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FABRICATION OF CERAMIC COMPOSITES: FORCED CVI

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Forced chemical vapor infiltration (CVI) is being developed as an efficient means for producing thick-wall ceramic matrix components. Recent efforts have focussed on process scale-up, modeling and the properties of the resultant material. Disks 24.6 cm in diameter and 1.27 cm thick have been produced. Composites of Nicalon™ fibers and SiC matrix have exhibited 480 MPa strength in flexure.

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1. Introduction

The past decade has seen the development of the forced flow-thermal gradient chemical vapor infiltration (FCVI) process as an alternative to isothermal-isobaric chemical vapor infiltration (ICVI) to meet differing structural composite requirements. Whereas ICVI can efficiently produce thin-wall, complex-shape parts, it requires a significantly long time to produce thicker-wall materials (> 3 mm). Using ICVI for thicker components requires many weeks to months of infiltration time, interrupted by occasional machining of the surfaces to open gas pathways that have become sealed due to overcoating. The FCVI of thicker sections can be effected in a single step and at sufficiently high rates to only require tens of hours or less.

In ICVI the reactant gases are allowed to flow around the preform and diffuse into the inner volume. In FCVI the reactant stream is forced to flow through the preform, thus only depending on diffusion to reach the finest porosity within, for example, fiber bundles. The imposition of a thermal gradient prevents premature sealing of the gas entrance surface, thus obviating the need for surface machining. Details of the processes have been extensively described elsewhere.[1-6]

The objective of the reported work was to scale-up the Oak Ridge National Laboratory (ORNL) FCVI technique to demonstrate fabrication of components approaching 30 cm in width and 2.5 cm in thickness. Previously, systems were available with capability to produce materials with a diameter of only 7.6 cm. The effort was designed as a demonstration of the ease of scaling the process and to provide for a comparison of the produced components with those prepared by other means.

This paper is an account of the scale-up FCVI unit specifications and the resultant infiltration system that was manufactured. The preform selected for the demonstration, a turbine rotor subelement prepared from a polar weave preform, is described along with the results of infiltration, including non-destructive evaluation and testing of the components. Additional efforts were undertaken to determine the mechanical properties of a densified cloth layup preform.

2. Scale-up FCVI facility

The specifications for the scale-up FCVI unit included requirements such as hot and cool surface temperatures and their control, minimal radial gradients, instrumentation,

and exhaust gas cleaning. These are indicated below:

Heating: Hot surface minimum temperature of 1500°C
              Radial gradients <10°C
              Variable cooling of cool surface

Fixturing: Hold preform shape
              Capacity to 30 cm diameter x 2.4 cm thickness
              Exclude reactants from heating elements

Instrumentation: Measure diametral temperature profile
                   Meter reactant flow
                   Measure reactant inlet pressure
                   Monitor power to heating elements
                   Provide for automated ramp to temperature and shut-down
                   Computer interface for data acquisition and control

Exhaust gas: Recirculating caustic scrubber
               Explosive gas dilution

3. FCVI system

The furnace and power supply components of the FCVI system were designed and constructed by Advanced Vacuum Systems of Ayer, MA. Figure 1 is a schematic of the furnace with the important features indicated. The furnace shell and lid are water-cooled. Access is gained through the top lid which rises on pneumatic lifters. The inside of the lid contains two concentric heating elements which are independently controlled, and therefore allow control of the radial temperature gradient. Also in the lid are two pneumatic hold-down pins, which press down on the preform fixture to compress the preform and seal the fixture against reactant gas leakage into the furnace cavity. The reactant gas inlet fits into the bottom of the fixture and the exhaust exits the fixture through a graphite tube that mates with a metal exhaust line. Graphite foil is used as gasket material in the fixture and to help seal the gas entrance and exhaust tubes.

