance. For these applications, which typically extend well above 1000 °C, CMC can also outperform other high-temperature structural materials such as carbon-carbon composites and monolithic ceramics. For example, if the CMC constituents are chosen to be oxides or silicon-based compounds, CMC service lives in oxidizing environments will be much longer than those of carbon-carbon composites. Also, if the CMC interfacial phases are designed to be weak enough to deflect and inhibit the growth of strength-limiting matrix cracks generated during system operation, CMC will display higher fracture toughness and consequently longer service life than competing monolithic ceramics. This strength and toughness advantage over monolithic ceramics is further enhanced if one of the composite phases consists of strong continuous-length fibers which act to maintain material integrity by bridging cracks that form in the host matrix (ref. 1). Also, as will be discussed here, the use of continuous fiber reinforcement with small diameter permits the formation of woven fiber structures which can then be infiltrated with matrix material to fabricate complex composite shapes much larger in volume than currently available for monolithic ceramics. It is these structural, shape, and size advantages that have effectively focused the majority of current CMC developmental efforts toward continuous fiber-reinforced ceramic composites (CFCC).

Although CFCC can out-perform other high-temperature structural materials, there are other process-related requirements that must be met before CFCC gain full technical and commercial acceptance. Prime among these is a fabrication route that will yield a composite microstructure that displays optimum, tailorable, and reproducible performance. *Optimum* performance typically implies that the fabrication route should not only maintain the structural properties of the fiber and matrix phases, which are generally strong, tough, and creep-resistant, but also allow these phases to interact in a synergistic manner. *Tailorable* performance implies that the fabrication route should allow the constituent phases to be assembled in versatile configurations so that the CFCC microstructure can be designed to best meet the structural, shape, and volume requirements for a wide range of components. *Reproducible* performance generally implies that the fabrication route should allow the interfacial and matrix phases to be well controlled and to be formed uniformly within a part and consistently from part to part. In addition to these microstructural requirements, the fabrication route must be able to make complex-shaped components in a *cost-effective* manner, that is, at a process cost competitive with those of other high-temperature structural materials.

Today, there exists many CFCC fabrication routes, but only _five_ general approaches have achieved to a large degree the performance and fabrication requirements needed to produce a wide variety of complex shaped components with microstructures capable of structural operation for long times at high temperatures. All of these five approaches are similar in that they first assemble small-diameter continuous-length fibers into configurations or architectures that have been designed to best meet both the performance and shape requirements of the final CFCC parts. After using various methods for applying interfacial coatings on the fibers, these particular approaches then form the constituent phases of the host matrix by *fluid infiltration*; that is, by gas, slurry, or liquid infiltration or combinations of these. Using nomenclature based on the matrix infiltration process, these general fabrication approaches include: (1) Chemical Vapor Infiltration (CVI), (2) CVI plus Directed Metal Oxidation (CDMO), (3) CVI plus Slurry (or polymer) infiltration plus Liquid Metal infiltration (CSLM), (4) Polymer (or sol gel) Infiltration and Pyrolysis (PIP), and (5) PIP plus Liquid Metal Infiltration (PLM). Table I lists these fabrication routes plus typical fiber lay-up approaches (see section II) and matrix compositions (see Section III) used by some of the current CFCC fabrication vendors. The use of continuous-length fiber architectures not only optimizes the strength and toughness of the composite, but also permits the formation of near-net shaped parts in a wide range of sizes, thereby minimizing the need for costly machining. Thus, in comparison to other fabrication approaches, these routes have important advantages in terms of CFCC component versatility and cost. However, the five routes do differ in the particular process steps that they employ, which can have a significant effect on the performance, tailorability, reproducibility, and cost of the CFCC components.

The scope of this paper is to examine in general detail the physical, chemical, and mechanical aspects of the five general matrix-infiltration routes for CFCC fabrication listed in table I. For each route, emphasis is placed on understanding issues related to its current ability for achieving low-cost complex-shaped CFCC parts with microstructures that display good performance, tailorability, and reproducibility. Because of the high technical payoff, these issues are examined in particular for CFCC application in advanced engineering systems that will operate at high temperature under aggressive environments. Thus emphasis will be placed on obtaining strong and creep-resistant fiber and matrix phases that are stable to temperatures well above 1000 °C. To form a basis for this discussion, Section II describes the general steps that are currently being employed and the key issues that need to be considered for a good matrix infiltration route. This not only includes matrix formation, but also the very important initial steps of fiber assembly and interface coating deposition. In Section III, the five general fabrication routes are then examined in terms of the process steps used for matrix infiltration around the fibers and interfaces. Besides fabrication details, advantages and

limitations inherent in each route are discussed. Finally, in Section IV, the current status of the various processing routes in achieving the general fabrication goals of performance, tailorability, reproducibility, and cost effectiveness are summarized and compared.

II. CFCC FABRICATION ISSUES

For judging the technical capabilities of various CFCC fabrication routes, focus is typically placed on the final steps of matrix formation. However, the performance and technical viability of the CFCC fabrication route also depend strongly on the initial steps of fiber architecture formation and interface coating deposition. Indeed, these initial steps can impact and limit the matrix formation steps so that CFCC fabrication is a complex integral process that requires optimization at all steps. The purpose of this section is to examine in a general manner these key fabrication steps so that one can better understand their effects on the microstructure and properties of CFCC components obtained from the five matrix-infiltration routes.

