Silicon carbide-based heat exchanger tubes are of interest to energy production and conversion systems due to their excellent high temperature properties. Fiber-reinforced SiC is of particular importance for these applications since it is substantially tougher than monolithic SiC, and therefore more damage and thermal shock tolerant. This paper reviews a program to develop a scaled-up system for the chemical vapor infiltration of tubular shapes of fiber-reinforced SiC. The efforts include producing a unique furnace design, extensive process and system modeling, and experimental efforts to demonstrate tube fabrication.

INTRODUCTION

Fiber-reinforced SiC-matrix composites are candidates for a number of high temperature applications due to their high-temperature strength, high thermal conductivity, light weight, thermal shock resistance, creep resistance, and damage tolerance. However, in the current commercial isothermal, isobaric chemical vapor infiltration process, thick-walled parts are difficult to densify. A leading alternative process is forced chemical vapor infiltration (FCVI) (1, 2). In FCVI, a preform is placed in a reactor where one side is heated and the other side is cooled, resulting in a thermal gradient across the preform. The reactant gases are constrained to flow from...
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
the cooled to the heated side, undergoing a surface, chemical vapor deposition reaction forming the ceramic matrix and an effluent gas. In the case of SiC deposited from chlorosilanes, the effluent HCl gas, has a poisoning effect on the reaction rate. This poisoning, combined with the depletion of the reactant, tends to retard the deposition rate. However, since the gases are traveling toward the hot side of the preform their temperature increases, resulting in faster deposition rates due to the Arrhenius behavior of the deposition reaction. Control over deposition is thus maintained by using the increase in temperature to offset reactant depletion and effluent gas buildup and poisoning effect.

In the current work, emphasis is on the development of composites with tubular geometries. In order to demonstrate the fabrication of a prototypical tube, the efforts have centered on component diameters approaching 100 mm with a 6.4 mm wall thickness. As a result, a unique furnace system was designed and constructed that facilitates the FCVI of such tubes with lengths of 300 mm. Supporting the developmental effort has been extensive process modeling which has successfully described and aided in the optimization of the FCVI of composite plates (3,4).

CVI MODEL

The modeling of CVI involves the mathematical description of transport and reaction phenomena within a simulation domain. The simulation domain for the tube FCVI system includes the fibrous preform, fixturing, and open gas space. The open spaces include the gas injection system and the area between the preform and the heating element. Fundamental processes to be modeled include heat transfer by conduction, convection, and radiation, transport and reaction of gaseous reactant species, and pressure-driven flow of the gas. Differential equations representing these phenomena can be written in the following steady-state form:

$$\nabla(\rho u \phi) = \nabla \cdot (\Gamma \nabla \phi) + S$$

where $\phi$ is temperature, pressure, or concentration, $u$ is the gas velocity, $\rho$ and $\Gamma$ are constants, and $S$ is a source term. Using the finite volume method of Patankar (5), the discretized version of this equation is solved over the simulation domain which is divided into control volumes.

Heat Transfer

The heat transfer equation contains both diffusion and convection components, and a source term:

$$\nabla(C_p u T) = \nabla \cdot (K \nabla T) + S$$
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 the volume element, such as heat from chemical reactions or from absorption of microwave energy. This source term also will be used to account for the 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 the adjoining volume elements. Since the radiation contribution may depend on the temperatures of more distant volume elements, these cannot be included as flux terms in the same manner. Instead, these are calculated and included as a source term. To do this a ray tracing program is coupled to the main finite-volume program as a pre-processing step. Based on the discretization of the simulation domain the ray tracing program calculates the view factors of the control volume surfaces. The view factors are then stored for later use. 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. The radiant energy is then added as a source term to the heat flow equation. To obtain a self-consistent solution several iterations of the heat flow equation are required to incorporate the non-linear behavior of the radiant energy exchange.

**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,

\[
\nabla \cdot \left( \frac{k}{\mu V} \nabla p \right) = 0
\]  

where \( k \) is the Darcy permeability for the material of each volume element, \( V \) is the gas molar volume, and \( \mu \) 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,

\[
\nabla (u \ C_i) = \nabla \cdot (D_{i,eff} \nabla C_i) + S
\]  

where \( C_i \) is the species concentration and \( D_{i,eff} \) is the effective diffusion coefficient for
Two species are included in the relationship for SiC deposition, methyltrichlorosilane (MTS) and HCl. The MTS is the input species which decomposes into solid SiC which deposits on the preform fibers and gaseous HCl, which is a by-product. The matrix deposition rate depends on the concentrations of both species. The carrier hydrogen, while playing a catalytic role, is not considered.

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.

MODELING TUBULAR GEOMETRY

In a preliminary effort, the CVI model has been applied to a system for preparation of tubular composites by FCVI. The preform is made up of seven layers of Nextel 312™ (alumino-borosilicate fiber, 3M Company, Minneapolis, MN) cloth. The calculations are performed in cylindrical geometry due to its ease of use and symmetry. The preform, fixturing, and open gas space are discretized into a grid of radial and axial volume elements. No discretization in the θ-direction is considered. The grid size chosen for the modeling domain is 31 radial volume elements by 49 axial volume elements. The preform itself is discretized into six radial volume elements and 29 axial volume elements. The preform is 37 cm in length and 6.4 mm in thickness with an inside diameter of 4.8 cm, and has a 40% fiber volume.