The bottom surface can be cooled with either a water-cooled plate or with forced air blown through annuli below the furnace. A baffle is fixed such that the flow of air can be directed to varying degrees into the inner or outer annulus, thus allowing control over the lower surface radial gradient. Temperature measurement is via thermocouples that are emplaced above and below the preform fixture (six each). Temperatures are maintained utilizing control thermocouples on the hot side (controlling power to the heating elements) and on the cool side (controlling positioning of the air flow baffle).

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The remaining system components were assembled on site. Reactant flow control is via a Tylan (Torrance, CA) Source V vapor source for methyltrichlorosilane (MTS) and MKS (Andover, MA) mass flow meters for hydrogen. Inlet reactant stream pressure is measured with a MKS Baratron. A caustic wet scrubber supplied by Vanair (Louisville, KY) was used for neutralizing the exhaust gas, which was previously diluted with air below the lower explosive limit for hydrogen. Figure 2 is a photograph of the system together with two infiltrated disks.

4. Preforms

The preforms used for demonstrating scale-up were constructed of a modified polar weave fabric developed for the U.S. Air Force Wright Laboratory "High Temperature, Non-Metallic Turbine Engine Evaluation" program under Allied-Signal Corp. (Phoenix, AZ) by Textile Technologies Inc. (Hatboro, PA). The preform was designed for a turbine engine compressor subelement and is 24.6 cm in diameter and 1.27 cm thick, with a 1.27 cm diameter central hole. The Allied-Signal program utilized preforms with a satin weave containing a glass matrix prepreg added to the fibers before weaving. However, the FCVI preforms required no prepreg, and it was observed that the use of the satin weave without prepreg resulted in inadequate fiber loading. The weave was thus modified to a plain weave, which yielded satisfactory preforms. The resultant fiber loading was ~33%.

Subsequent to the demonstration phase of the effort, a composite disk was produced for more extensive mechanical properties testing. A similar dimension preform of plain weave Nicalon™ cloth was laid up using 55 layers of cloth, oriented ±30°.

For all preforms the sizing (i.e., the organic coating on as-received fiber tows) was removed by heating in the furnace, and this step was followed by the deposition of ~200 nm of pyrolytic carbon on the fibers. This was accomplished by placing the preform in the FCVI furnace and holding the top surface temperature at 1100°C, the pressure fixed at 6.6 Pa, and flowing propylene diluted in argon through the preform. After two hours the furnace was shut-down and the preform turned over. The process was then repeated. This ensured that the coating was applied uniformly throughout the preform. Weight gain measurements confirmed the average coating thickness.

5. Densification

The preforms were infiltrated utilizing constant flows of 5 g/min MTS, 5 l/min H_2, and a hot surface temperature of 1200°C, and required ~40 h. The results are shown in Table I.

Table

6. Spin Testing

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The polar weave composites were spin tested to determine their strength in potential turbine rotor environments. The results of spin testing performed at Williams International, Inc. (Walled Lake, MI) were inconclusive due to eccentricities in the densified preforms. Specimen no. 2 was spun up to 21,080 rpm and became unstable, causing shearing of the mounting quill. (The equivalent stress was 193 MPa.) The disk struck the wall of the spin test pit, yet remained intact. A second test was performed with the same disk which again sheared the quill at 20,850 rpm, indicating a destructive harmonic at that speed. This time the disk delaminated due to striking the edge of the groove left in the lead wall by the first test.

Specimen no. 3 was designed to overcome the test problems encountered with no. 2. The disk was made thinner to allow the test rig to overcome any imbalance. In addition, the holes in the fixture top plate were made smaller to reduce puckering in the cloth. This specimen, however, proved to have an eccentric placement of the center hole which caused the disk to encounter a critical point at 14,700 rpm, stalling the apparatus. The disk was intact, but only tested to 70.2 MPa.

7. Characterization Procedures

Characterization studies were conducted on test bars taken from sections cut from a composite disk prepared as a cloth layup (no. 4). The disk was cut into sections 45 mm long and labeled I through V (Fig. 3). Sections II through V were then cut into four plates and labeled as shown. The top layer refers to the position in the FCVI furnace that is nearest the heating elements. Each plate was then cut into 3 mm x 4 mm x 45 mm bend bars labeled as shown in Fig. 3. This allows one to reference each bar to its exact position within the FCVI disk.

