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Carbon Fiber Reinforced Ceramic Composites For Propulsion Applications

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Abstract

This report presents a critical review of the processing techniques for fabricating continuous fiber-reinforced CMCs for possible applications at elevated temperatures. Some of the issues affecting durability of the composite materials such as fiber coatings and cracking of the matrix because of shrinkage in PIP-process are also examined. An assessment of the potential inexpensive processes is also provided. Finally three potential routes of manufacturing C/SiC composites using a technology that NC A&T developed for carbon/carbon composites are outlined. Challenges that will be encountered are also listed.

1. Introduction

Monolithic Ceramics are generally processed starting from powders, which are given appropriate shapes by pressing, casting, and extrusion, and then sintered at high temperatures for densification and improvements in mechanical and possibly other properties. However, the monolithic ceramics are generally weak and brittle and fail catastrophically because of their low fracture toughness. In contrast, reinforcement of ceramics with strong fibers and/or whiskers has been done in the past 15-20 years for enhancing strength and toughness of the monolithic ceramics [1-5]. Consequently, an accelerated pace of research and development has ensued in the immediate past to understand both the theoretical and experimental behaviors of ceramic matrix composites (CMCs). This included micromechanics based modeling of CMCs, fiber development, processing techniques to fabricate CMCs, and experimental determination of their mechanical properties. Furthermore, issues of environmental-related degradation of CMC properties associated with oxidation-induced changes in constituent (fiber, interface, and matrix) properties have been actively studied in the recent past [6]. The current state of CMCs and associated technologies has advanced sufficiently to such a state that component level assessments/applications are being pursued. In spite of these extraordinary developments, the cost of the CMCs in comparison to the monolithic ceramics is still high because of the expensive reinforcements and processing routes. In addition, durability of the fibers and fiber-matrix interfaces, particularly at elevated temperatures, remains an issue as most of the non-oxide fibers and interfaces can readily oxidize at elevated temperatures rendering composites to loose most of their useful mechanical properties.

Therefore, one of the objectives of this report is to critically review the processing techniques for fabricating continuous fiber-reinforced CMCs for applications at elevated temperatures. Some of the issues affecting durability of the composite materials such as fiber coatings and cracking of the matrix because of shrinkage in PIP-process are also examined. An assessment of potential cost saving processes is also provided. The processing route to fabricate carbon/carbon composite developed at NC A&T is discussed as well as modifications to enhance durability of the composite system for use at high temperature. This is followed by a description of three low-cost proposed routes for producing C/SiC composites and the research challenges that need to be addressed.

2. Background

A continuous fiber-reinforced ceramic-matrix composite is made from fibers (uniaxially aligned or woven), that are converted into a porous preform into which a ceramic matrix is incorporated by a variety of techniques. Unlike sintering of the monolithic ceramics, which can produce fully dense ceramics, processing of dense CMCs is a non-trivial task. The presence of continuous fibers restricts densification of the matrix because of the constraint on shrinkage of the matrix from reinforcing fibers. Consequently, conventional sintering approaches are unable to produce dense CMCs. Therefore, different processing methods must be used to produce a dense matrix of a CMC. Processing techniques such as filament winding/densification, lamination and densification, sol-gel infiltration and densification, chemical vapor infiltration, polymer infiltration and pyrolysis (PIP), resin transfer molding (RTM), and melt infiltration have been developed to fabricate CMCs [7, 8]. Each of these techniques is critically reviewed here, which can be used to fabricate either an oxide fiber-reinforced oxide matrix composite or a non-oxide fiber reinforced non-oxide matrix CMCs. Consequently, this review is done independent of the materials system although a particular attention is paid to CMC systems containing SiC and C fibers, SiC and C matrices, and a few oxide fibers, and oxide matrices. In comparison to many fibers, SiC and C fibers are most promising for reinforcing ceramic matrices because of their superior mechanical properties at elevated temperatures. Oxide fibers in oxide matrices are promising because of their inherent oxidative stability at high temperatures. The fiber/matrix combination must be selected so that the residual stresses after processing is minimized. Generally, this is achieved by selecting fiber matrix to have similar coefficients of thermal expansion or fiber coefficient of thermal expansion slightly higher than the matrix. This creates a compressive pre-stress in the weaker component of the composite, i.e. the matrix. In addition to the strong fiber and matrix, interface between the fiber and matrix must be appropriately selected so that a weakly bonded interface is created for promoting interface debonding, crack-deflection, fiber-bridging and toughening [1-5]. It is also desirable for the interface to remain stable at elevated temperatures during processing and in service in oxidizing environments to maintain the toughening potentials of CMCs. Some of these relevant issues will also be considered in this review. However, readers are encouraged to refer of the relevant literatures for more exhaustive reviews on the micro-mechanics of CMCs and associated requirements on fiber, matrix, and interface properties to achieve a significant strengthening and toughening [1-5].

3. Processing Techniques of CMCs

Basic composite processing can be classified into four methods based on the approaches of matrix incorporation into the fiber bundles or pre-forms as follows.

A. Slurry Infiltration
B. Sol-gel and Polymer Infiltration
C. In Situ Chemical Reactions and Infiltration (Lanxide^{TM}, CVD and CVI)
D. Melt infiltration

Some of these infiltration approaches also require additional high-temperature processing steps to convert and densify the matrix as described in detail below.

3.1. Slurry Infiltration

In its most rudimentary form, a slurry is prepared from the matrix forming powder in an aqueous or non aqueous liquid medium that also contains an appropriate dispersant for stabilizing the slurry, wetting agent, and binder. The binder is added for developing bonds between ceramic particles. The slurry is then infiltrated into the fiber preform or fiber bundle via either a filament winding method or vacuum filtering approaches. The filament winding approach is shown in Fig. 1. The filament winding approach, after drying, produces a layer of uniaxial laminate, which is stacked on top of each other and laminated under low pressure and temperature to form a laminated composite. This composite is then heated to remove the binder and sintered or hot-pressed to achieve a dense composite.

