

Recent Advances in Forced-Flow, Thermal-Gradient, CVI for Refractory Composites

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Abstract:

Chemical vapor infiltration (CVI) is simply chemical vapor deposition (CVD) on the internal surfaces of a porous preform and has been used to produce a variety of developmental and application materials. The greatest use of CVI is to infiltrate continuous filament preforms taking advantage of the relatively low-stress CVD process. In CVI, reactants are introduced in the porous preform via either diffusion or forced convection and the CVD precursors deposit the appropriate phase(s). As infiltration proceeds, the deposit on the internal surfaces becomes thicker. Thus, after some length of time, the growing surfaces meet bonding the preform and filling much of the free volume with deposited matrix. The forced-flow/thermal-gradient technique (FCVI) developed at Oak Ridge National Laboratory (ORNL) overcomes the

problems of slow diffusion and restricted permeability and has demonstrated a capability to produce thick-walled, simple-shaped, SiC-matrix components in times of the order of hours. A model has been developed for the process that predicts flow, thermal, and density profiles as a function of time. The results have been compared to an initial set of experiments and indicate qualitative agreement. It is expected that improved property relationships, such as permeability and thermal conductivity as a function of density, will allow the model to closely represent the FCVI process and be useful in fabrication and product optimization.

1. Introduction

Chemical vapor infiltration (CVI) is simply chemical vapor deposition (CVD) on the internal surfaces of a porous preform and has been used to produce a variety of developmental and application materials. The greatest use of CVI is to infiltrate continuous filament preforms taking advantage of the relatively low-stress CVD process.

Chemical vapor infiltration originated in efforts to densify porous graphite bodies by infiltration with carbon.¹ The technique has developed commercially such that half of the carbon/carbon composites currently produced world-wide are made by CVI (the remainder are fabricated by curing polymer impregnated fiber layups). The earliest report of CVI for ceramics was a 1964 patent for infiltrating fibrous alumina with chromium carbides.²

In CVI, reactants are introduced in the porous preform via either diffusion or forced convection and the CVD precursors deposit the appropriate phase(s). As infiltration proceeds, the deposit on the internal surfaces becomes thicker. Thus, after some length of time, the growing surfaces meet, bonding the preform and filling much of the free volume with deposited matrix.³

The major advantage CVI has over competing densification processes is the low thermal and mechanical stress to which the relatively sensitive fibers are subjected. Chemical vapor I infiltration can occur at temperatures much more moderate than the melting point of the deposit, and therefore, usually well below the sintering temperature. In addition, the process imparts little mechanical stress to the preform as compared to more traditional techniques such as hot pressing.

The most widely used commercial process is isothermal/isobaric CVI (ICVI) which depends only on diffusion for species transport. It generally operates at reduced pressure (1-10 kPa) for

deposition rate control. This diffusion-dependent process is slow, requiring several, week-long infiltration times. It is commercially attractive, however, because large numbers of parts of varying dimensions are easily accommodated in a single reactor.

The forced-flow/thermal-gradient technique (FCVI) developed at Oak Ridge National Laboratory (ORNL) overcomes the problems of slow diffusion and restricted permeability, and has demonstrated a capability to produce thick-walled, simple-shaped, SiC-matrix components in times of the order of hours.⁴⁻⁶

Chemical vapor infiltration is a maturing technology with specialty manufacturing in place and the emergence of broader markets imminent. A number of recent advances have made the technology more attractive and provided a broader base for applications. These include obtaining an understanding of fiber-matrix interface chemical and thermomechanical issues,⁷ ability to design preforms for specific applications,⁸ and development of process models for use in optimization. This paper will review some current efforts in FCVI process modeling and the development of a technologically useful geometry, a ceramic composite tube prepared by FCVI.