Bars were randomly selected from each layer and density measurements made using the Archimedes method to obtain closed porosity and geometric (bulk) density to determine the sum of open and closed porosity. After drying, the effectiveYoung's modulus was measured for each bar by using an impulse excitation technique. This technique measures the resonant frequency of bend bars by exciting them mechanically with a singular elastic impulse. A transducer (contact accelerometer) senses the resulting mechanical vibrations of the bend bars and transforms them into electrical signals. The resonant frequencies, dimensions, and mass of the bend bars were then used to calculate the effective Young's modulus. Fifteen measurements were made for each bar to obtain an average value. The flexural strength as a function of specimen density at 300°C in air (~50% relative humidity) was characterized in four-point bending (20 mm inner span versus 40 mm outer span) under a loading rate of ~40 MPa/s. The tensile edges of the test specimens were beveled with a 6-µm diamond polishing lap.

8. Mechanical Properties

Figure 4 shows the results of both Archimedes and geometric densities as a function of bend bar position through the thickness and diameter of the FCVI disk. The closed porosity (Archimedes density) is reasonably constant through the thickness, with the specimens from the bottom layer having a slightly higher closed porosity. However, there was considerable variation in the open porosity that appeared generally as large, incompletely filled spaces in the open structure of the cloth weave or between cloth layers. Specimens from the bottom layer had open porosity levels of 10 to 15%. The specimens from the second and third layers had the lowest open porosity (< 6%) and the porosity level in the top layer specimens were between these two extremes.

Measurements of the effective Young's modulus are shown in Fig. 5 as a function of the bulk density. As expected the modulus increases linearly with the density. As a result, the fracture strength in four-point flexure should also decrease with increase in open porosity, and this is seen in Fig. 6. In the present study, these variations in mechanical properties with density can be correlated with the position in the section of the FCVI disk; the highest densities, Young's modulus, and strength being associated with the two layers located in the central plane (with respect to the thickness) of the disk. The bottom layer exhibits the lowest values for these characteristics, and the top layer has values that lie between these extremes.

9. Conclusions

The demonstration of scale-up in FCVI was successfully accomplished with the fabrication of 24-cm diameter disks. The Tyranno™ polar-weave preforms were relatively well-infiltrated, with spin-test strengths of at least ~200 MPa. A Nicalon™ cloth layup preform was densified, sectioned, and characterized with respect to density. The specimens' mechanical properties of Young's modulus and flexural strength were found to be proportional to density. The most dense specimens (~10% void volume) were found to have an effective modulus of ~240 GPa and a flexural strength of ~480 MPa.

ACKNOWLEDGEMENTS

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<u>Table I. Results of the infiltration runs.</u>

Spec. No.	Weave/ Fiber	No. Plies	Thickness (cm)	Run Time (h)	Void Fraction
1	Polar/ Tyranno™	50	1.59	40	16.5%
2	Polar/ Tyranno™	50	1.59	40	16.4%
3	Polar/ Tyranno™	40	1.27	40	13.6%
4	Plain/ Nicalon™	55	1.59	51	15.3%

FIGURE CAPTIONS

Figure 1.   FCVI furnace schematic for large-scale component fabrication

Figure 2.   Photograph of the FCVI furnace with two infiltrated disks.

Figure 3.   Plan for sectioned Nicalon™/SiC composite.

Figure 4.   Open and closed porosity in the sectioned specimens for the various of layers.

Figure 5.   Measurements of effective Young's modulus as a function of density.

Figure 6.   Flexure strengths as a function of density.

