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**MODELING OF FORCED CVI
FOR TUBE FABRICATION**

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INTRODUCTION

The forced flow/thermal gradient chemical vapor infiltration process (FCVI) can be used for fabrication of tube-shaped components of ceramic matrix composites¹. Recent experimental work at Oak Ridge National Laboratory (ORNL) includes process and materials development studies using a small tube reactor for tubes 20 cm long and 2.5 cm ID². Adaption of FCVI for this geometry involves significant changes in fixturing as compared to disk-shaped preforms previously fabricated. We have used our computer model of the CVI process to simulate tube densification and to identify process modifications that will decrease processing time.

MODEL DEVELOPMENT

Our "finite volume" method for modeling of FCVI has been described previously³. It involves dividing the CVI system into an orthogonal array of volume elements. A value for each process parameter (temperature, pressure or reactant concentration) is specified at the grid point located at the center of each volume element. This array of discrete values approximates the real, continuous variation of the temperature, of the pressure and gas flow, and of the reagent concentration and reaction rate over the region of interest. A series of steady-state solutions to this model produces a simulation of the densification process.

Modeling of Radiant Heat Transfer

For the tube infiltration system at ORNL (Figure 1) heating of the preform is accomplished primarily by radiation from the hot reactor wall which is held at a set temperature. Earlier versions of our CVI model included only

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conductive heat transfer, which proved suitable for disk infiltration where radiative effects are minor.

Radiant heat flux, q , between two non-reflecting solid surfaces separated by a non-absorbing medium is given:

$$q = F_{12} \sigma (T_1^4 - T_2^4)$$

where T_1 and T_2 are the surface temperatures, σ is the Stefan-Boltzmann constant and F_{12} is the "view factor" relating the two surfaces. This heat flux is in addition to that resulting from conduction through the medium between the two surfaces.

One method of including radiation effects is to artificially increase the thermal conductivity of the medium, thus increasing the conductive flux to account for radiation. While suitable for simple geometries this method cannot be applied in a general way to more complex geometries. We have modified our CVI model to correctly calculate view factors between surfaces separated by a gas space and to include the resulting flux in the energy balance for these volume elements.

Figure 1. ORNL system for CVI of tube-shaped components.

Figure 2. ORNL tube densification system is modeled using a 20x20 grid.

Comparison to Experimental Temperature Measurements

The model predicted temperature profile has been compared to experimental measurements. Figure 2 shows the finite volume grid for the ORNL tube infiltration system which features a cooling tube through the center of the tube, a gas injector located at the mid-point and the fiber preform wrapped onto a porous graphite mandrel. (Note that the radial and axial directions in the figure use different scales.) The region between the gas

injector and the mandrel can include a graphite gas distributor, insulation or simply empty gas space. Heat transfer through this region has a major effect on the temperature profile through the preform.

Temperature measurements at ORNL were made by inserting three thermocouples between the mandrel and the preform at different positions along the tube length, and by directing an optical pyrometer at the outer surface of the preform. This arrangement does not allow concurrent monitoring of the furnace temperature. For the configuration where the space between the gas injector and the mandrel is empty, a preform surface temperature of 1180°C resulted in a temperature of 739, 703 and 740°C at the bottom, middle and top of the preform inner diameter⁴.

The thermal model for the CVI system uses the thermal conductivities shown in Table 1 for the graphite mandrel and reactor fixturing, the preform and the gas. The boundary conditions for the temperature model are somewhat uncertain. We set a fixed temperature of 50°C along the inner diameter of the model and adiabatic boundaries at the

Table 1. Thermal conductivities for thermal model of tube CVI system.

MATERIAL ID	THERMAL CONDUCTIVITY W/CM/K
graphite	0.40 T ^{0.29}
preform (30% fiber)	0.01
gas (H ₂)	0.004

top and bottom. The temperature at the outer diameter of the model, corresponding to the furnace heating element, is also fixed, but the value for this temperature is adjusted to produce a temperature at the preform surface that matches experimental observation.

A furnace temperature of 1275°C produces the temperature profile shown in Figure 3. The temperatures at the preform surface and at the mandrel-preform interface show reasonably good agreement with experimental measurements. However, the temperature variation from top to bottom does

Figure 3. Model temperature profile is a good match to experimental measurements.

not match experiment. In the model, the temperature in the middle of the tube is somewhat higher than that at the two ends. The experimental values above show the middle to be about 36°C cooler than the top and bottom. This discrepancy may be due to model approximations involving the tube ends. In the model, the tube ends are cooled by direct contact with the graphite endcaps which form a high thermal conductivity path to the water cooling in the tube center. In the actual experimental configuration, the thermal contact

between the tube ends and the endcaps is not perfect and produces less cooling of the tube than indicated in the model.