2. Fundamentals of CVI

During CVI, the primary objective is to maximize the rate of matrix deposition and minimize density gradients. Unfortunately, there is an inherent competition between the deposition reaction and the mass transport of the gaseous reactant and product species. The most common ceramic matrix is SiC, and its deposition via the thermal decomposition of methyltrichlorosilane (MTS) will be considered the model system for the current discussion.⁹⁻¹¹

Deposition reactions that are too rapid usually result in severe density gradients where there is essentially complete densification near the external surfaces and much lower densities in the

interior regions. Alternatively, exceptionally slow deposition reactions require an uneconomically long time to densify a part. Control of temperature is critical because chemical reactions exhibit Arrhenius behavior such that the rates increase exponentially with temperature. Therefore, relatively low temperatures slow the deposition rate substantially more than does diffusion. Alternatively, low pressure decreases concentration and the diffusive flux to the deposition surface. The deposition down the length of a pore provides a simple model of this problem, and the effect of the CVI parameters of temperature and total pressure can be clearly seen in the review by Naslain.⁷ Assuming a first-order reaction for the simulation of the deposition of SiC, deposit thickness profiles show smaller gradients at lower temperature and pressure.

Several CVI efforts have described non-isothermal, non-isobaric processes. In these systems, there are additional complexities associated with heat transfer and forced convection as infiltration proceeds and the pore structure of the material changes. To accurately describe infiltration behavior, descriptions of the complexities associated with these transport processes should be combined with the complex microstructure evolution and chemical kinetics. Regardless of these complexities and the current inability to fully describe them, understanding the general relationships between the relevant kinetic processes has led to the practical solution of many CVI problems. Simple reactant gas depletion within the CVI reactor or poisoning of the deposition process by reaction by-products (e.g., HCl in the CVI of SiC from MTS) also reduces the deposition rate.¹² In the thermal gradient process, controlling the temperature difference prevents the gas entrance surfaces from becoming sealed until after the interior of the component has reached an acceptable density.⁶ Figure 1 illustrates the competition between temperature and

depletion/HCl formation in the infiltration of SiC from MTS. Depletion is defined as the percent of input MTS consumed in depositing SiC, and the resultant production of HCl via the reaction:



The rates computed for the curves use the more complex kinetic expressions that include the “poisoning” effect of HCl¹², and we can see the strong effect of depletion (Fig. 1). It is this type of competitive relationship that permits high-density composites to be prepared by the non-isothermal, non-isobaric processes.

3. Modeling CVI

The modeling of CVI involves the mathematical description of transport and reaction phenomena within a simulation domain. Fundamental processes to be modeled include heat transfer by conduction, convection, and radiation; transport and reaction of gaseous reactant species; and pressure-driven gas flow. Differential equations representing these phenomena can be written in the following steady-state form:

$$\nabla(\mathbf{r}u\mathbf{f}) = \nabla \cdot (\Gamma \nabla \mathbf{f}) + S \quad [2]$$

Where \mathbf{f} is temperature, pressure, or concentration, u is the gas velocity, \mathbf{r} and Γ are constants and S is a source term. Using the finite volume method of Patankar,¹³ the discretized version of this equation is solved over the simulation domain that is divided into control volume elements.

3.1 Heat Transfer

The heat-transfer equation contains both diffusion and convection components and a source term such that

$$\nabla(C_p u T) = \nabla \cdot (K \nabla T) + S \quad [3]$$

where C_p is the heat capacity of the flowing gas and K is the thermal conductivity of the material. The source term S contains any heat generated or absorbed by a volume element such as the heat from chemical reactions. This source term will also be used to account for thermal radiation.

Calculation of the diffusive and convective contributions to the heat balance for each volume element is straightforward given the flow rate and heat capacity of the gas, the thermal conductivities of the materials, and the thermal boundary conditions. The heat-flux terms for each volume element depend only on these quantities and on the temperatures of adjacent volume elements. Since the radiation contribution may depend on the temperatures of nonadjacent volume elements, it cannot be included as a flux term in the same manner. Instead, the radiation contribution is calculated and included as a source term. Based on the discretization of the simulation domain, a ray-tracing program calculates the view factors of the control volume surfaces. During the solution of the heat-transfer equation, the view factors are used to calculate the energy exchange between the radiating surfaces by standard formulas based on the nodal temperatures. To obtain a self-consistent solution, several iterations of the heat transfer equation are required to incorporate the nonlinear behavior of the radiant energy exchange.

