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NEAR-NET-SHAPE FABRICATION BY FORCED-FLOW, THERMAL-GRADIENT CVI*

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Forced-flow, thermal gradient chemical vapor infiltration (FCVI) has been developed for the rapid densification of ceramic matrix composites. For preforms of >3 mm thickness FCVI can produce a near-net-shape part in less than one day as opposed to isothermal, isobaric CVI which requires several weeks to densify such a component. Efforts at ORNL and elsewhere have resulted in capability to produce prototypical thick-walled heat exchanger tubes and turbine disk blanks. This paper will review recent modeling and experimental efforts related to the FCVI of cylindrical forms.

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 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

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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. CVI 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 It is the current state of development of this process based on recent work at ORNL that is the subject of this report.

2. FUNDAMENTALS OF MODELING

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.

Deposition reactions which 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.

Several CVI modeling 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 structure of the material changes. For models such as these to accurately describe infiltration behavior, accurate descriptions of the complexities associated with these transport processes will have to 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. 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. 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 reduce the deposition rate.⁷ 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

3. FCVI MODEL

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:

$$\nabla(\rho u \phi) = \nabla \cdot (\Gamma \nabla \phi) + S \quad [1]$$

Where ϕ is temperature, pressure, or concentration, u is the gas velocity, ρ and Γ are constants, and S is a source term. Using the finite volume method of Patankar,⁸ 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:

$$\nabla(C_p u T) = \nabla \cdot (K \nabla T) + S \quad [2]$$

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 also will 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 non-adjacent 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 non-linear 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 [1]. For pressure-driven gas flow,

$$\nabla \cdot \left(\frac{k}{\mu V} \nabla P \right) = 0 \quad [3]$$

where k is the Darcy permeability for the material of each volume element, V is the gas

molar volume, 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,

$$\nabla(u C_i) = \nabla \cdot (D_i^{\text{eff}} \nabla C_i) + S \quad [4]$$

Where C_i is the species concentration and D_i^{eff} is the effective diffusion coefficient for species i . Both MTS and HCl are included in the SiC deposition rate. 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 "snap-shots" of the densification process.

4. MODELING TUBULAR GEOMETRY

The model has been applied to a system for preparation of composite tubes by FCVI. The preform is made up of concentric layers of Nextel™ 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 Figure 1. The fibrous tubular preform exterior is radiatively heated by a graphite coating chamber and its interior cooled with a water-cooled cooling 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 sides of the preform to reduce axial heat loss.

The reactor configuration shown in Figure 1 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 40% 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.

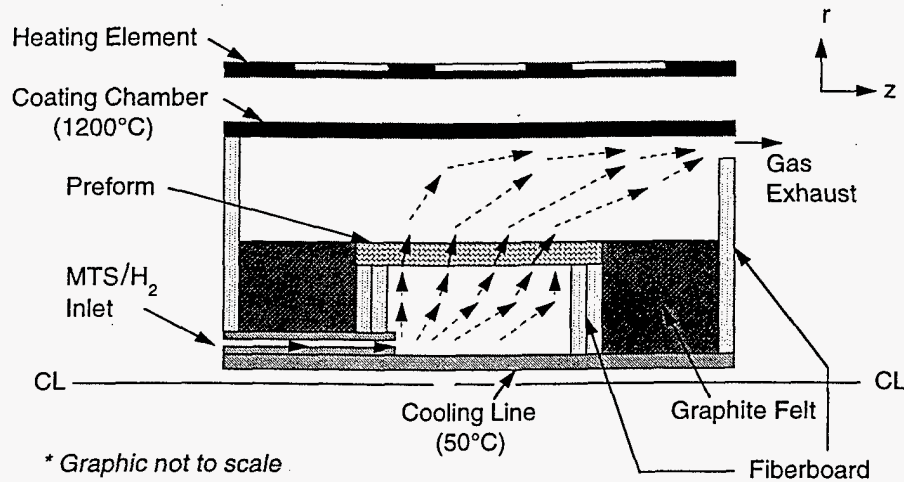


FIGURE 1
The FCVI experimental reactor configuration

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.

Several key boundary conditions are applied to the model. A parabolic temperature profile is imposed on the length of the graphite coating chamber. The coating chamber temperature is 1200°C at the center and 1000°C at the ends. These temperature values describe the thermal profile seen experimentally. 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. Atmospheric pressure is fixed at the gas exhaust and the ends of the domain are specified as adiabatic.

The modeling results presented in this paper investigate three key parameters that influence the FCVI process: The graphite coating chamber temperature; the molar feed ratio of hydrogen to MTS, and the total flow. The external temperature range is 1100°C to 1200°C, the hydrogen/MTS molar feed ratio range is 5 to 10, and the total flow range is 3 to 9 l/min.

Figures 2-5 show the FCVI parameter effects on the transient density. The baseline FCVI parameters used are shown in Table 1.

Table 1

Baseline FCVI parameters

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

Figure 2 shows the coating chamber temperature effect on the transient density profile where increasing the coating chamber mid-line temperature results in higher densities. Figure 3 shows the hydrogen/MTS molar feed ratio effect which indicates that reducing the molar feed ratio results in higher theoretical densities. The effect of the total flow on the transient density profile is seen in Fig. 4 and shows that increasing the total flow results in higher densities.