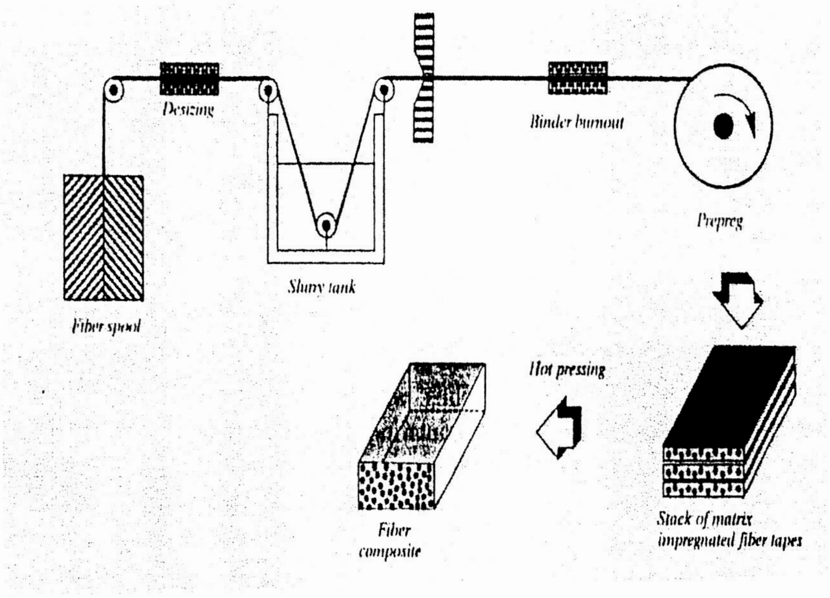

Figure 1. Processing of CMCs by slurry infiltration process [8].

A large number of composites were processed by this technique, particularly those with a glass matrix because glass matrix becomes soft at temperatures much below its melting point. Initial works used carbon fibers [9-12] but then SiC fibers (Nicalon) were extensively used to prepare SiC-glass composites. A wide rage of glass compositions (high-silica, borosilicate, aluminosilicate) as well as glass-ceramics (lithium aluminosilicate/LAS and magnesium aluminosilicate/MAS) were tried. The Nicalon-LAS composite showed impressive mechanical properties (strength of 830 MPa and K_{IC} of 18.9 MPa.m$^{1/2}$) [13,14]. Extension of this approach to process crystalline matrices were also tried with less success because crystalline matrices require higher processing temperatures during hot-pressing, which can lead to fiber damage/degradation. Also, crystalline matrices do not show a sufficient viscous flow during hot-pressing so that it becomes more difficult to infiltrate the matrix materials between the fiber of a fiber tow thus leading to porous matrix or void spaces between fibers. This may result in poor mechanical properties because of insufficient load sharing by the fiber/matrix in the voided regions. Incorporation of the liquid phase sintering aids has improved this situation for composites of Si_3N_4 matrix [15].

A particular limitation of the slurry infiltration and hot-pressing approach has been its inability to produce composites with complex shapes. This is because hot-pressing is only conducive to planar/simpler geometry. Hipping is an option for densification of a more complex geometry. Both of these (hot-pressing and hipping) approaches are expensive for fabricating CMCs and limited to simpler shapes. Slurry infiltration is also inadequate because unless very fine powders are used it is difficult to infiltrate the fiber bundles. Consequently, slurry infiltration alone is not an attractive process for fabricating CMCs.

3.2. Sol-gel and Polymer Infiltration Process (PIP)

A sol is made up of a colloidal suspension of very fine particles in a liquid medium. Developing surface charge on the particles stabilizes the suspension. Since the sol particles are very fine, they have much better capabilities than a slurry to infiltrate the small spaces among fiber bundles. Similarly a polymer can be used as a preceramic precursor, which can be melted at a relatively low temperatures and then readily infiltrated into a fiber bundles or fiber preform to fabricate CMCs. After infiltration of the fiber preform, the sol-gel or the polymer is pyrolysed to sufficiently high temperatures to convert the sol-gel or the polymer to ceramic matrix. The advantages of this process are (1) ease in infiltration, including injection-molding, (2) lower processing temperatures, (3) potential for forming multiphase matrices, and (4) compositional homogeneity. The polymer infiltration and pyrolysis process is particularly advantageous for producing covalently-bonded non-oxide matrices (C, SiC or Si_3N_4) at temperatures much lower than the conventional sintering temperatures used for powders. Extensive studies have been done to synthesize C, SiC, and Si_3N_4 matrices using a variety of polymeric precursors [16-21].

One of the limitations of this processing route has been the large shrinkage upon pyrolysis of the gel or polymer. This leads to a shrinkage cracks in the matrix phase because of the constraint by reinforcing fibers in the preform. Consequently, the matrix phase is not dense and requires several infiltration and pyrolysis cycles to fill the open porosity. An effective method to reduce shrinkage has been to add solid particles of appropriate size into the gel or polymer so that a majority of the volume is filled by particles and only a small amount of polymer is needed. This approach also avoids too many repeated infiltration and pyrolysis cycles to achieve a higher density for the matrix. BN, SiO_2, SiC, and Si_3N_4 fine-particle fillers have been used for a polymer-derived SiC matrix [22]. Another approach for reducing shrinkage in polymer infiltration route has been to use polymers with much higher ceramic yield upon pyrolysis. There are now promising polymers (polycarbosilane) available in the marketplace from Starfire Systems and others with ceramic yields approaching as high as 80-85% [23]. The pyrolysis of this polymer forms a nanocrystalline SiC at 1250-1700° C, which is stable to 1800° C in air. The SiC formed from this polymer also has an excellent oxidation resistance to very high temperatures and can be used as protective coatings on fibers or composites at high temperatures. This polymer is stable in air and inexpensive because it is a by product of silicone manufacturing process. A combination of high yield polymer and addition of fillers can be used to fabricate dense SiC_f-SiC CMCs with a single infiltration cycle at a relatively low cost. In addition, this polymer can also be used to provide external coatings of SiC for additional oxidation resistance. Consequently, the PIP process is promising for creating CMCs for operations at high temperatures at relatively lower cost than other methods [24].