FCVI System Allows Rapid Densification of Composites

Columns (top): I II III IV V
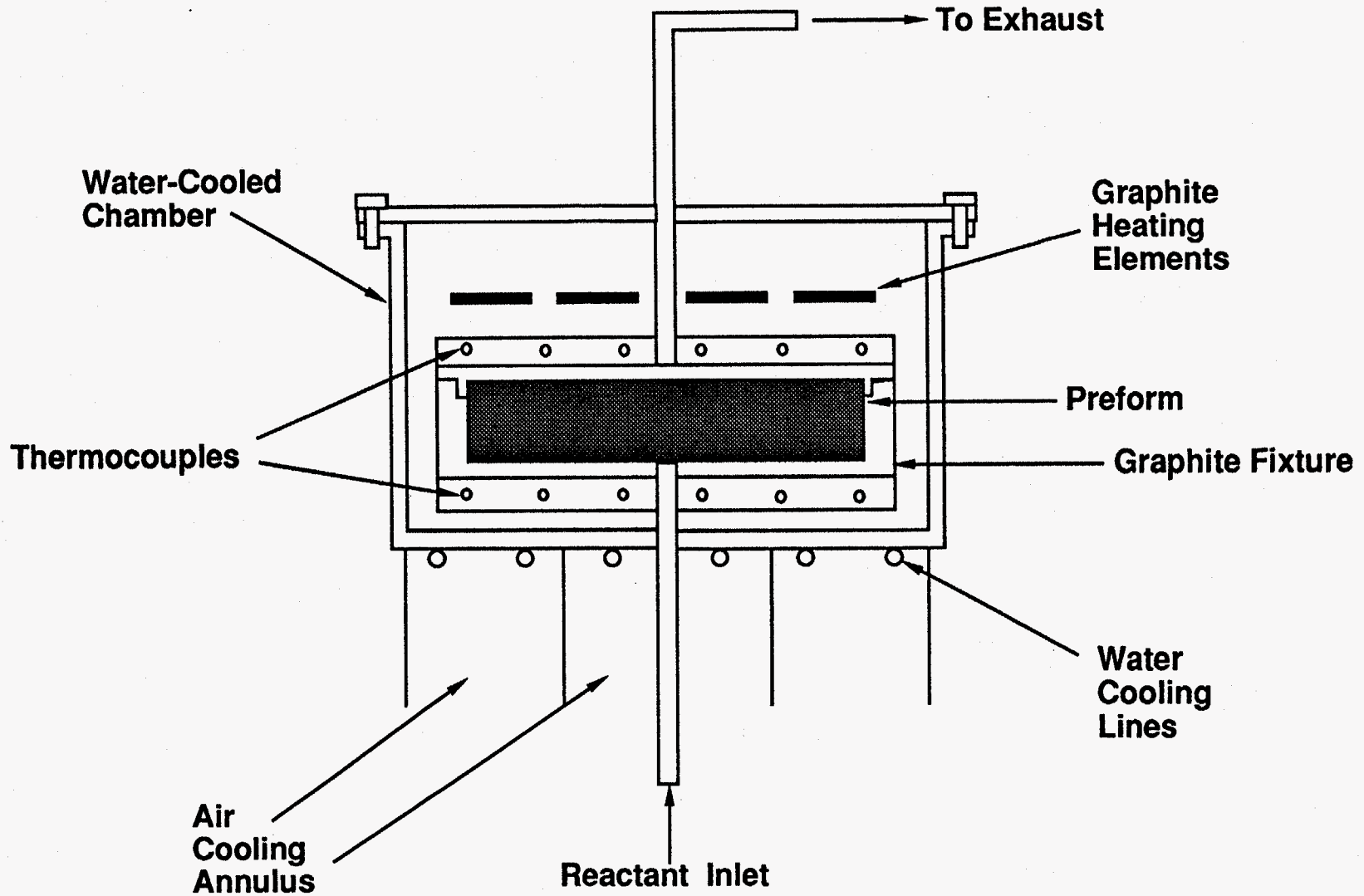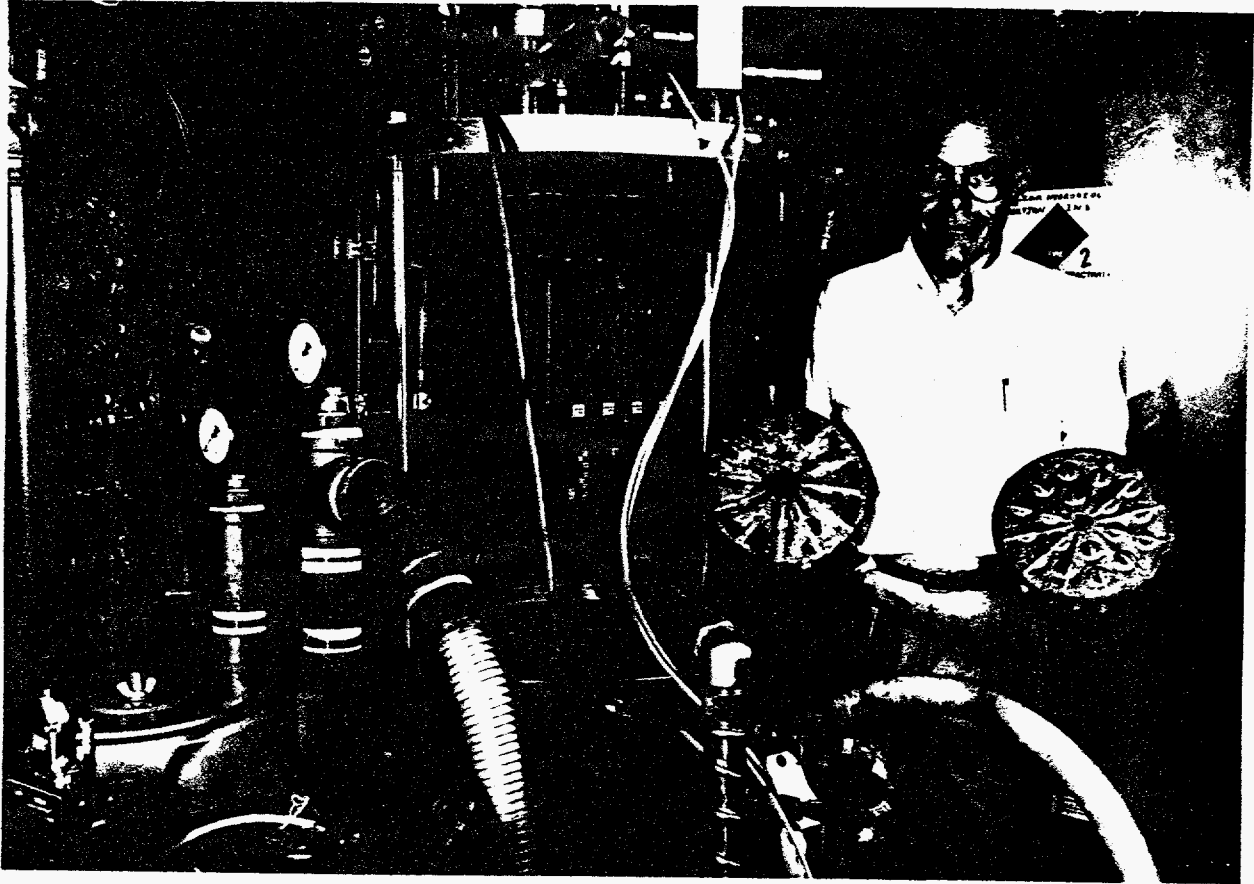
"Top Layer"