The initial temperature profile produced by the model is displayed in Figure 5. 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. Little axial temperature gradient is seen throughout the preform length with the exception of the very ends. Both preform ends are at higher temperatures with little radial temperature gradient. This is due to the assumption of adiabatic ends.

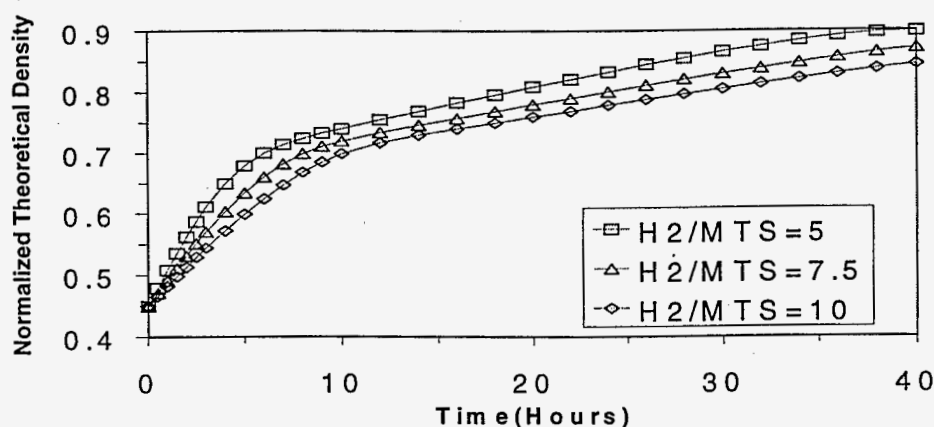


FIGURE 2
Coating chamber mid-line temperature effect on theoretical density

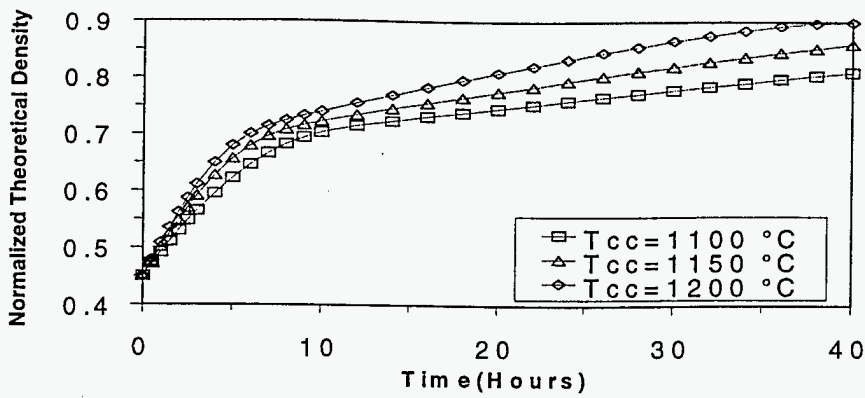


FIGURE 3
Hydrogen/MTS molar feed ratio effect on theoretical density

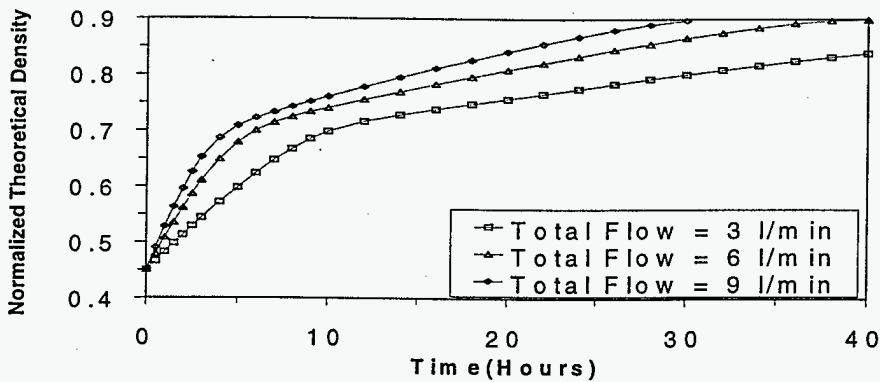


FIGURE 4
Total flow effect on theoretical density.

