RAPID FABRICATION OF CERAMIC COMPOSITE TUBES USING CHEMICAL VAPOR INFILTRATION

T.L. Starr and D. Chiang
School of Materials Science and Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0245

T.M. Besmann, D.P. Stinton, J.C. McLaughlin and W.M. Matlin
Oak Ridge National Laboratory
Oak Ridge, TN 37831

ABSTRACT

Ceramic composite tubes can be fabricated with silicon carbide matrix and Nicalon fiber reinforcement using forced flow-thermal gradient chemical vapor infiltration (FCVI). The process model GTCVI is used to design the equipment configuration and to identify conditions for rapid, uniform densification.

The initial injector and mandrel design produced radial and longitudinal temperature gradients too large for uniform densification. Improved designs have been evaluated with the model. The most favorable approach utilizes a free-standing preform and an insulated water-cooled gas injector.

Selected process conditions are based on the temperature limit of the fiber, matrix stoichiometry and reagent utilization efficiency. Model runs for a tube 12" long, 4.0" OD and 1/4" wall thickness show uniform densification in approximately 15 hours.

INTRODUCTION

Chemical vapor infiltration is an effective method for fabrication of tube shapes for fossil energy applications. Equipment design and process conditions are significantly different than for disk-shaped components fabricated previously. A new, larger tube infiltration system has been installed at Oak Ridge National Laboratory (ORNL). Our previously developed process model (GTCVI) is being used to design the fixturing and process conditions for rapid, uniform densification.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
MODEL OF TUBE CVI SYSTEM

The "finite volume" method for modeling of FCVI has been described previously\textsuperscript{22}. For the new, larger 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 preset temperature. A mixture of hydrogen and methyltrichlorosilane (MTS) is introduced from a water-cooled gas injector in the center of the tube preform. The design of the gas injector and of the mandrel which supports the preform is expected to have a strong effect on densification performance. Process parameters include the temperature of the reactor wall, the overall gas flow rate and the concentration of MTS in the infiltration gas. In this paper we report on our efforts in applying the model to the new infiltration system, in using the model to design the injector and mandrel, and in specifying process conditions for rapid, uniform densification.

Our simulation of the ORNL reactor involves dividing the system into an orthogonal array of volume elements as seen in Figure 1. Each volume element consists of a material in the CVI system and its properties should match those of the actual material used. In some cases, such data is easily available. For example, the mandrel in the preliminary design is machined from H451 graphite. Thermal conductivity data from the manufacturer for this material is used in the model. In other cases, measured material properties are not available and must be estimated. In this situation, we perform "sensitivity" experiments with the model using a range of estimates for the material property to determine the effect on the temperature profile. For example, the reactor wall is a carbon-carbon composite material made by the furnace manufacturer. Thermal conductivity data for this material is not available and is difficult to estimate. Fortunately, since the wall is relatively thin and is located at the temperature control point, a large uncertainty in the thermal conductivity produces only a small uncertainty in the temperature at the preform. Similarly, data for the carbon fiber insulation at the ends of the reactor is not available. Our analysis indicates that this property is not critical to the calculation of temperature profile within the preform.

PRELIMINARY DESIGN

The preliminary injector/mandrel design is shown in Figure 1 and consists of a 1" OD stainless steel injector and a graphite mandrel upon which Nicalon plain weave cloth is wound to form a 4" OD tube preform. A large number of holes and grooves are machined into the mandrel to allow free passage of reactant gas. (We estimate a 50% reduction in the mandrel thermal conductivity due to this machining.) For this design, the CVI model predicts the temperature profile shown in Figure 2 with the reactor wall temperature of 1200°C assumed uniform along the length of the tube. (The furnace setpoint is maintained by a control pyrometer at the midpoint of the tube.) Model results show a significant longitudinal temperature gradient with the ends of the preform cooler than the center. In the end regions, there is good thermal contact with the cool injector through the high thermal conductivity graphite. In the tube middle the thermal contact
Figure 1. The new tube CVI system at Oak Ridge National Laboratory (left) is modeled using a 15x26 volume element grid (right). (Note that the radial and axial scales are different.)
relies on radiation across the gas space which is less efficient at the temperatures involved.

Also in Figure 2 the model temperature profile is compared to experiment. Temperatures were measured prior to infiltration with embedded thermocouples placed between the preform and mandrel, pressed against the outside of the preform, and extended into the gas space between the mandrel and injector. (There is some uncertainty in the radial position of this last thermocouple.) At the tube midpoint, there is good agreement between model and experiment. The temperature difference between the cool and hot side of the preform is in the range 300-350°C. Both model and experiment show temperatures at the tube ends lower than those in the middle. However, the measured temperatures also indicate that the setpoint temperature is not maintained uniformly along the length of the heating element.