3.2 Mass Transport and Reaction

The flow of the carrier gas and the concentrations of reacting species are determined by differential equations in the form of equation [2]. For pressure-driven gas flow

$$\nabla \cdot \left(\frac{k}{\mu V} \nabla P \right) = 0 \quad [4]$$

where k is the Darcy permeability for the material of each volume element, V is the gas molar volume, P is the total pressure, and μ is the gas viscosity. This formulation of gas transport does not include source or convective (inertial) terms. It will not be accurate for high-velocity gas flow in open reactors but is suitable for the pressure-driven gas flow through semi-permeable materials, as is the case for FCVI. The transport equation for the reacting species includes convection, diffusion, and source terms,

$$\nabla(u C_i) = \nabla \cdot (D_i^{\text{eff}} \nabla C_i) + S \quad [5]$$

where C_i is the species concentration and D_i^{eff} is the effective diffusion coefficient for species i . Both MTS and HCl concentrations are included in the transport rates. The SiC matrix is deposited on the fiber surfaces throughout the preform volume. The matrix deposition rate depends on the temperature and concentrations of both species.

The coupled systems of differential equations for temperature, pressure, and chemical species concentration are solved in the steady state. For a selected time increment, the local reaction rate is used to calculate a new density for each preform volume element. A new steady-

state solution is then calculated and the density incremented again producing a series of "snapshots" of the densification process.

4. Modeling Tubular Geometry for FCVI

The model has been applied to a system for preparation of composite tubes by FCVI. The preform is made up of concentric layers of NextelTM 312 (alumino-borosilicate fiber, 3M Company, Minneapolis, MN) fibrous tubular sleeves. The model calculations are performed in cylindrical geometry due to its ease of use and symmetry. The FCVI experimental reactor configuration used is shown in Fig. 2. A graphite coating chamber radiatively heats the fibrous tubular preform exterior and its interior is cooled with a water-cooled line. The MTS carried in hydrogen is injected inside the preform. The gas mixture infiltrates through the preform thickness and exhausts at atmospheric pressure. Ceramic fiberboard is used to seal the preform ends. Graphite felt insulation is placed on both ends of the preform to reduce axial heat loss.

The reactor configuration shown in Fig. 2 is discretized into a two-dimensional array of finite volume elements. Neglect of the circumferential direction reduces the cylindrical discretization to only radial and axial components. The preform is 37 cm in length and 6.4 mm in thickness with an inside diameter of 5.1 cm, and has a variable fiber volume. The array size chosen for the model domain is 35 radial volume elements by 49 axial volume elements. The preform itself is discretized into four radial and 29 axial volume elements. The reason for only four radial elements through the wall thickness even though there are large thermal and concentration gradients is the inhomogeneity of the material. The 1.6 mm radial elements capture a maximum of three cloth layers, thus smaller elements would not capture sufficient material to make average property values meaningful.

The transport properties for all materials in the model domain are defined in separate material files. The thermal conductivities for the graphite, graphite felt, stainless steel, and ceramic fiberboard are functions of temperature. The gas-mixture heat capacity, viscosity, thermal conductivity, and binary diffusivities of MTS and HCl in hydrogen are also functions of temperature. The thermal conductivity, permeability, effective diffusivity, and surface area of the preform are functions of density. For the calculations used here, the initial specific surface of the preform was arbitrarily assumed to be significantly lower than that determined from the total fiber surface (850 cm^{-1} vs 1500 cm^{-1}) due to fiber tow contacts that limit the available area for matrix deposition.

Several key boundary conditions are applied to the model. A constant temperature of 50°C is assumed along the centerline of the water-cooled line. Both total molar flux and MTS mole fraction are specified at the hydrogen/MTS inlet and atmospheric pressure is fixed at the gas exhaust.