II.1. Fiber-Related Issues

Key to a CFCC fabrication route for producing complex fiber architectures and composite shapes is the ability of the reinforcing fiber to be shaped with bend radii as small as possible. However, in bending a fiber with diameter D, the minimum radius, R_{min}, that can be achieved without fiber fracture is given by $R_{min} = ED/2\sigma$ where E and σ are the fiber modulus and bend strength, respectively. For commercially available ceramic fibers suitable for long-term high-temperature use in oxidizing environments (SiC and Al_2O_3-based compositions), modulus values typically are ~400 GPa and bend and tensile strengths do not generally exceed ~4 GPa due to process-related flaws (ref. 2). Thus, the practical limit for shaping these fibers is $R_{min} \approx 50D$, indicating a strong need to utilize fibers with the smallest diameters available to allow the most versatility in shape forming. Additional fabrication advantages of the smallest diameter fibers are their ability to reinforce CFCC parts with thin sections and to be easily assembled and shaped using conventional weaving and braiding processes (ref. 3). In order that these processes form complex architectures, it has been empirically determined that the fibers should display R_{min} values no >~2 mm. This in turn implies that CFCC fabrication routes should only use commercial fibers with diameters <~40 μm if their strengths are consistently near 4 GPa, and <~20 μm if their strengths are consistently near 2 GPa.

Fortunately, there exists today a variety of commercially available SiC- and Al_2O_3-based fibers that have diameters in the range 10 to 20 μm and tensile strengths equal or greater than 2 GPa (ref. 2). These are typically made from Si-based polymers or oxide slurries, respectively, which are formed in the "green" state by the continuous spinning of multifilament tows with fiber counts of ~500. The "green" tows are then passed through high temperature furnaces to form the final ceramic fiber product. For small diameter fibers, the use of multifilament tows has the advantage of reducing the risk of fiber breakage during handling in the weak "green" state or in subsequent fiber architecture formation in the stronger ceramic state. It also has the advantage of reducing fiber process costs by allowing a high mass-throughput during the production processes. In this last regard, it would appear desirable to spin fiber counts much higher than ~500 as is the typical case with carbon-based fiber tows. However, as will be discussed, higher filament counts can inhibit subsequent CFCC fabrication steps in which it is desirable to infiltrate interfacial and matrix materials uniformly around all fibers within the tow.

Currently all matrix infiltration routes to structural CFCC parts begin their production by the use of small diameter fibers in multifilament tow form. Generally fiber architectures are employed that are as dense as possible in order to maximize the fiber volume fraction and load-carrying ability of the composite if the matrix should crack. To form these architectures, two different lay-up approaches are typically chosen: pre-preg and preform. In one version of the pre-preg approach (pre-preg A), the tows are treated in a manner similar to that typically used for commercial formation of filament wound polymer matrix composites. That is, after the individual tows and their fibers are pre-coated with interfacial coatings (to be discussed), the tows are laid up in unidirectional sheets or mattes that are then impregnated with a matrix-precursor resin to form pre-pregged plies. These plies are then laid up at selected angles to each other and pressed together in an autoclave to form the final CFCC shape as a two-dimensional cross-plied laminate. The "green" laminate is then subjected to various infiltration and high-temperature treatment methods to form the ceramic matrix around the cross-plied fiber architecture.

Another version of the ***pre-preg approach*** route (pre-preg B) is to have the tows woven into a two-dimensional fabric cloth using weave patterns suitable for the CFCC application. Figure 1 shows an example of a two-dimensional fabric in which the tows have been woven in two directions (0 and 90°) with a five-harness satin weave pattern. After fabric formation, the interface coatings are applied in a separate step. The coated fabric is then impregnated with a matrix-precursor resin, laid up as plies into the final CFCC shape, subjected to autoclave processing to form a green two-dimensional woven laminate, and processed further to form the ceramic matrix. Thus the pre-preg A and B approaches differ primarily in cross-plied versus woven 2-D fiber architecture and in the manner in which the fiber interfacial coatings are applied.

For the ***preform approach*** to fiber lay-up, the multifilament tows are first formed into two or three-dimensional fiber architectures using weaving or braiding. One common method (preform A) is to pre-cut uncoated or dry fabric plies and stack the plies into a two-dimensional preform which is then placed into tooling that has the shape of the final CMC part. The stacked fabric could be held together dry or with a fugitive binder. The tooling typically has predrilled holes which allow one or more interfacial coatings to be subsequently applied by chemical vapor infiltration on all fibers in the preform. The matrix material is then infiltrated into the porosity remaining in the preform. As discussed in Section III, this can be accomplished by gas, liquid, or slurry infiltration or by any combination of these methods. An example of a matrix infiltrated 8-ply 0/90° SiC/SiC CFCC produced by the preform A approach is shown in by the micrograph in figure 2.