3.3. In Situ Chemical Reactions and Infiltration (Lanxide^{TM}, CVD and CVI)

Early nineteen eighties saw new approaches to processing of CMCs. These included in situ reactions to synthesize matrix into a porous preform by processes of liquid metal oxidation (Lanxide^{TM}), Chemical Vapor Deposition (CVD), and Chemical Vapor Infiltration (CVI).

In the Lanxide^{TM} process (Fig. 2), a porous fibrous preform was placed into a molten Al and then the chamber was exposed to air to grow Al_2O_3 scale as a matrix phase [25]. This led to oxidation of the Al at the air-Al interface and produced Al_2O_3. However, solid Al_2O_3 is highly passivating because of the very slow diffusion of oxygen through the Al_2O_3 scale at ~800-1200° C. However, a novel approach of adding impurities such as Mg led to the formation of a non-passivating Al_2O_3 oxide scale, which had continuous channels of liquid Al along the grain boundaries of the Al_2O_3 scale. This provided a continuous availability of liquid Al at the surface where air continued to oxidize Al and grew the scale unabated. This approach produced Al_2O_3

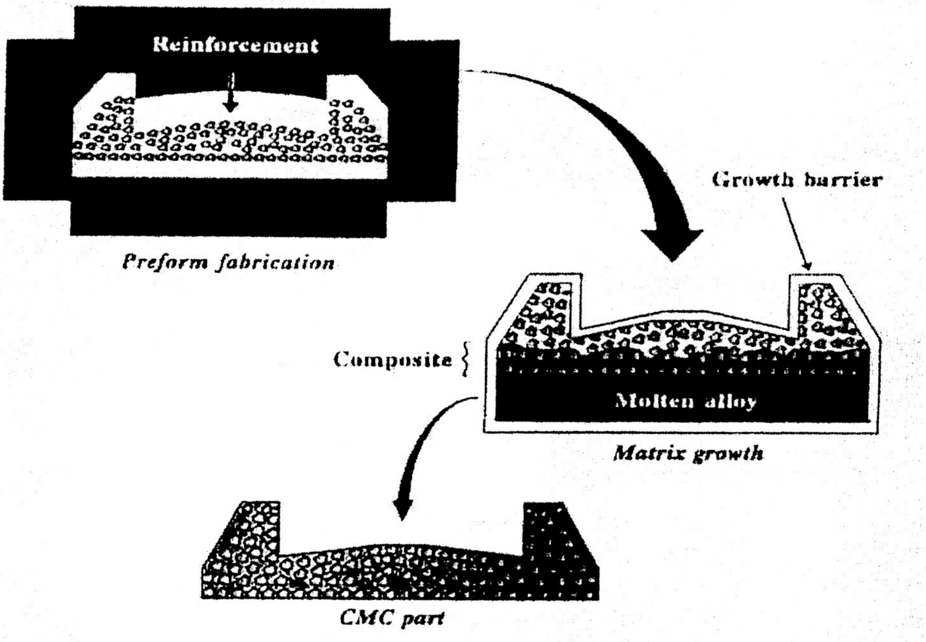

Figure 2. Processing of CMCs by directed metal oxidation of Lanxide Corporation [8].

matrix-Nicalon composite with full density and capability for a net and complex shape. A similar approach was used to grow AlN-Nicalon composite by the Lanxide process in which Al melt was exposed to N_2 to form AlN. The fiber coatings of BN and SiC was applied to Nicalon SiC fibers to prevent oxidation of the fibers in air at temperatures > 800° C and to create a weakly bonded fiber-matrix interface for toughening by fiber bridging and pullout mechanisms. While this process created a lot of excitements for several years in CMCs, it is currently not in practice because the process was limited to only select matrices and required long time to grow sufficiently thick composites.

Chemical vapor deposition is another technique for forming matrix materials in situ by way of chemical reactions in the gas phase. This process is extensively used in processing of microelectronic devices and deposition of coatings of all types. Initial attempts to use CVD for synthesizing CMCs were for coating fibers to either protect them during processing or service and to create an optimum interface for interface debonding and pullout [1,36,38]. Advantages of CVD coatings are its uniformity of thickness and composition as well as its ability to deposit multilayered coatings for achieving several functionality [26,27]. These fiber coatings also offer optimum wetting character for ease in processing by slurry, polymer, and melt infiltration.