Figures 3-6 describe densification utilizing the CVI model. The baseline FCVI parameters used are:

Coating Chamber Mid-Line Temperature:	1200°C
Hydrogen/MTS Molar Feed Ratio:	5
Total Flow (STP):	6 l/min

The initial temperature profile produced by the model for the unfiltered preform is displayed in Fig. 3. The model utilized boundary values provided by measurements of the temperature of the exterior graphite reactor chamber at three axial positions. The radial temperature gradient is quite uniform along the preform length with a slightly higher radial gradient in the tubular preform

region directly above the injector. Higher temperatures at the preform ends are a function of the fiber-board which insulates those regions from the cooling line.

Figure 4 shows the computed transient radial temperature gradient profile at a nominal axial position. As infiltration proceeds, SiC matrix is deposited throughout the tubular fibrous preform increasing the preform thermal conductivity and reducing the radial temperature gradient.

The computed mass volume (percent density) profile of the composite after 12 hours of infiltration is shown in Fig. 5. The density near the mid-line is greatest due to the initially higher temperatures in this volume causing more rapid SiC deposition. Also seen is an axial asymmetry due to the introduction of the reactant flow into the volume of the tube at the left side, as seen in Fig. 2. After 32 h (Fig. 6), near completion, the density distribution has become more flat, however, the effect of the non-uniform axial temperature profile and the introduction of the precursor flow is still evident. As is the case in FCVI, such nonuniformities will eventually be eliminated as reactants are directed to less infiltrated areas due to their higher permeability.

Utilizing the baseline process parameters, an average mass volume for the tubular components can be predicted as a function of infiltration time. Figure 7 contains plots of the average density of an infiltrated tube as a function of infiltration time under the above-specified conditions. Shown are the results of computations assuming a fiber loading of 35 vol.% for the two initial specific area values, 1500 cm^{-1} and 850 cm^{-1} .

5. Experiment

Several tubular preforms have been infiltrated by FCVI utilizing the standard conditions described above. These tubular preforms were fabricated by pulling concentric Nextel™ 312

braided tubular sleeves (2.75 tows/cm) over a mandrel and rigidized by resin impregnation and curing. The tube preform specifications are:

Inside Diameter:	5.08 cm
Outside Diameter:	6.64 cm
Length	35.6 cm
Fiber Volume	34.4%

Initial temperature measurements were obtained using optical pyrometry at three positions along the length of the reactor chamber: inlet side, 1087°C; mid-line, 1203°C; and outlet side, 1104°C. Infiltration was allowed to proceed for specific time periods and then the reactant flow was replaced with inert gas and the system allowed to cool to room temperature.

6. Results

The results of four experimental runs are given in Table I and Fig. 7. The mass volume is determined from the geometric volume of the component and the weight gain. It is apparent that mass volume, or void fraction, changes nonlinearly with infiltration time. The initial lower slope in the mass volume is due to the steep temperature gradient through the preform that limits deposition of SiC due to the lower temperatures of the inner volume. As infiltration proceeds, the through-thickness thermal conductivity of the component increases with the density, increasing the temperature of the inner volume and allowing more rapid infiltration. Figure 8 is a photograph of a Nextel™ 312 cloth sleeve, a rigidized preform, and a densified tubular composite.

Table 1. Results of FCVI Experimental Runs and Modeling

Identification	Run Time (h)	Observed Avg. Mass Vol.	Predicted Avg. Mass Vol.
CVI 1211	6	45.6%	39.7%
CVI 1223	12	67.6%	54.0%
CVI 1217	24	74.5%	69.6%
CVI 1218	32	78.0%	79.5%

An asymmetry in axial infiltration is seen in the partially infiltrated tubes. These have apparently higher densities near the precursor inlet side due to the tendency for the reactants to initially flow out of the tube through the area of the wall closest to the inlet tube. As infiltration progressed (for the tubes with longer infiltration times), this effect was not as apparent.