A second preform approach (preform B) is to avoid the need for tooling by using weaving or braiding approaches which shape the fibers into a near-net three-dimensional shape of the final CMC part. Such architecture may be needed, for example, to assure fiber reinforcement in many directions because of the structural requirements of the CFCC part. This preform can then be infiltrated with interface and matrix material as just described. A third possible preform approach is to first coat individual tows as in pre-preg A and then form the preform by weaving or braiding processes that minimize the risk of damaging or degrading the coating. This approach is rarely practiced because it generally results in low-density fiber architectures or in architectures with a high incidence of interfacial coating damage. Thus the currently viable preform approaches differ from the pre-preg approaches in that the interfacial fiber coatings are applied through a denser, more complex network of fibers, but the available fiber architectures can be considerably more versatile.

II.2. Interface-Related Issues

The interfacial coating phases or *interphases* between the fiber and matrix must provide a variety of functions if CFCC are to meet their performance and fabrication requirements. Prime among these is the ability to provide a weak fiber-matrix interfacial bond after CFCC fabrication and during service, even in the presence of matrix cracks and aggressive environments. In addition, the interphase composition and formation processes should be protective and not degrading to the fiber properties, again either during CFCC fabrication or service. It is also desirable that the interphase performs its functions in a consistent and reproducible manner throughout the CFCC microstructure so that performance is the same for all similar CFCC parts. For some thermostructural applications, it may also be desirable that the interphase provides high thermal conductivity to reduce thermal stresses within the CFCC. Finally, the interphase formation processes should be cost effective.

Today, essentially all matrix-infiltration routes using nonoxide fibers are employing interfacial fiber coatings based on carbon or on boron nitride with thickness typically ranging from 0.1 to 1.0 μm. These compositions have demonstrated the ability to provide weak interfacial fiber-matrix bonds for crack deflection and also to be nondegrading to fiber properties. However, for stability in aggressive environments, both are lacking in terms of providing long CFCC lives in the presence of matrix cracks. Research efforts are ongoing to find methods to eliminate this deficiency by examining new coating concepts based on multilayers, alternate compositions, and/or weak porous phases (refs. 4 to 8).

Nevertheless, the current use of environmentally unstable carbon and BN interphases generally necessitates the application of protective over-coatings on these materials. The typical approach is to use CVI to provide thin SiC coatings (~0.5 to 5 μm) over the carbon or BN coatings. Thus, in effect, each fiber in a tow consists of a single-fiber microcomposite with a thin C or BN interface and a thin SiC over-coating which then becomes part of the matrix microstructure (fig. 3). These over-coatings are generally chosen to protect the interfacial coatings and fibers from reactions with the other matrix phases that are introduced during CFCC fabrication. Since the C and BN can be affected by long exposures to ambient environments, it is important that the over-coating be deposited as soon as possible on the interfacial coatings, preferably before exposure to the ambient. The over-coatings may also act to protect the fibers and interphases from aggressive gases such as oxygen and water vapor during CFCC service. In this regard, the interphases and over-coatings are sometimes repeated in multilayer concepts in order to provide environmental protection layers in the presence of service-generated matrix cracks (refs. 4, 7 and 8).

From the above discussion, it should be clear that an important requirement for a good CFCC fabrication route is to provide reliable and uniform interphase coatings and over-coatings throughout the CMC microstructure. All of the five general matrix-infiltration routes used today provide both types of coatings by CVI. Three methods are generally employed: (1) coating fibers in multifilament tows by passing one or more tows continuously through reaction furnaces; (2) coating woven fiber fabric in batch or continuous modes; and (3) coating fiber preform architectures in a batch mode. Clearly there are various cost-related issues with each of these methods, which will not be discussed here. However, one can examine the tailorability and reliability issues for each case. The importance of such an examination is that coating methods 1, 2, and 3 generally correspond, respectively, to those used for the pre-preg A, B, and the preform A-B fiber lay-up approaches.

For example, a major issue with the CVI process for fiber coatings is control of the uniformity of the coating thickness (and perhaps of the coating composition). Since the coatings are formed by penetration of the precursor gases into the architecture followed by reaction and deposition on the fiber surfaces, the gases become depleted in reaction species from the outside to inside of the architecture. Since all fiber surfaces in a complex architecture are generally at the same temperature, the CVI deposition process always results in thicker coatings on the outside fibers compared to those on the inner fibers. This ratio of outer to inner coating thickness generally increases with thickness of the fiber architecture and with deposition temperature and pressure Thus lower temperatures and pressures can improve uniformity, but since these result in lower deposition rates, they are typically not cost-effective options. Therefore interphase uniformity generally decreases from coating methods 1 to 3 as described above, so that the pre-preg A architecture approach typically yields the most consistent and reproducible interphase coatings.

However, in terms of assuring interphase reliability throughout CFCC fabrication, it is important to understand that the pre-preg approaches require the coated tow or fabric to be handled and then subjected to bending stresses in order to form the final CFCC shape. Since the interphase and over-coating are on the fiber surface, these constituents can be subjected to sufficient stress to lose their integrity and functionality. For this reason, CFCC fabrication routes that employ pre-preg A and B approaches typically do not attempt to fabricate complex shapes with small radii. Thus, although the pre-preg approaches have a considerable advantage in that they can draw on the commercial experience and facilities used for polymer composite fabrication, they cannot generally accommodate complex and versatile fiber architectures as well as the preform approach. (This arises simply from the fact that polymer matrix composites do not require the complex interphase coatings that CFCC do.) On the other hand, the uniformity of fiber coatings remains an issue with the preform approaches, often necessitating its use only for thin section architectures and parts.