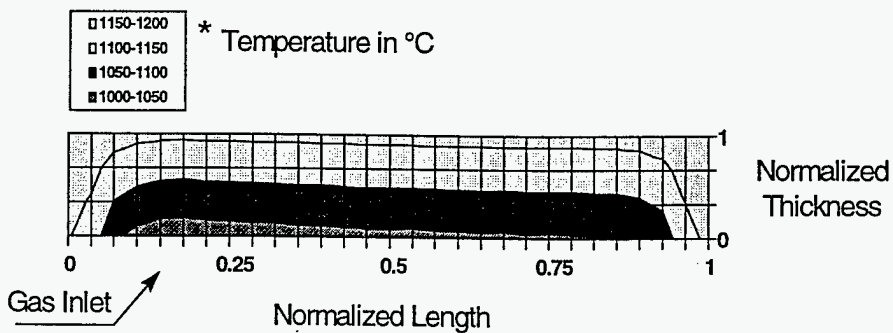


FIGURE 5
Initial temperature profile of the tubular prefor

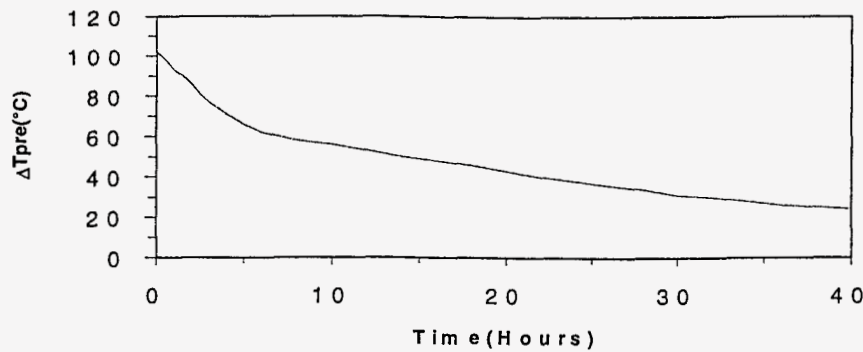


FIGURE 6
Transient temperature gradient profile.

Figure 6 shows the transient radial temperature gradient profile. As infiltration proceeds, silicon carbide matrix is deposited throughout the tubular fibrous preform increasing the preform thermal conductivity and reducing the radial temperature gradient.

Figure 7 displays an uninfiltrated, fibrous tubular preform, a fully infiltrated, dense composite tube, and an individual Nextel™ 312 tubular sleeve. The tubular preform shape is maintained in the composite tube. The tubular preform dimensions, fiber volumes, infiltration times, and theoretical densities for each FCVI-fabricated composite tube are presented in Table 2. For each composite tube, the estimated experimental theoretical density is compared to the model prediction at the given infiltration time.

5. EXPERIMENT

Several tubular preforms have been infiltrated by FCVI. These tubular preforms were fabricated by pulling concentric Nextel™ 312 tubular sleeves over a mandrel and rigidized by resin impregnation and curing. Preform fiber volumes between 40% and 50% were achieved with the tubular preform fabrication techniques utilized.

The FCVI infiltration conditions used were a hydrogen flow of 5l/min, a hydrogen/MTS molar feed ratio of 5, an external temperature of 1200°, and a cooling line temperature of 50°C. The infiltration was conducted until a 100 kPa-backpressure was realized in the preform interior.

6. CONCLUSIONS

FCVI modeling efforts of tubular geometries have identified infiltration conditions necessary to achieve dense composite tubes. Increasing the coating chamber mid-line temperature, decreasing the hydrogen/MTS molar feed ratio, and increasing the total flow will reduce infiltration time and yield higher densities at a given time.

Application of the model infiltration conditions has indicated that dense composite tubes can be fabricated by FCVI. Experimental composite tube theoretical densities between 80% to 94% have been realized. At the corresponding infiltration times, reasonable density agreement between the model and experiment is seen. Future efforts focus on model validation through comparison with experiment. Theoretical density variation at intermediate infiltration times will be compared to model prediction.

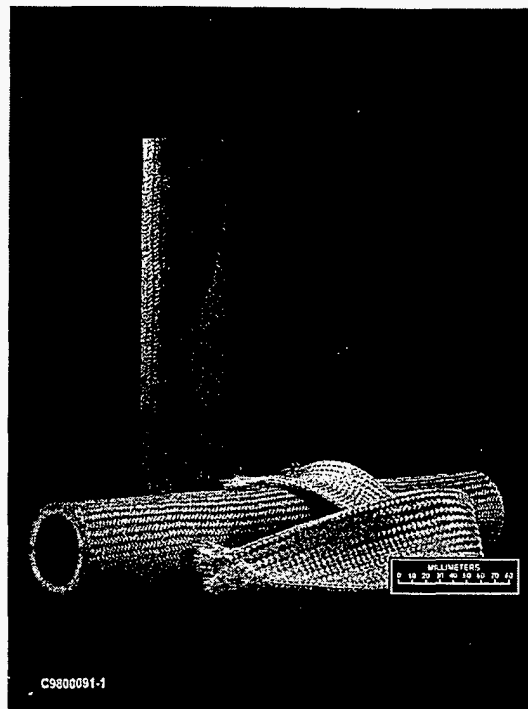


FIGURE 7

An uninfiltred, fibrous tubular preform, dense composite tube, and Nextel™312 tubular sleeve.

Table 2
Summary of FCVI-fabricated composite tubes.

Tube Identification	<u>CVI 1103</u>	<u>CVI 1132</u>	<u>CVI 1173</u>
Inside Diameter	4.8 cm	5.1 cm	5.1 cm
Wall Thickness	6.4 mm	5.1 cm	4.8 cm
Fiber Volume	35%	44%	50%
Infiltration Time	24 Hours	28 Hours	24 Hours
Theoretical Density(Exp.)	80%	75%	87%
Theoretical Density(Mod.)	81%	81%	79%

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