Figure 9 is a typical microstructure for a component infiltrated to a relatively high density. The lower magnification image (Fig. 9a) reveals the fiber bundles within the woven material. The white phase is deposited SiC, which is seen to infiltrate and overcoat the bundles. The dark areas are void volume. The oval Nextel™ 312 fibers are apparent at higher magnification (Fig. 9b). The gray phase is some minor amounts of residual carbon that resulted from the pyrolysis of the phenolic resin used to rigidize the preform.

7. Discussion

In this initial work, the comparison between experiment and model of the mass volume infiltrated as a function of time shows reasonable agreement when the smaller value for initial specific area is used (Fig. 7). The model and experiment indicate an early exponential increase in density which after 10 to 12 h undergoes a transition to a slower, monotonic increase that is typically seen in CVI.¹¹ It is at this point the fine porosity within the fiber bundles is either fully infiltrated or the bundle surface is sufficiently sealed so that the high-surface area bundles are no

longer available for deposition. Since the mass deposition rate is proportional to surface area, the result is a sharp decline in the rate of mass gain. Thus, the model accurately represents the onset of this transition.

The predicted axial asymmetry due to the precursor inlet being positioned at one end of the preform appears to be qualitatively observed in the partially infiltrated tubes. This is an effect of the precursor flow predominately following a path through the preform wall closest to the inlet tube. As the density of that region grows disproportionately compared to the downstream volume, its permeability also decreases disproportionately. The result is that, with time, a greater flux of precursor will be directed to the lower density, downstream regions, eventually obtaining uniform densification.

The model results are governed by the material properties input to the computations. These include critical relationships such as the permeability and thermal conductivity of the material as a function of density and orientation. Currently, there is little information with regard to these variables, thus, the relationships were largely based on earlier work with other fiber systems.¹⁴⁻¹⁶ The observed results support the need to improve these relationships which has been one of the objects of the current work.

The model and experimental results both indicate that the mass volume can be increased with greater infiltration times (Fig. 7). The mass volume is, however, ultimately limited by the fiber architecture to approximately 90%.¹⁴⁻¹⁶ This limitation is a feature of the pore-size distribution and structure that causes some porosity to be closed before it can be filled.

8. Conclusions

The modeling efforts for the tubular FCVI system utilizing observed temperature boundaries have indicated a non-uniform, initial densification profile. The profile, however, becomes significantly more uniform with time, as expected, in the self-correcting FCVI process.

The initial experiments have shown that densification generally follows the trends indicated by the modeling results. Discrepancies in the relative values highlight the need to obtain improved property data as a function of density.

As has been the case with the development of FCVI-densified plates, it is expected that the production of high-density tubes should be possible. The current work is encouraging for the relatively high densities already achieved and for the semi-quantitative agreement with the model. Increased accuracy in the model that should result from improved property modules and will allow derivation of processing conditions for more efficient fabrication of high-density tubes.

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Figure Captions:

1. Plot of computed SiC deposition rate versus temperature or percent depletion of 20 mol% MTS in hydrogen illustrating the competing effects.
2. Schematic of the tubular FCVI reactor illustrating the gas flow paths, heat source and centerline cooling.
3. Computed thermal profile within the composite tube wall before the onset of infiltration.
4. Computed average thermal gradient through the wall of the tube as a function of infiltration time.
5. Density profile within the tube wall after 12 hours of infiltration. The fractional values are relative to a full density value of unity, with an initial value of 0.35 indicative of the initial 35% mass volume of fiber.
6. Density profile within the tube wall near completion (32 hours of infiltration).
7. Comparison of computed and experimental percent mass volume (theoretical density) as a function of infiltration time.
8. Photograph of a Nextel™ 312 cloth sleeve, a rigidized preform, and an infiltrated tube.
9. Optical micrographs a polished cross-section of an infiltrated composite at (a) low and (b) high magnification.