Most CVD processings for surface coating are done under conditions in which the deposition is rate controlled by diffusion of gaseous reactants and products in the gas phase. Consequently, filling a porous preform with a matrix by CVD is not readily possible because surface gets coated first and then access to the interior void is limited to small depths. To overcome this limitation of the CVD process, CVI methods were developed to process CMCs. In this CVI approach, the CVD process is done at low reactant concentration, pressures, and temperatures. This leads to CVD process controlled by reaction at the surface rather than the diffusion in the gas phase, and deposit matrix materials much more uniformly throughout the interior of the porous fiber preform. This process was initially demonstrated for fabricating SiC-Nicalon composite in France and USA but a similar process has been used to synthesize C-C composites as well [26,28]. One of the limitations of this process is that it is extremely slow and may take 100 hours to fill a 1/4" thick preform. Another limitation of this process is that it is unable to fill all porosity so achieving a density higher than 90-95% of the matrix phase is not possible because of the development of the closed porosity. To overcome this limitation, researchers at ORNL and universities have developed a forced flow CVI technique (Fig. 3) in which applications of thermal and pressure gradients in a chamber containing a fiber preform with specially designed gas flow has significantly reduced the processing time to 10-12h and achieved a density up to 90% of the theoretical density for SiC and Si_3N_4 matrices of a CMC [29-31]. Other advantages of the CVI technique are single step process, complex and net shape capability, and ability to deposit a wide range of matrix materials. An important disadvantage of this process is that it is still slow and expensive.

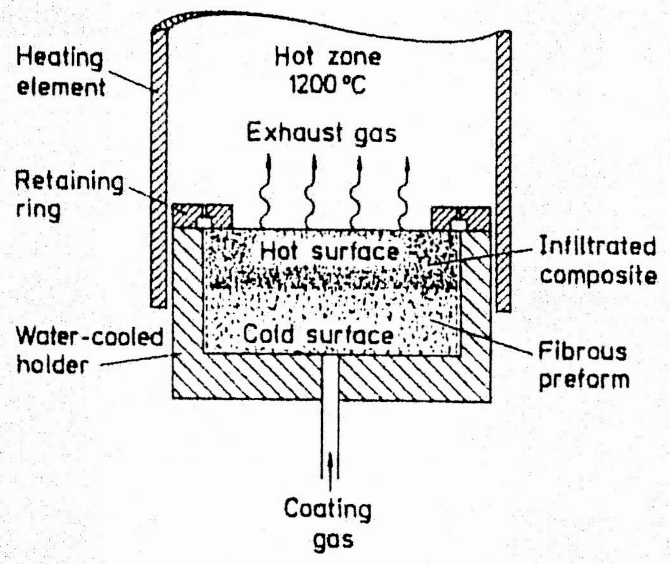

Figure 3. Schematic of CVI process under pressure and temperature gradients [30].

Another reaction-based in situ process has been used to form reaction-bonded matrix of a CMC. An example of this is Si_3N_4 matrix reinforced with SiC fibers, in which Si powder in a porous SiC fiber reinforced preform, is prepared and then Si is nitrided at elevated temperatures to form Si_3N_4 matrix. Excellent properties have been displayed by these composites as reported by Lucke et al [32] and Corbin et al. [33]. BN-BN composites are also processed by a similar approach [34].

3.4. Melt Infiltration

In this process, a fiber-reinforced porous preform is infiltrated with a molten material to fill the void spaces and form a fully dense composite. This approach is most popular for making metal-matrix composites because of their low melting temperatures and low viscosity of the molten metals. In contrast, this approach is relatively less widespread for processing CMCs because of their high melting temperatures and possibly high melt viscosity. But, this approach has become most promising for synthesizing SiC-based CMCs because of the fact that it produces fully-dense and net-shape composites in a relatively short times. Nonetheless, there are a few items that need to be considered for processing of CMCs by melt infiltration. These include, damage to fibers because of the reaction with the melt and low rates of infiltration because of high viscosity of melt. This process also requires excellent wetting of the preform with the molten matrix to avoid resistance to infiltration. Some of these issues can be handled via suitable coatings on the fibers for enhanced wetting and fiber protection.

One of the most promising applications of the melt infiltration process to fabricate SiC-based CMCs has been to infiltrate molten Si into a porous preform containing C, SiC, and coated SiC fibers. The Si melts at 1410°C where the viscosity of the molten Si is very low (like water at room temperature). The molten Si gets wicked into the preform and reacts with C to form SiC in situ. This is an exothermic reaction that also leads to volume expansion upon SiC formation, which fills the void spaces in the preform. There is little or no distortion of the preform and the entire process leads to a fully dense matrix consisting of SiC and Si. The amount of free Si can be controlled by suitable selection of the overall porosity and C/SiC ratio. In fact composites with free Si content in the matrix ranging from as low as 10% to 40% can be readily processed. Even, Si-free matrix can be produced by this approach but this requires a careful control of the level and size of the porosity and the C/SiC ratio in the preform. The initial work on this system was carried out at GE R&D center utilizing SCS-6 SiC and/or C fibers in a carbon matrix [35-40]. Si-melt is extremely reactive to SiC and C fibers thereby destroying all of the useful mechanical properties of fibers. Consequently, these fibers were protected from molten Si by a CVD fiber coatings of BN, BN/C, or BN/SiC. To date this coating system has proved effective in not only protecting the fibers from reaction with molten Si but also in creating an optimum fiber-matrix interface for enhancing toughness by debonding and fiber pullout mechanisms [36,37].

There have been substantial improvements in the processing approaches to fabricate SiC-Si matrix composites reinforced with SiC fibers since the initial demonstration at GE R& D center by researchers at NASA-Glenn [41,42], and industrial organizations such as Carborundum, Honeywell/GE Composites. For example, NASA-Glenn developed a polymer route to forming porous C-matrix, and Carborundum developed slurry-infiltration to form the porous matrix phase [43]. Each of these approaches was followed by infiltration by molten Si to reactively form fully dense SiC-Si matrix. In addition, small diameter SiC fibers of Nicalon, Hi-Nicalon, and Sylramic are currently used for manufacturing CMCs because of their superior thermal stability and weavability. At the present time, there are two approaches for forming the porous preform for melt infiltration. In one case, the BN/SiC coated fibers are aligned to form a sheet of fiber mats. These are then stacked on top of each other with matrix forming materials and cured. Then, this preform is infiltrated with molten Si to form a fully dense CMCs. In the other approach, a woven fiber preform is coated with BN/SiC fiber coating in a CVI reactor. The matrix forming materials are then slurry cast to form the multilayered preform, which is then infiltrated with molten Si to form the CMC. There have been attempts to use B- and Si-doped molten Si infiltrants as well as Mo-doped Si to form $MoSi_2$/SiC in the matrix phase [41,42,44]. Composites fabricated by these approaches are currently being tested in gas turbine environments of aircraft engines and land-based turbines by several industrial organizations such as GE and UTRC.