The transport properties for all materials in the modeling domain are defined in separate material files. The thermal conductivities for the graphite, stainless steel, preform, and ceramic fiberboard which make up the structure of the system are functions of temperature. The hydrogen heat capacity, viscosity, and binary diffusivities of MTS and HCl in hydrogen are also functions of temperature. The thermal conductivity, permeability, and surface area of the preform are functions of fractional density.

Several key boundary conditions are applied to the model. The preform is heated by a cylindrical furnace which surrounds it and is lined with a graphite coating chamber. The thermal gradient is imposed by a stainless steel cooling line that is positioned along the centerline of the system. The temperatures of the graphite coating chamber and stainless steel cooling line are fixed. The total molar flux and mole fraction of MTS are specified at the gas inlet, which is at the centerline on the left side of the preform. Atmospheric pressure is fixed at the gas exhaust and the ends of the domain are specified as adiabatic.

The modeling considered in this paper investigates three key parameters that affect the CVI process: The temperature of the graphite coating chamber; the ratio of
hydrogen to MTS (alpha), and the hydrogen flow rate. The temperature range is 1100°C to 1200°C, the alpha range is 5 to 10, and the hydrogen flow rate range is 2.5 to 7.5 l/min.

Figure 1 shows the preform density profile after 24 hours of infiltration at the baseline modeling parameter values of 1200°C, an alpha of 5, and a hydrogen flow rate of 5 l/min. The profile represents a longitudinal section of the tube with the hot side at the top and the cooled side at the bottom. $\tau$ is the dimensionless thickness and $\eta$ is the dimensionless length. Figure 2 illustrates an increase in alpha to 10 and Fig. 3 uses a hydrogen flow rate of 7.5 l/min. Figures 4 and 5 show preform temperature profiles at the baseline conditions at the start of infiltration and after 12 hours, respectively.

The density profiles in Figs. 1-3 show approximately the same radial and axial gradients. The densities are highest at $\tau=1$ and $\eta=0$ and 1. The fractional density is higher in these areas because of the higher temperature. The higher temperature at the ends is due to the graphite felt insulation placed just outside the preform. In Fig. 2, the absolute density values are somewhat lower across the preform. The higher alpha used in Fig. 2 lowers the MTS concentration in the gas phase and thus lowers the SiC deposition rate. Due to the greater reactant flux, the absolute densities in Fig. 3 are slightly higher than those of Fig. 1.

In Fig. 4, the temperature gradient across the preform thickness at $\eta=0.5$ is about 80°C. At lower $\eta$, near the gas inlet, the gradient is greater due to the radial convective gas cooling. Figure 5 shows the temperature profile after 12 hours of infiltration. The radial temperature gradient is reduced to 50°C due to enhanced radial heat conduction by the SiC matrix in the gas inlet region.

EXPERIMENT

An initial infiltration experiment has been attempted utilizing a tubular preform of the same material and dimensions as that described in the modeling efforts. The Nextel™ preform was rigidized by impregnation with a resin to prevent it from sagging in the horizontal furnace. The infiltration conditions utilized were a hydrogen flow of 5 l/min, an alpha of 4.5, a coating chamber temperature of 1200°C, and a centerline coolant temperature of 50°C. The infiltration time was 24 hours.

Figure 6 is a photograph of the tube showing that, at least superficially, it is well-infiltrated. The average fractional density based on weight is approximately 80%. However, adjustments for the somewhat heavy overcoating of the inner surface of the tube may cause some uncertainty. The model estimated an average preform fractional density of 76% after 24 hours of infiltration.
CONCLUSIONS

The efforts to model the FCVI of tubular geometries has indicated generally successful conditions for infiltration. Decreasing the coating chamber temperature increases the densification time. This reduces the temperature across the preform, causing slower deposition rates. Increasing alpha also increases the densification time. At higher hydrogen flow rates, the densification time decreases. However, a higher gas flow imposes a higher temperature gradient near the gas inlet.

Application of the modeling conditions to experiment gave initial indications that high quality composite tubes can be fabricated, which is also indicated by the experimental results. Future efforts will be focused on better validating the model through comparison with experiment, optimizing processing time and composite density, and increasing the preform outer diameter to 10 cm.

ACKNOWLEDGEMENTS

The comments and suggestions of T. N. Tiegs and L. L. Snead are gratefully acknowledged. This research was supported by the U. S. Department of Energy, Office of Fossil Energy, Advanced Research and Technology Development Materials under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

REFERENCES


Figure 1: Density profile at baseline conditions.

Figure 2: Density profile when alpha = 10.

Figure 3: Density profile when hydrogen flow rate = 7.5 l/min.
Figure 4: Baseline temperature profile at the start of infiltration.

Figure 5: Baseline temperature profile after 12 hours of infiltration.

Figure 6: Photograph of Nextel 312™, SiC matrix composite tube fabricated by FCVI.