It should be noted that other methods might be developed to replace CVI deposition of CFCC interphase coatings and thus minimize the risk of coating nonuniformity for the preform approach. One potential method is to develop ceramic fiber reinforcements that contain some or all of the chemical ingredients required for the desired coating. Then by some special pre-treatment of the preform architecture, these coating ingredients could be made to migrate to the fiber surface to form an *in-situ* interfacial coating. If the ingredients are controlled and limited within the fiber, coating thickness should be uniform on all fibers. Indeed, in-situ carbon-rich interfacial coatings have been grown on ceramic-grade Nicalon SiC fibers, but at the expense of reducing fiber strength due to the formation of new flaws on the fiber surface (ref. 9). Thus, although the in-situ interfacial coating concept appears promising, considerable research efforts would appear to be required to develop fibers that are not only structural, but also can provide the proper interphase chemistry without degrading in strength during the interphase formation process.

II.3. Matrix-Related Iss ies

When dealing with complex fiber architectures, it generally follows that the matrix formation process will require development of innovative processes that will allow infiltration of matrix precursor materials into the architecture. Section III will discuss in more detail the infiltration processes currently being used by the five general approaches listed in table I. The purpose here is to examine the general property requirements of the final CFCC product and how these can influence the matrix formation steps.

Like the interface over-coating, which is in effect the initial matrix phase, a prime requirement for the final matrix phases is to protect the fibers and interphases from aggressive gases such as oxygen and water vapor during CFCC service. Clearly the matrix can perform this function if, in its most dense form, it displays long-term durability in these environments. Thus silicon and oxide-based compounds are preferred for the matrix composition. Assuring high matrix density then requires (1) matrix formation processes which do not result in porosity open to the CFCC external surfaces, and (2) matrix structural properties that minimize the risk of matrix cracking during CFCC service. A very important additional reason for both requirements is that the CFCC part will typically be subjected to small stresses in directions where there is no or only a small amount of fiber reinforcement (for example, interlaminar regions). Thus zero porosity and high structural performance will minimize the risk of matrix cracking in these directions. In effect then, these requirements together dictate that the matrix composition and microstructure be chosen to be similar to those of the best structural monolithic ceramic that could be used for the intended service conditions. However, this CFCC matrix must be formed by infiltration into a complex fiber architecture by processing approaches which are typically nonconventional for monolithic ceramics.

Based on the need for the best monolithic-type performance from the matrix material, one might select matrix compositions based on the following compounds: silicon nitride, silicon carbide, and alumina. Here it is assumed that the applications with the highest payoff for CFCC are at temperatures above 1000 °C and that if the CFCC can meet these applications, they can also meet those at lower temperatures. Although these three compositions are practically possible, the performance requirement that the matrix material have a thermal expansion very close to that of the commercially available SiC and Al_2O_3-based fibers effectively eliminates silicon nitride and Al_2O_3 as matrix choices for the SiC fibers, and silicon nitride and SiC as matrix choices for the Al_2O_3-based fibers. Thus, as will be discussed, the five CFCC matrix-infiltration routes primarily produce SiC- and Al_2O_3-based matrices, even though there exists expansion-driven matrix cracking in the as-fabricated SiC/Al_2O_3 CFCC (CDMO route). The SiC/SiC CFCC can also display good thermal conductivity, a performance advantage for reducing thermal stresses during service. The lack of high thermal conductivity and oxide-based fibers that are creep-rupture resistant for long times above 1000 °C are two factors currently limiting the commercial availability of oxide/oxide CFCC.

Another important concern during matrix infiltration is property retention for the fiber and interphases. The potential for degradation can arise either from intrinsic instabilities in the fiber and interphases due to the temperature requirements for matrix formation, or from chemical and physical interaction between the matrix precursors and these constituents. The first possibility arises because many commercially available small-diameter fibers are only processed to maximum temperatures near 1200 °C and most CVI interphases to maximum temperatures near 1000 °C. On the other hand, the newer CFCC fabrication routes using liquid silicon infiltration require matrix formation steps above 1400 °C. The existence of SiC over-coatings on the fiber architecture can minimize the interaction concern, but there is still some risk that the metals used in the liquid metal fabrication routes can diffuse through the over-coating grain boundaries and attack the fibers and interphases.

One final concern for matrix formation is the fact that, although the matrix-infiltration fabrication routes can produce near net shape parts, some matrix processes result in open-porosity. Also all routes will probably require some minor machining that will also expose fibers and interphases. Thus there is a general need to provide the CFCC matrix and finished part with an environmentally resistant over-coating. Again the typical approach would be chemically vapor deposited SiC for the SiC/SiC composites. However, there can be issues concerning the over-coating causing critical changes in the dimensions of the CFCC part, as well as with the adherence of the

over-coating especially if the environment were to enter the matrix porosity. Clearly these risks would be significantly reduced if the matrices were fully dense and the fibers and interphases were stable in the CFCC service environment.