The dense CMCs fabricated by this technique have excellent oxidation resistance to very high temperatures because of the SiC/Si matrix. In addition, these composites retain their superior mechanical properties to very high temperatures (approaching 1300-1450°C). However, a concern on the stability of the BN/SiC fiber coating against environmental attack upon cracking of the matrix phase remains because it can lead to oxidation of the coatings and strong bonding at the interface. This situation is expected to degrade mechanical properties of composites. In spite of these limitations, this composite system has enormous potential for applications in a variety of systems at very high temperatures as is evident from industrial activities.

3.5. NC A&T Process for C/C Composites

Carbon-carbon composites were processed at NCA&T by the RTM process in which a carbon source of Primaset PT-30 cyanate ester resin and T-300 carbon fiber heat treated fabric were used. The PT-30 resin has several advantages such as high char yield (65%), low viscosity, and low volatiles during processing, which makes it very attractive candidate for RTM. Consequently, RTM-based processing of C-C composites was pursued at NCA&T [45,46]. Figure 4 shows a comparison of the conventional resin solution method and the RTM process. Both processes use green part, which is carbonized to convert the polymer to carbon. After this, in the case of the resin solution method, several infiltration and carbonation cycles are done to densify the composite. In contrast, the RTM process used only a limited impregnation/cure and carbonization cycles to achieve good densification. For example a 5% void content requires only 2 cycles Vs 5 cycles for the resin solution method (Fig. 5). Consequently, the RTM approach is much more efficient in filling voids. The C/C composites fabricated by RTM showed across the board increase in mechanical properties such as higher modulus, strength, and interlaminar shear. Although these properties are good for C/C composites it may not be adequate for applications at very high temperatures in oxidizing environments. Some of the improvements that will be needed for higher temperature applications include (1) enhanced oxidation resistance of the carbon matrix, and (2) improvement in the interlaminar properties. Several approaches can be taken to improve oxidation resistance of the matrix. Fillers can be added to the carbon matrix to fill the voids and if these fillers form SiO_2 scale then the oxidation resistance can be enhanced. Also, fillers that promote low melting glass formation upon oxidation can also be beneficial. In addition, external coatings of SiC can be beneficial for oxidation protection as well as PIP infiltration of a preceramic polymer. However, the problem with the C fiber is notably its poor oxidation resistance but abnormal coefficient of thermal expansion (much too low along the fiber axis), which makes selection of a suitable external coating for oxidation resistance a problem as most of the coatings tend to crack because of the low expansion of C/C composites. A promising approach of infiltration of the C/C composites with molten Si to seal the open channels and produce a dense matrix has the potential for significantly increasing the oxidation resistance of C/C composites because the Si melt will react with the C and form SiC in situ and will fill the big voids by SiC/Si. This way a dense and impervious C/C-Si-SiC composite can be obtained. Still the matrix may crack upon thermal cycling because of the higher coefficient of thermal expansion of the C-Si-SiC matrix thus formed in comparison to C fibers. To alleviate this problem, use of other fibers such as Hi-Nicalon should be beneficial. Consequently, a hybrid process based on RTM of C/C composites, incorporation of fillers, PIP infiltration of a preceramic polymer (SiC former), and Si-melt infiltration is expected to significantly enhance the high temperature capability of C/C composites fabricated at NCA&T. The infiltration of C/C composite by molten Si may also require protective coatings on C fibers to avoid fiber-Si reaction. Coatings of SiC may be beneficial for this as it can also lead to optimum fiber-matrix bonding for creating a toughened C/C composite.