ρ_{avg} = 2.439 (82.68%)

	II	III	IV	V
E		2.456		2.457
D			2.426	
C	2.448	2.437		2.456
B		2.337		2.491
A	2.48		2.42	

"2nd Layer"

ρ_{avg} = 2.590 (87.80%)

	II	III	IV	V
E	2.593	2.503	2.604	2.545
D	2.52	2.608	2.554	2.635
C	2.555	2.626	2.561	2.625
B	2.567	2.591	2.604	2.623
A	2.618	2.634	2.614	2.626

"3rd Layer"

ρ_{avg} = 2.647 (89.74%)

	II	III	IV	V
E	2.649	2.668	2.663	2.601
D	2.681	2.640	2.684	2.590
C	2.666	2.664	2.680	2.612
B	2.657	2.674	2.645	2.613
A	2.658	2.673	2.672	2.558

"Bottom Layer"

ρ_{avg} = 2.32 (78.66%)

	II	III	IV	V
E	2.433		2.326	
D		2.264		2.373
C			2.333	
B	2.342			
A		2.288		2.204

VOID VOLUME DISTRIBUTED BETWEEN OPEN AND CLOSED POROSITY
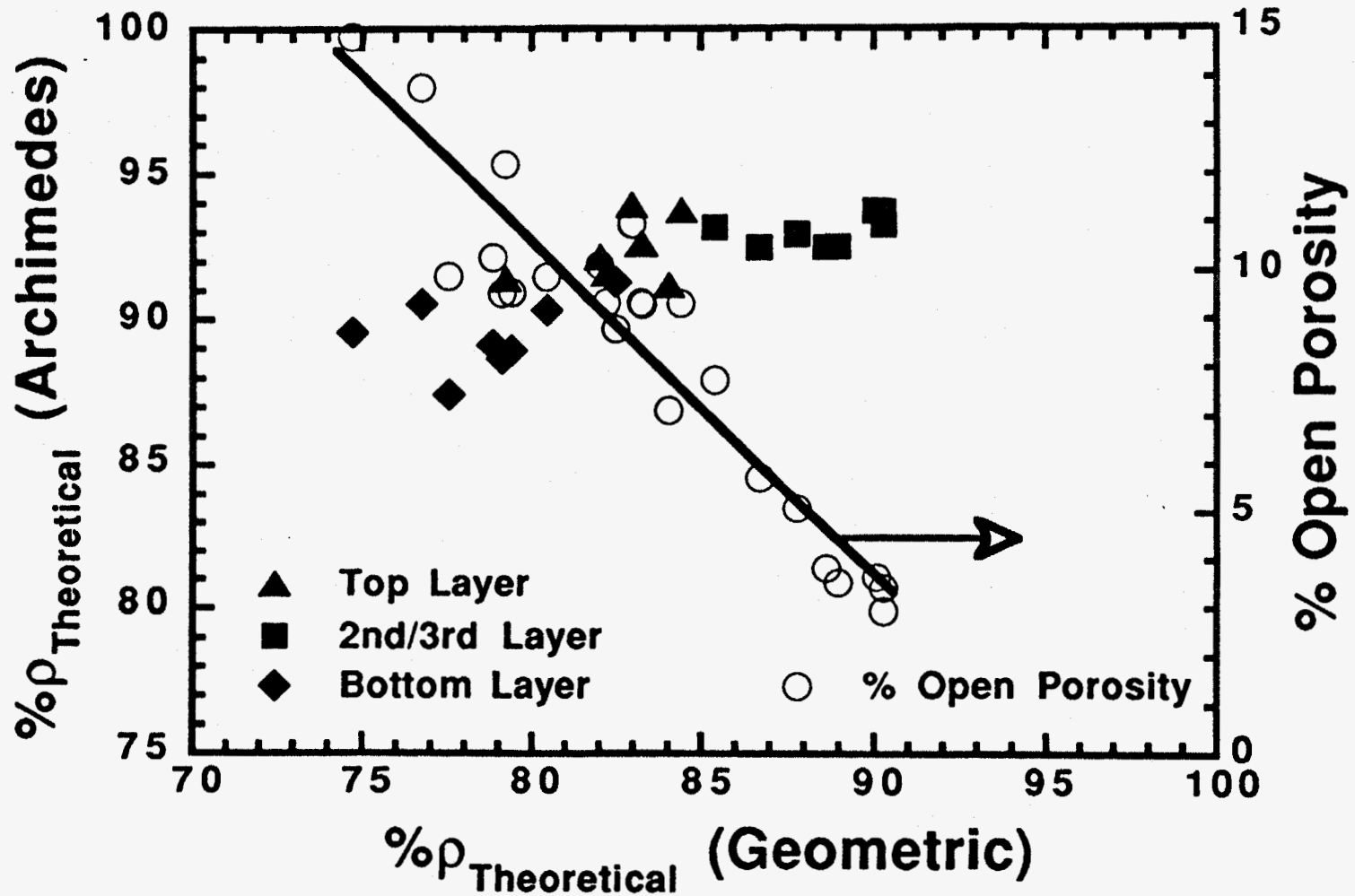
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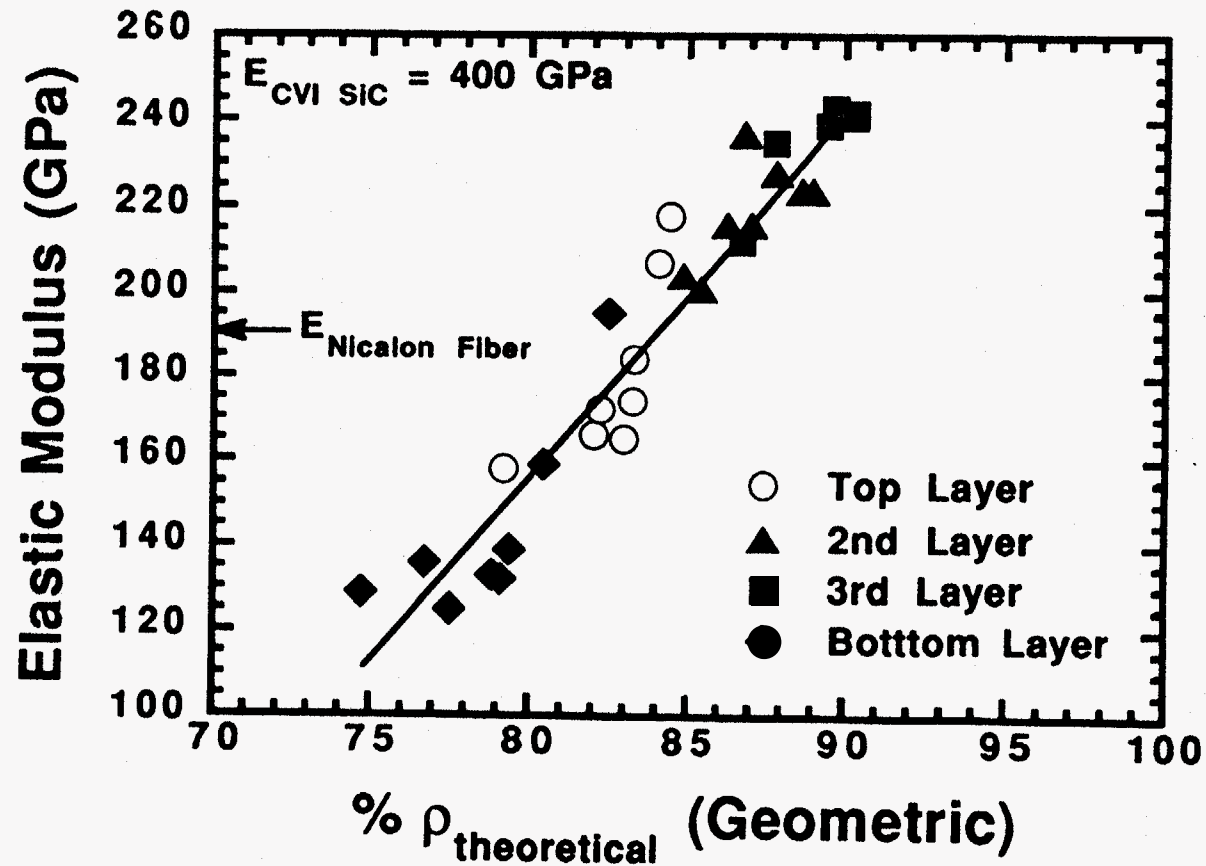
Flexural Strength versus Composite Density