III. MATRIX-INFILTRATION ROUTES FOR CFCC FABRICATION

A variety of methods such as chemical vapor infiltration, directed metal oxidation, slurry infiltration, liquid metal infiltration, polymer infiltration and pyrolysis, reaction forming/bonding, sol-gel, gel-casting, electrophoresis, glass-ceramic, etc. have been used for fabrication of ceramic matrix composites. Of these, only the first five approaches and their combinations (cf. table I) are being used to make a large variety of CFCC components. These fabrication routes will be briefly described in this section. The advantages and limitations of each fabrication method will also be discussed. All of these approaches involve infiltration of matrix precursor materials by gas or slurry or liquid processes and thus are suitable for various kinds of continuous fiber architectures. These techniques are also amenable to fabrication of components having large and complex shapes with near net-shape capability.

III.1. Chemical Vapor Infiltration (CVI)

In CVI, gaseous precursors of the ceramic matrix are infiltrated into a porous fiber preform where, by chemical decomposition, they react *in situ* to form the matrix on all exposed surfaces within the preform. In the most commonly used isothermal approach the preform is held at constant temperature of about 900 to 1100 °C, a range required for a good combination of gas infiltration rate and decomposition rate. Almost any ceramic matrix can be deposited by appropriate choice of the reactant gases or vapors. The most important example is the production of SiC matrix composites using the decomposition of methyltrichlorosilane (CH_3SiCl_3) in the presence of hydrogen at about 1000 °C:

$$CH_3SiCl_3(g) \rightarrow SiC(s) + 3HCl(g).$$
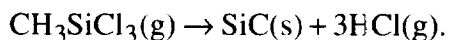
Various experimental parameters such as temperature, pressure, and flow rate of the gases as well as the preform temperature need to be optimized in order to attain the desired microstructure and properties of the matrix. Also, these variables need to be adjusted so as to delay the closing of the porosity at the preform surface until an appropriate high density has been obtained in the interior.

A number of variations of the CVI process, depending upon whether the preform is uniformly heated or not and how the reacting gases contact the preform are available (refs. 10 and 11). These are isothermal, thermal gradient, isothermal-forced flow, thermal gradient-forced flow, and pulsed flow CVI. Detailed descriptions of these CVI processes for matrix fabrication are beyond the scope of this section. Each has its own advantages and disadvantages in terms of matrix porosity, matrix microstructure, and/or matrix processing time. As indicated in table I, there are many organizations using the CVI method for CFCC components, but most use the preform A approach for forming the fiber architecture. Table II shows typical property data for three CFCC systems fabricated by CVI with three different fiber types.

The CVI method for matrix infiltration has several advantages. It is amenable to the fabrication of CFCC components having irregular, large, and complex shapes with near-net shape capability. High temperature properties are generally good because high purity matrices with controlled

microstructures can be obtained. This results typically in a SiC material with high thermal conductivity and high creep resistance. Also CVI is typically carried out at relatively low temperatures, so that there is little risk of fiber damage. In addition, the fiber-matrix interface can be tailored by pre-coating the fiber preform during an initial CVI step using different reagents but the *same* reactor. Porous CFCC components fabricated by other techniques can be further densified using CVI as long as the pores are open to the surface allowing the infiltration of the gaseous reactants.

One of the major limitations of the CVI method is the long reaction times needed for the densification process (typically greater than 100 hr). This raises the cost of the CFCC in comparison to processes that may require only minutes to complete the matrix infiltration. Also, it is not possible to obtain fully dense matrices using CVI. The presence of residual closed porosity of 10 to 15 percent may shorten the useful life of the CMC component particularly after matrix cracking in an oxidizing environment at elevated temperatures. In relation to fully dense CFCC, the porosity can also reduce the CFCC thermal conductivity and proportional limit stress (and strain) required for matrix cracking (cf. table II).

III.2. CVI plus Directed Metal Oxidation (CDMO)

The CDMO process is based on the DIMOX process developed by Lanxide Corporation. In the approach most often used (refs. 12 and 13), a fiber preform, which has been precoated with a BN interphase coating and a CVI SiC protective over-coating, is brought in contact with molten aluminum alloy held in a suitable container in air for the growth of an alumina matrix according to the following reaction:

$$2\,Al(l) + 3O_2(g) \rightarrow Al_2O_3(s).$$
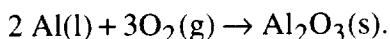
When the aluminum metal is infiltrated, the alumina matrix slowly builds up within the fiber preform and fills up the space in between the fibers, even within the closely packed fiber tows. In the presence of certain minor alloying elements such as Mg, Cu, Zn, Fe, etc, alumina matrices can grow very rapidly from the surface of the melt. The reaction continues even after the build up of an Al_2O_3 layer because the reaction product is not continuous, but contains microscopic channels through which the molten metal wicks to the surface and reacts with the gaseous atmosphere. All preform surfaces, except the one in contact with the molten metal or alloy, are coated with a gas-permeable barrier material by spraying or dipping. The barrier material is not easily wet by molten aluminum. When the growth front comes in contact with the barrier layer, the reaction product formed is impervious to the flow of molten Al, thus stopping the reaction and further growth. Proper control of the reaction kinetics during this process is very important. Growth rates of matrix in the preform is ~2 cm/day.