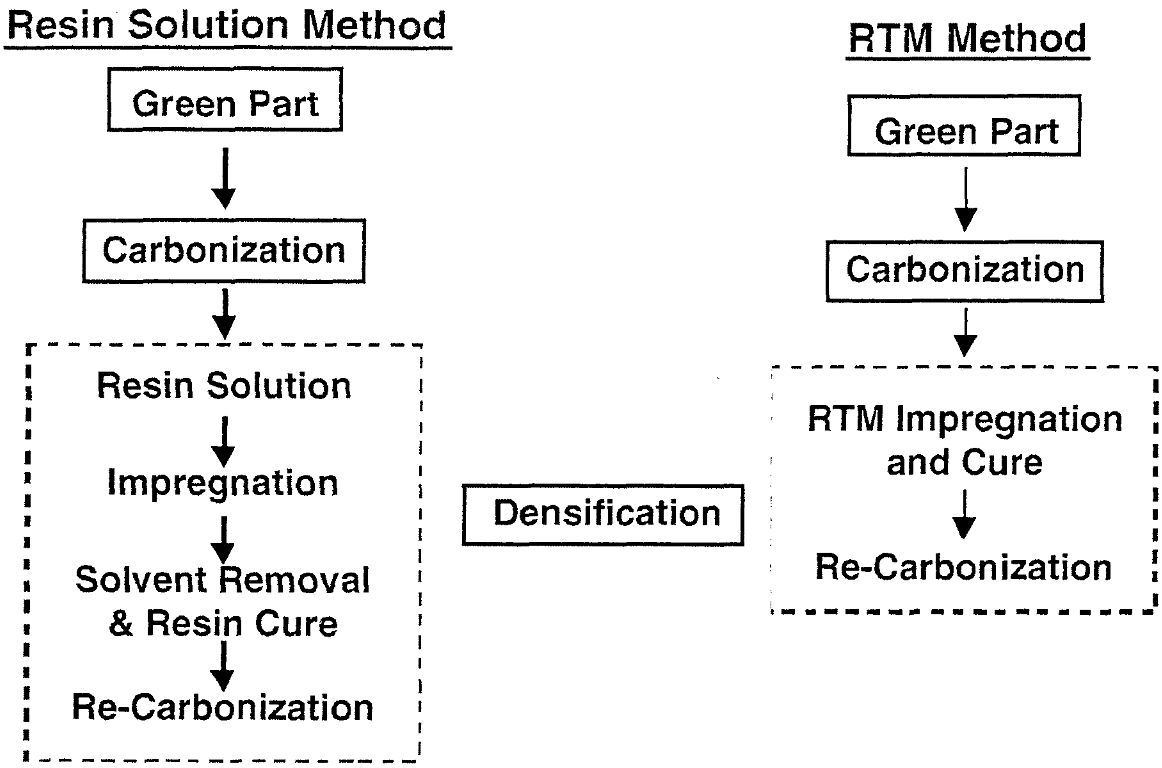

Figure 4. Processing of C/C composites by resin solution and RTM techniques [46].

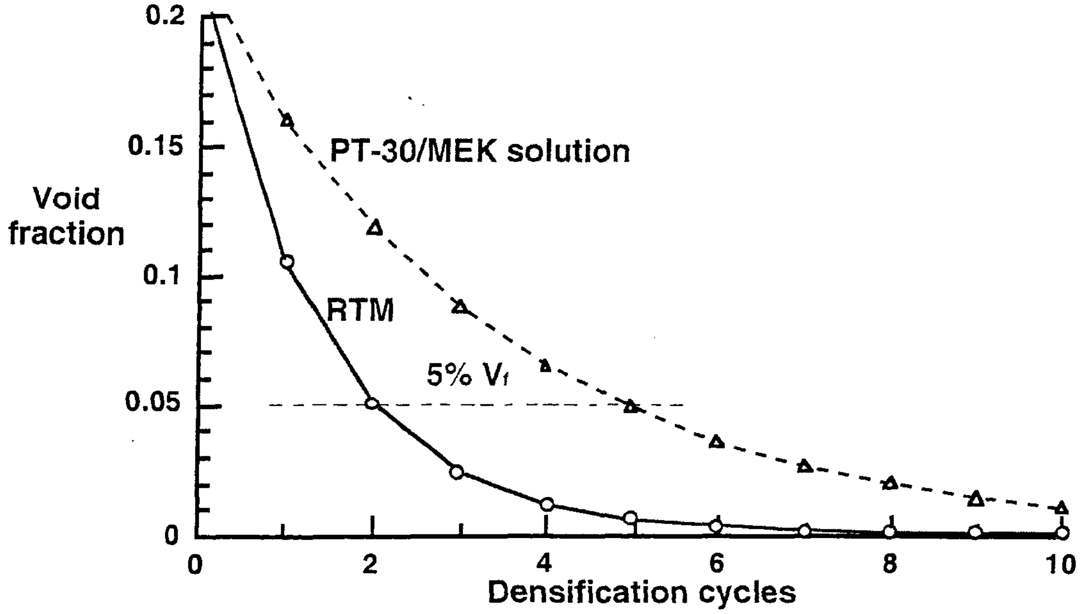

Figure 5. Dependence of void content on the number of densification cycles for the RTM and resin solution approaches [46].

4. Proposed Manufacturing of C/SiC Composites

Three potential methods of manufacturing C/SiC composites are proposed and are schematically shown in Fig. 6. In one proposed route, a coated fiber preform will be subjected to a treatment of processing cycles of impregnation with a resin of high carbon yield, followed by pyrolysis and a final step of silicon melt infiltration to prepare the C/SiC composite product of high density. In the second approach, a SiC precursor resin will be used to impregnate the coated fiber preform followed by pyrolysis and repetition of these PIP steps to obtain the final product. In the third approach, the coated fiber preform will be treated with PIP cycles with a high ceramic-yield precursor resin, followed by a final PIP cycle with a high carbon-yield resin and followed by silicon melt infiltration to obtain high density C/SiC composite.