Model and experimental densification runs with this fixture design revealed a number of difficulties. The 300-350°C temperature gradient through the preform is too large for good infiltration, yielding poor densification of the innermost part of the preform when the outer part is fully dense. Also, the longitudinal temperature gradient produces a longitudinal density gradient in the tube. Both of these results are due fundamentally to the high thermal conductivity of the dense graphite mandrel. Also, a practical shortcoming of this design is the difficulty of removing the tube from the mandrel after infiltration which requires boring out - destroying - the graphite mandrel. The CVI model has been used to investigate alternative designs that avoid these difficulties.

LOW THERMAL CONDUCTIVITY MANDREL

A second design approach replaces the dense graphite mandrel material with a rigid carbon-bonded carbon fiber (CBCF) insulation material which has a thermal conductivity approximately two orders of magnitude lower than that of dense H451 graphite. (Measured data provided by the supplier.) With this change (and increasing the diameter of the injector to 2.5" OD) the thermal gradient through the mandrel thickness is reduced to 150-170°C and the longitudinal temperature variation is less than 20°C. Model runs show relatively uniform densification although the inner part of the tube reaches a somewhat higher density than the outer.

While this design avoids the temperature and density inhomogeneity of the preliminary design, it still presents the difficulty of removing the tube at the end of the process and the cost of destroying the mandrel after each run. A third design approach addresses these issues.

FREE STANDING PREFORM

Although the mandrel has a strong role in controlling the temperature gradient in the tube preform, its primary function is to maintain the preform shape and fiber loading during
Figure 2. Model temperature profile matches experiment at tube midpoint (left). Perforated ends are cooler than midpoint due to conduction through graphite and non-uniform furnace temperature (right).
the initial stages of infiltration. The 3M company has developed technology for preparing rigidized preforms of braided fiber, eliminating the need for a mandrel. Several "sleeves" of braided Nextel 312 fiber are pulled over a metal cylinder, one at a time, forming a multi-layer tube preform. This is compressed to the desired wall thickness and rigidized with a phenolic resin. We have fabricated preforms with diameters 1", 2" and 3 1/2" and wall thicknesses of 2 layers, 1/8" and 1/4". The volume fraction fiber in these preforms is estimated to be 35-40%.

Model calculations for a furnace configuration with no mandrel - only gas space between the injector and preform - show a temperature gradient of 390-420°C (assuming sufficient water flow to maintain the injector internal temperature at 50°C). This large temperature gradient results from strong radiative cooling of the preform inner surface and would lead to non-uniform densification during CVI. We have examined two different approaches for reducing the magnitude of this temperature gradient.

In the first approach, a coolant - gas or liquid - with higher temperature capability is used, allowing operation of the injector at a higher internal temperature. For an injector temperature of 500°C the temperature gradient in the preform is reduced to 280-300°C, still somewhat larger than desired. Also, the operation of the stainless steel injector at this temperature in the presence of MTS and H₂ is likely to present problems of material degradation.

In the second approach, the water-cooled injector is sheathed with a thickness of CBCF material to reduce the heat flow. A gas space is maintained between the free-standing preform and the insulation material. With 1/4" of CBCF and 1/4" of gas space, the temperature gradient in the preform is reduced to 180-200°C, which is in the range needed to produce uniform densification.

PROCESS OPTIMIZATION

Using the insulated injector design described in the preceding section, we still must select "optimum" values for the processing parameters of setpoint temperature, gas composition and gas flow rate. In general, processing time is reduced by increasing any of these parameters, however, the "optimum" value of each is constrained by certain limits. For Nicalon, fiber degradation becomes significant at temperatures above 1200°C and the setpoint temperature is chosen as 1250°C to keep the temperature below this limit within the preform. For a preform of 30 vol% fiber in the form of a tube 12" L x 4" OD and 1/4" wall thickness, densification to 95 vol% requires 1200 g of SiC. With an estimated 50% utilization efficiency, MTS delivery of 14 g/min yields a processing time of 10 hours. Previous experience with SiC deposition has shown a tendency to produce non-stoichiometric, silicon-rich material at low H₂:MTS ratios. Based on this we select a gas composition of 20 mole% MTS. With the MTS delivery rate above, this composition is achieved with 9 L/min (STP) H₂ flow.
The GTCVI model was used to simulate tube infiltration using the processing parameters derived above. Densification of the preform is shown in Figure 3. MTS utilization efficiency is somewhat lower than estimated, however, after 15 hours the tube has an average density of 92% (8% porosity), varying only from 90 to 93% at different points within the tube.

SUMMARY

Initial modeling of the new ORNL tube infiltration system has been completed. Experimental temperature profiling and computer modeling of densification led to improved design of the injection and mandrel configuration. Selected process conditions for a free-standing preform design shows full densification in approximately 15 hours.

ACKNOWLEDGEMENT

Research sponsored by the U.S. Department of Energy, Office of Fossil Energy, Advanced Research and Technology Development Materials Program, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research. We appreciate the assistance of the 3M Company in fabrication of free standing tube preforms.

REFERENCES


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.
Figure 3. Model-predicted densification for free-standing preform with insulated water-cooled injector requires approximately 15 hours with selected process conditions. Final density is uniform throughout the tube.