One advantage of the CDMO route is that it is a low-cost process with near-net shape capabilities. Only a minor dimensional change occurs during the process since the matrix fills the pores within the preform without disturbing the placement of the reinforcing fiber phase. Complex-shaped large CFCC components can be fabricated. One drawback of this method is the presence of residual aluminum phase (~5 to 10 percent) in the matrix which must be removed if the CFCC is to be used above the aluminum melting point (660 °C). This residual metal can be leached away by treatment with an acid leaving behind open porosity. Matrix cracking also occurs during the fabrication process due primarily to a thermal expansion mismatch between the alumina matrix and the protective CVI

SiC over-coating, which can provide up to 50 percent of the total matrix volume. This cracking and the residual porosity from the removed aluminum phase reduce the proportional limit stress and thermal conductivity of the CFCC system (cf. table II). Another drawback is that the total CDMO process requires the initial CVI step for SiC, which can take many hours to deposit. At the present time, AlliedSignal Composites (formerly DuPont Lanxide Corporation) is the sole fabricator of CFCC components using the CDMO route.

III.3. CVI plus Slurry and Liquid Metal infiltration (CSLM)

The CSLM matrix infiltration route is similar to the CDMO route in that the matrix is formed by a liquid metal infiltration and a CVI SiC interphase over-coating is needed to protect the fibers and interphase coating from metal attack. In this case, however, the liquid metal is typically silicon or one of its low-melting alloys, which form reaction-bonded SiC matrices that are more compatible with SiC fibers and the SiC interphase over-coating in terms of thermal expansion. Before metal infiltration, fine-grained SiC particulates are slurry cast into a fiber preform that has already been processed with interphase coatings and the SiC interphase over-coating (ref. 14). After removal of the slurry carrier liquid, silicon or a silicon alloy is infiltrated into the particulate-filled preform at a temperature of above 1400 °C. The melt infiltration is complete within a few hours or less. The infiltrated silicon or its alloy bonds the SiC particulates together and forms a matrix material that is stronger and denser than that obtained by the CVI route. The volume fraction of free silicon in the reaction-bonded matrix may range up to 50 percent, but due to its high melting point, long-term matrix use temperatures near 1200 °C are possible.

To reduce the free silicon content, some versions of the CSLM route also infiltrate carbon slurries or carbon-yielding polymers prior to metal infiltration (ref. 15). Although effective in converting excess silicon into SiC, it is generally difficult to eliminate all free silicon throughout a CFCC component. That is, some excess carbon and silicon are typically left unreacted in the matrix. If the unreacted carbon is exposed at the CFCC surface, porosity in the matrix could increase by carbon reaction with oxidative environments.

One advantage of the CSLM route is the production of a fairly dense SiC-based matrix. This typically results in CFCC with better proportional limit strength and thermal conductivity than CFCC fabricated by the complete CVI route. This can be seen in table II, particularly for CFCC with the same fiber and interphase types. The higher density and closed porosity of the CSLM route are also useful for eliminating the need for a final seal coat on the outer CFCC surfaces. Another advantage over the CVI route is reduced matrix processing time at high temperatures. However, this is compensated somewhat by the extra step of slurry infiltration.

One possible disadvantage of the CSLM route is the use of temperatures above 1400 °C for liquid silicon infiltration. This can be further exasperated by local temperature rises caused by the exothermic reaction between silicon and any excess carbon. These high temperatures can cause strength loss in those SiC fiber types that are produced at temperatures below 1400 °C (e.g., Nicalon and Hi-Nicalon). The temperatures can also increase the risk of fiber and interphase attack by diffusion of excess free silicon through the grain boundaries in the CVI SiC protective over-coating on the fibers. The free silicon may also cause problems during CFCC service such as enhanced matrix creep. Also if hot spots should exist in a CFCC component, possible changes in the CFCC properties could occur due to silicon diffusion to free surfaces on the component (silicon sweating).

III.4. Polymer/Sol-Gel Infiltration plus Pyrolysis (PIP)

General aspects of the polymer precursor approach to ceramics and ceramic matrix composites have been described earlier (ref. 16). The polymeric precursor should have certain characteristics. It should show high ceramic char yield in order to obtain high matrix density in the least number of PIP cycles. Highly branched and cross-linked polymeric precursors or those containing a high content of ring or caged structures show high ceramic yields. On the other hand, long chain polymers result in low ceramic yield because of their tendency to break up into low molecular weight volatile species during pyrolysis. The important characteristics of the polymeric precursors are the correct elemental stoichiometry, controllable molecular weight, good chemical stability during storage and use, low toxicity, low cost, and ability to cross-link at low temperatures.

A number of steps are involved in the fabrication of CFCC via PIP processing. The first step typically involves the stacking of fiber mattes that have been individually infiltrated with polymer (pre-preg B approach). These are then pressure-molded in an autoclave, before being thermally treated through cure and pyrolysis temperatures. This results in a CFCC preform that contains an amorphous and highly porous ceramic matrix. The next step is to infiltrate this structure with liquid polymer and repeat the curing and pyrolysis cycles. This last infiltration and some or all of the thermal treatment step is typically repeated over 10 times to achieve a CFCC with sufficient matrix density to provide adequate CFCC physical and mechanical properties. The resulting CFCC may be heat treated at higher temperatures for crystallization of the amorphous matrix, relaxation of residual stresses, and final consolidation. This method has also been extensively used for fabrication of carbon/carbon composites.