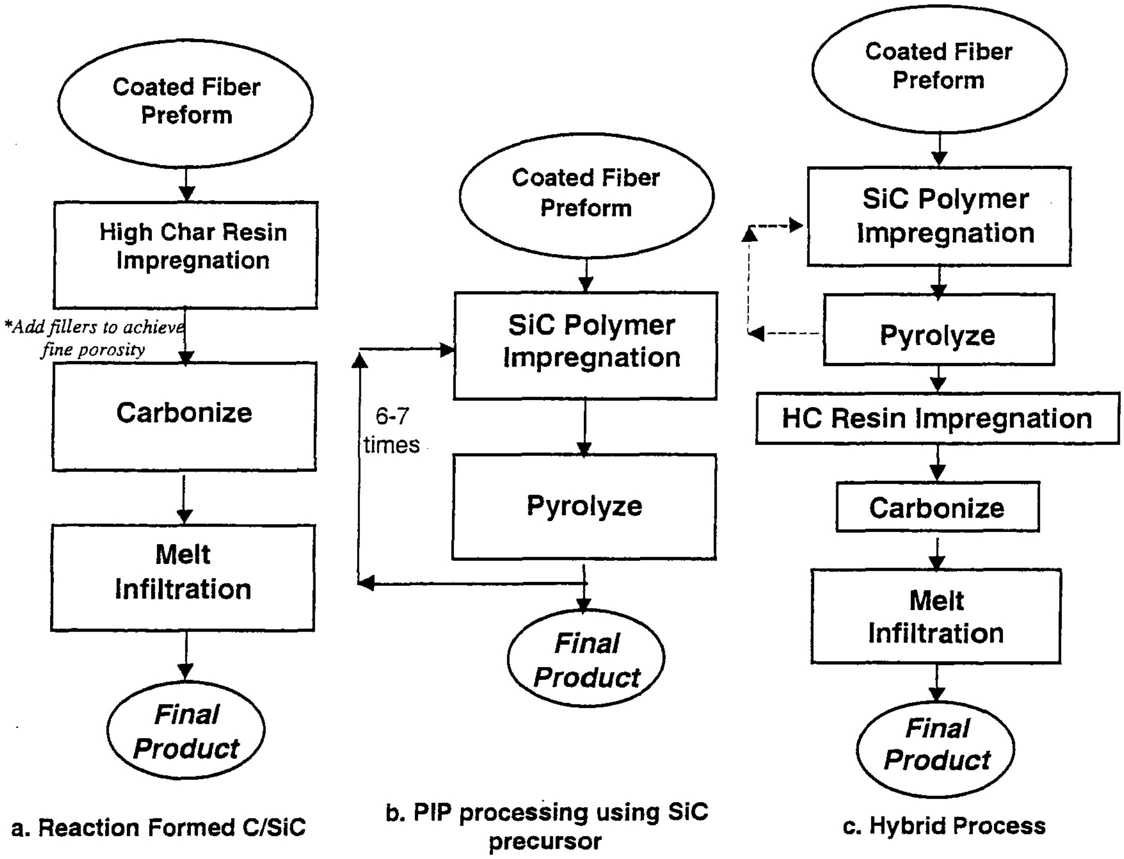

Figure 6. Methods of manufacturing C/SiC composites.

4.1. Research Challenges

The mechanical properties of carbon fiber based silicon carbide composites are superior to those of carbon/carbon composites. The C/SiC materials can be produced using basically a similar process used in carbon/carbon composites of polymer-impregnation-pyrolysis (PIP) [48,49]. However, to eliminate the residual porosity in the C/C composite processes, such as, either high-pressure liquid pitch infusions followed by pyrolysis or chemical vapor deposition (CVD) or chemical vapor infiltration (CVI) of pyrolytic carbon need to be employed. Both of these approaches involve capital-intensive process equipment and these processes are time consuming and expensive.

Following the same processing route as the carbon-carbon composite [47], C/SiC composites also are left with residual porosity. In the case of C/SiC, fully dense composites can be obtained by a final step of silicon infiltration wherein the carbon available can react with silicon to form silicon carbide. Molten silicon is very reactive and can attack the carbon fibers if the fibers are unprotected and exposed to the Si melt. Thus there are three major research challenges: (i) How to create a porous structure in the matrix for complete Si infiltration and reaction with carbon without an excess of residual silicon? (ii) Can the reactivity of molten silicon with carbon be controlled by alloying with other metals? (iii) What type of coatings on carbon fibers will be necessary to protect them from attack by silicon, smooth transition of CTE match from carbon fiber to SiC matrix, and for operation in oxidative environment

5. Conclusions and Recommendations

Conclusions of this critical review are summarized as follows:

Monolithic ceramics, produced for pressing and sintering the respective powders at high temperatures, are generally brittle and fail catastrophically because of their low fracture toughness. Micromechanics based modeling and experimental studies have shown that incorporating strong fibers enhances the mechanical strength and toughness of ceramic matrix composites. The current state of the ceramic matrix composites is such that component level applications are being pursued. In spite of these developments the cost of the CMC's in comparison to monolithic ceramics is still very high due to expensive fibrous reinforcements and processing routes.

Continuous fiber-reinforced ceramic-matrix composite is made from uniaxially aligned or woven fibers that are converted into a fibrous perform into which ceramic matrix is introduced. The presence of continuous fibers in the CMC restricts the densification of the ceramic matrix by conventional techniques because of the constraint on shrinkage of the matrix by the reinforcing fibers. Thus, sintering approaches are unable to produce fully dense CMC's and different processing methods are necessary to develop a dense matrix of CMC.

Processing techniques such as filament winding/densification, lamination plus densification, sol-gel infiltration followed by densification, chemical vapor infiltration and reaction, polymeric ceramic precursor infiltration and pyrolysis, resin transfer molding and melt infiltration have been developed to fabricate the CMCs. These techniques have been reviewed in this report, which can be utilized to produce either oxide or non-oxide matrix CMCs.

There is a great deal of interest in SiC/SiC or C/SiC composites for NASA propulsion system applications. SiC fibers are very expensive with prices ranging from $3,500 to $10,000 per kg. If carbon fibers can be utilized with appropriate fiber coatings, the production cost of the SiC CMCs can be significantly lowered. Further, a combination of different processing techniques can lead to low-cost SiC based CMCs of improved mechanical strength and fracture toughness characteristics. A research and development program to evaluate the use of carbon fibers with multilayer protective coatings against attack in oxidative environments, CTE mismatch and slippage against the matrix and to develop a hybrid process for C/SiC composites is highly recommended.