TUBE DENSIFICATION

Using the thermal model described above the densification process can be simulated. Process control parameters include the temperature of the furnace, the overall gas flow rate and the concentration of methyltrichlorosilane (MTS) in the infiltration gas. We have examined four sets of processing conditions, as described in Table 2.

Table 2. Four sets of processing conditions are modeled.

	A	B	C	D
Furnace temperature (C)	1275	1250	1250; 1300 after 10 hours	1300
H ₂ flow (sccm)	630	1000	1000	2000
H ₂ /MTS	10	6	6	6

Set A corresponds to process conditions used at ORNL early in 1993. Densification times under these conditions were found to be very long, greater than 60 hours. Model results agree with experiment, as shown in Figure 4, showing only about 80% full density after 40 hours of processing.

Figure 5 shows intermediate density profiles for the tube after 20 and 58 hours of infiltration. The lower density near the top and bottom of the tube results from the lower model temperatures at these positions. As seen previously with disk-shaped preforms, the temperature at the cool side (ID)

Figure 4. Densification time varies with different processing conditions.

Figure 5. Model shows density variation in tube after 20 hours (left) and 58 hours (right) for the initial gas flow and composition.

Figure 6. Midpoint temperature at the cool side of the tube preform rises as density increases.

of the preform rises as density increases (Figure 6) producing an increase in densification rate in this area later in the run.

Examination of the reactant concentration at the outlet of the reactor for these process conditions suggests that the densification rate is limited by depletion of the reactant. Examination of Figure 7 indicates that nearly 90% of the MTS introduced into the system is converted to matrix material. Thus, the densification rate is limited by the MTS flow rate.

This is confirmed by the following calculation. For a tube preform 0.7 cm thick and 30% fiber loading, 102 cm³ of matrix is needed to reach full density. The given flow conditions correspond to 0.46 g/min MTS or 2.3 cm³/hr of SiC at 100% utilization. Thus, the minimum time to full density is 44 hrs.

Set B corresponds to more recent experiments at ORNL with higher MTS and H₂ flow rates and a slightly lower furnace temperature. Model densification time matches observed time of 40 hours. Although the utilization of MTS is lower on a percent basis, the higher overall flow yields more rapid densification.

Figure 7. MTS utilization varies with time and processing conditions.

PROCESS OPTIMIZATION

"Optimized" process parameters should yield high strength material densified in a short time and with efficient reagent use. The requirement of high strength material yields two process limitations: 1) limit the temperature in the composite to 1200°C to avoid thermal degradation of fiber properties, and 2) maintain H_2 :MTS ratio greater than 5 to avoid deposition of free silicon.

The furnace temperature of 1250°C yields a maximum temperature in the composite that is lower initially than the 1200°C limit and decreases further as the composite becomes more dense (Figure 8).

Conditions C and D correspond to adjusted conditions that should produce reduced processing times. In set C we see the effect of increasing the furnace temperature by 50°C after 10 hours of processing. Densification time is reduced by approximately 5-6 hours and the highest temperature in the

Figure 8. Temperature at tube O.D. decreases during run as density increases.

composite rises above 1200°C only briefly. Set D corresponds to a higher temperature from the beginning of the process and a doubling of the gas flow rate. The corresponding densification time is about 20 hours (Figure 4). Although the temperature in the composite is slightly higher than 1200°C initially, it drops below this limit after 6 hours of processing (Figure 8). Initially between 80-90%, MTS utilization drops below 60% after 10 hours of processing.

SUMMARY

These model runs suggest a strategy for optimizing and controlling the tube CVI process. Since the thermal conductivity of the composite increases during densification, the outer diameter of the tube grows progressively cooler. To maintain a high deposition rate throughout the run the furnace temperature should be increased so as to maintain the highest permissible temperature at the tube O.D. (1200°C for Nicalon). The overall gas flow rate then is adjusted

to yield approximately 80% MTS utilization. Higher MTS use would reduced densification rate due to reagent depletion while lower MTS use would increase material and cleanup costs. We plan to use this strategy with the model to select an "optimum" process profile including temperature and gas flow variation. Experimental measurement of preform temperature and outlet gas composition may be useful process monitors for tube CVI.

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