The main advantage of the PIP method is the use of typical methods employed in the fabrication of polymer matrix composites in order to fabricate complex-shaped CFCC components. The main drawback of this method is the long CFCC processing times and repeated impregnation/pyrolysis cycles in order to obtain sufficiently high matrix density. Also due to polymer shrinkage during pyrolysis, matrix cracking generally results within the CFCC. Re-impregnation fills these cracks to some degree, but matrix strength and thermal conductivity generally remain low. Another problem is the high cost of polymer precursors.

III.5. PIP plus Liquid Metal Infiltration (PLM)

The PLM matrix-infiltration route has been developed to eliminate the fabrication times and costs associated with the multiple re-impregnation steps inherent in the PIP route. After the initial step of using the pre-preg B approach to form a fiber architecture filled with a highly porous carbon matrix, liquid silicon is infiltrated into the structure in a manner similar to the CSLM route. The carbon and silicon react to form a dense matrix consisting of SiC plus excess silicon and carbon. In the present form practiced by the German Aerospace Center (ref. 17), low-cost carbon fibers are used with no interphase coatings or interphase over-coatings. This significantly reduces the high costs typically associated with the fiber and interphase production. Thus this process has the primary advantage of being the lowest cost approach for CFCC. However, the liquid silicon does react with the carbon fibers at the outer edges of the reinforcing tows so that the structural properties of CFCC from the PLM route are not as good as the other matrix infiltration methods. Also the poor oxidation resistance of the carbon fibers necessitates the application of a SiC over-coating on the CFCC, thereby limiting this material to only low-stress and/or short-term applications.

IV. SUMMARY

The primary routes used today for the fabrication of CFCC components are based on the five general matrix-infiltration approaches listed in table I and discussed in Section III. Each approach has its advantages and limitations in terms of achieving the four important process-related goals of (1) optimum performance, (2) tailorable or versatile structures, (3) reproducible microstructures and properties, and (4) cost-effective fabrication steps. As discussed in Section II, there are a variety of factors that influence the attainment of each of these goals. For example, for *optimum performance*, the route should have a low risk for degrading the fiber and interphase properties while providing a matrix material that is dense, strong, creep resistant, and thermally conductive. For *tailorable structures*, the route should be able to achieve good CFCC performance and net-shape capability using the wide variety of fiber architectures that may be required for complex-shaped components of various sizes. For *reproducible properties*, the route should repeatedly produce the same local microstructures throughout the entire volume of the CFCC component. Finally, for *cost-effectiveness*, the route should minimize the number of process steps and carry on these steps in the shortest times and at the lowest temperatures possible.

With process-related criteria such as these, it is possible to assess and compare in a very qualitative manner the capabilities of the five matrix-infiltration routes. This is done in table III where the process and material details for each route are judged against the four key fabrication goals. In this table, the rankings high (H), medium (M), and low (L) refer to the route's relative ability to achieve the various aspects of the fabrication goals. In general, it can be seen that no route ranks high in all categories. Typically those routes yielding high performance matrices are not cost-effective; while those that are low cost do not show good performance. Also, although the matrix infiltration routes are conducive to net and complex shapes, attainment of high microstructural uniformity throughout a CFCC component is generally not possible. Thus, today, the best fabrication route for the CFCC end-user is not clear and compromises need to be made depending on the details of the CFCC application. However, with time, this problem should be reduced as research continues to develop advanced CFCC constituents and fabrication routes.

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TABLE I.—FIVE GENERAL MATRIX-INFILTRATION APPROACHES FOR CFCC COMPONENT FABRICATION

Matrix-infiltration approach	Typical fiber lay-up approach[a]	Typical matrix phases[b]	Some current practicing organizations
Chemical Vapor Infiltration (CVI)	Preform A	SiC	• AlliedSignal Composites[c] • B.F. Goodrich • Hypertherm • Man Technologie • Refractory Composites • SEP
CVI plus Directed Metal Oxidation (CDMO)	Preform A	$SiC + Al_2O_3 + Al$	• AlliedSignal Composites[c]
CVI plus Slurry/Polymer plus Liquid Metal Infiltration (CSLM)	Preform A	$SiC + Si$	• AlliedSignal Composites[c] • B.F. Goodrich
	Preform A	$SiC + Si + C$	• AlliedSignal Composites[c]
	Pre-preg A		• General Electric
Polymer/Sol-Gel Infiltration plus Pyrolysis (PIP)	Pre-preg B	Si-O-N-C	• Dow Corning
	Pre-preg B	$Al_2O_3 + SiO_2$	• Composite Optics • General Electric
PIP plus Liquid Metal Infiltration (PLM)	Pre-preg B	$SiC + Si + C$	• German Aerospace Center

[a]See Section II for details.
[b]See Section III for details.
[c]Formerly DuPont Lanxide Corporation.