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References:

1. J. Llorca and R. N. Singh, J. Am. Ceram. Soc., 74[11], 2882-90 (1991).
2. A. G. Evans, J. Am. Ceram. Soc., 73[2], 187-206 (1990).
3. Y. L. Wang, U. Anandkumar, and R. N. Singh, J. Am. Ceram. Soc., 83[5], 1207-14 (2000).
4. M. D. Thouless and A. G. Evans, Acta Metall., 36, 517-22 (1988).
5. B. N. Cox, Acta Metall. Mater., 39, 1189-201 (1991).
6. J. A. Celemin, J. Y. Pastor, L. Llorca, U. Anandkumar, and R. N. Singh, Comp. Sci. and Tech., 59, 253-262 (1999).
7. J. A. Cornie, Y. M. Chiang, D. R. Uhlmann, A. Mortensen, and J. M. Collins, Ceramic Bull., 56[2], 293-304 (1986).
8. K. Chawla, Composite Materials, p. 213-226, Springer, New York (1998).
9. R. A. J. Sambell, D.H. Bowen, and D.C. Phillips, J. Mater. Sci., 7[6], 663-75 (1972).
10. R. A. J. Sambell, A. Briggs, D.C. Phillips, and D.H. Bowen, J. Mater. Sci., 7[6], 676-81 (1972).
11. D. C. Phillips, J. Mater Sci., 9[11], 1847-54 (1974).
12. D. C. Phillips, J. Mater Sci., 7[10], 1175-91 (1972).
13. J. J. Brennan and K. M. Prewo, J. Mater. Sci., 17[8], 2371-83 (1982).
14. K. M. Prewo and J. J. Brennan, J. Mater. Sci., 15[2], 463-68 (1980).
15. J. K. Guo, Z. Q. Mao, C. D. Bao, R. H. Wang, and D. S. Yan, J. mater. Sci., 17, 3611-16 (1982).
16. Y. Hasegawa, M. Iimara, and S. Yajima, J. Mater. Sci., 15, 720-28 (1980).
17. R. West, L. D. David, P. I. Djurovich, H. Yu, and R. Sinclair, Am. Ceram. Soc. Bull., 62[8], 899-903 (1983).
18. D. Seyferth and G. H. Wiseman, J. Am. Ceram. Soc., 67[7], C132-C133 (1984).
19. D. Seyferth and G. H. Wiseman and C. Prud'honne J. Am. Ceram. Soc., 66[1], C13-C14 (1983).
20. W. S. Coblenz, C. H. Wiseman, P. B. Davis, and R. W. Rice, pp 271-85, in Emergent Process Methods for High-Technology Ceramics, Ed: R.F. Davis, H. Palmer III, and R,L. Porter, Plenum, New York (1984).
21. J. J. Lannutti and D. E. Clark, Cerm. Eng. Sci. Proc., 5[7-8], 574-82 (1984).
22. J. Jamet, J. R. Spann, R. W, Rice, D. Lewis, and W. S. Coblenz, Cer. Eng. Sci. Proc., 5[7-8], 677-94 (1984).
23. Starfire Systems, 877 25th Street, Watervliet, NY 12189.
24. G. Ziegler, I. Richter, and D. Suttor, Composites A30, 411-417 (1999).
25. A. W. Urquhart, Mater. Sci. Eng., A144, 75 (1991).
26. J. W. Warren, Cerm. Eng. Sci. Proc., 5[7-8], 683-93 (1985).
27. J. W. Warren, Eoropian Pat. Applcation 021797, March 9 (1984).
28. R. Naslain and F. Langlais, Conf. on Tailoring Multiphase and Composite Ceramics, Penn. State Univ., July (1985).
29. A. J. Caputo and W. J. Lackey, Ceram. Eng. Sci. proc., 5[7-8], 654-67 (1984).
30. A. J. Caputo, W. J. Lackey, and D. P. Stinton, Ceram. Eng. Sci. proc., 6[7-8], 694-706-67 (1985).
31. S. Vaidyaraman, W. J. Lackey, and P. K. Agrawal, Carbon, 34[5], 609-617 (1996).
32. J. W. Lucek, G.A. Rosetti, and S. D. Hartline, unpublished work.

33. N. D. Corbin, G. A. Rosetti, and S. D. Hartline, Am. Ceram. Soc. Bull., 64[12], 1539 (1985).
34. R. Y. Lin, J. Economy, and H. D. Batha, Am. Ceram. Soc. Bull., 55[9], 781-84 (1976).
35. W. B. Hillig, J. Am. Ceram. Soc., 71, C-96 (1988).
36. K. L. Luthra, R. N. Singh, and M. K. Brun, Am. Ceram. Soc. Bull., 72, 79-85 (1993).
37. K. L. Luthra, R. N. Singh, and M. Brun, in High Temperature Ceramic Composites, Proc. Of 6th European Conf, on Composite Materials, Bordeaux, France (1993), Ed: R. naslain, J. Lemon, and D. Doumeing.
38. R. N. Singh and A. R. Gaddipati, US Patent # 4889686 (1989).
39. R. N. Singh and W. A. Morrison, US Patent # 4944904 (1990).
40. M. P. Borom, W. B. Hillig, R. N. Singh, W.A. Morrison, and L.V. Interrante, US Patent # 5015540 (1991).
41. M. Singh and D. R. Behrendt, Mat. Sci. & Eng., A 194, 193-200 (1995).
42. D. R. Berendt and M. Singh, J. Mater. Synth. Proc., 2, 133-39 (1994).
43. J. J. Brennan, Acta Mater 48, 4619-4628 (2000).
44. R. P. Messner and Y. M. Chiang, J. Am. Ceram. Soc., 73, 1193-1200 (1990).
45. K. N. Shivakumar, V. S. Avva, M. J. Sudersan, F. L. Abali, A. Cunningham, and R. L. Sadler, US Patent # 6325608 (2001).
46. F. Abali, K. Shivakumar, N. Hamidi, and Robert Sadler, An RTM Densification method of Manufacturing Carbon-carbon Composites Using primaset PT-30 Resin, CARBON Journal, 2002.