TABLE II.—TYPICAL PROPERTIES OF 2-D CFCC FABRICATED BY DIFFERENT MATRIX-INFILTRATION ROUTES

Property at room temperature	CFCC matrix infiltration route					
	CVI	CVI	CVI	CDMO	CSLM	PIP
Fiber type (vol %)	T300 Carbon (45%)	Nicalon SiC (40%)	Hi-Nicalon SiC (40%)	Nicalon SiC (35%)	Hi-Nicalon SiC (40%)	Nicalon SiC (50%)
Interface	C	C	BN	BN	BN	Proprietary
Matrix	SiC	SiC	SiC	Al_2O_3	SiC + Si	Si-N-C-O
Proportional limit strength, MPa	62	75	130	42	140	60
Interlaminar shear strength, MPa	26	32	43	63	50	14
Thermal conductivity through thickness, W/m-°K	6.5	9.5	10	8.7	19	1.3

TABLE III.—COMPARISON OF MATRIX-INFILTRATION
ROUTES FOR CFCC FABRICATION: RELATIVE
ABILITY FOR ACHIEVING FABRICATION
CRITERIA: H - HIGH, M - MEDIUM, L - LOW

| Fabrication criteria	CFCC matrix infiltration method				
	CVI	CDMO	CSLM	PIP	PLM
Optimum performance					
Fiber-interphase stability	H	M	M	H	L
Structural matrix: High strength/creep resistance	M/H	L/L	H/M	M/L	H/M
High matrix thermal conductivity	M	L	H	L	M
Tailorable structures					
Near net shape capability	H	H	H	H	H
Complex shape capability	H	H	H	M	M
Conducive to 3-D architecture	H	H	H	L	L
Reproducible properties					
Uniform interphase coating	L	L	L	M	M
Uniform matrix microstructure	L	L	L	L	L
Cost-effectiveness					
Low-cost interphase steps	H	H	H	M	M
Low-cost matrix steps	L	M	M	L	H
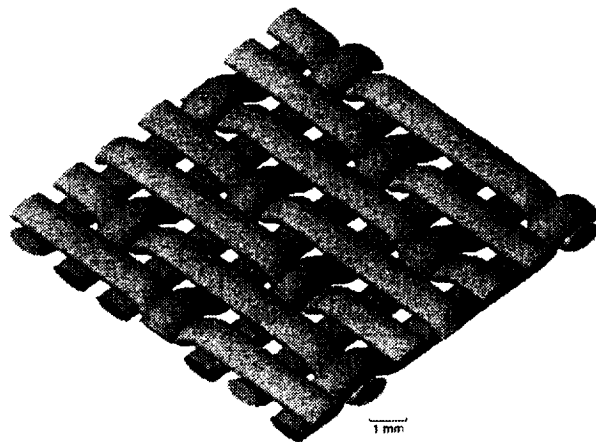
Figure 1.—0/90° 2-D fabric composed of multifilament
tows woven in a 5-harness satin pattern [18].

Figure 2.—SEM micrograph showing polished cross-
section of a matrix infiltrated 8-ply 2-D SiC$_f$/SiC
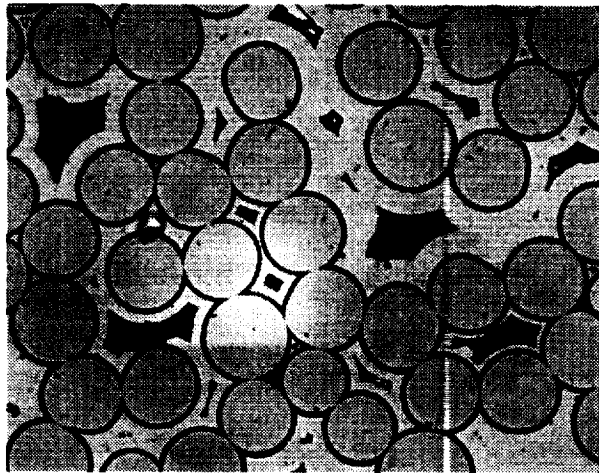composite.

Figure 3.—High magnification SEM micrograph
showing fibers within a tow, each covered with
a BN interface coating (dark) which are in turn
covered by a CVI SiC overcoating.

REPORT DOCUMENTATION PAGE

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE November 1998	3. REPORT TYPE AND DATES COVERED Technical Memorandum

4. TITLE AND SUBTITLE

Fabrication Routes for Continuous Fiber–Reinforced Ceramic Composites (CFCC)

6. AUTHOR(S)

James A. DiCarlo and Narottam P. Bansal

5. FUNDING NUMBERS

WU–523–21–13–00

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135–3191

8. PERFORMING ORGANIZATION REPORT NUMBER

E–11424

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

National Aeronautics and Space Administration
Washington, DC 20546–0001

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

NASA TM—1998-208819

11. SUPPLEMENTARY NOTES

Responsible person, Narottam P. Bansal, organization code 5130, (216) 433–3855.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unclassified - Unlimited
Subject Category: 24   Distribution: Nonstandard

This publication is available from the NASA Center for AeroSpace Information, (301) 621–0390.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The primary approaches used for fabrication of continuous fiber-reinforced ceramic composite (CFCC) components have been reviewed. The CFCC fabrication issues related to fiber, interface, and matrix have been analyzed. The capabilities, advantages and limitations of the five matrix-infiltration routes have been compared and discussed. Today, the best fabrication route for the CFCC end-user is not clear and compromises need to be made depending on the details of the CFCC application. However, with time, this problem should be reduced as research continues to develop advanced CFCC constituents and fabrication routes.

14. SUBJECT TERMS

Ceramic composites; Fabrication methods; Interfaces

15. NUMBER OF PAGES
22

16. PRICE CODE
A03

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	