14:21:19 OCA PAD AMENDMENT - PROJECT HEADER INFORMATION 08/02/95

Active

Project #: E-18-X09	Cost share #:	Rev #: 7
Center # : 24-6-R9280-000	Center shr #:	OCA file #:
		Work type : RES
Contract#: 86X-SL260C	Mod #: ADMINISTRATIVE	Document : CONT
Prime #: DEAC05-840R21400		Contract entity: GTRC

Subprojects ? : Y
Main project #:

CFDA:
PE #:

Project unit:	MSE	Unit code: 02.010.112
Project director(s):		
STARR T L	MSE	(404)853-0579

Sponsor/division names: OAK RIDGE NAT'L LAB / MARTIN MARIETTA
Sponsor/division codes: 240 / 001

Award period: 920801 to 950228 (performance) 950524 (reports)

Sponsor amount	New this change	Total to date
Contract value	0.00	219,871.00
Funded	0.00	219,871.00
Cost sharing amount		0.00

Does subcontracting plan apply ?: N

Title: CHARACTERIZATION OF CVI

PROJECT ADMINISTRATION DATA

OCA contact: Anita D. Rowland 894-4820

Sponsor technical contact	Sponsor issuing office
T. M. BESMAN	G.V. ROGERS, JR.
(615)574-6852	(615)576-1406
MARTIN MARIETTA ENERGY SYSTEMS, INC. BLDG. 4515, MS-6063 OAK RIDGE, TN 37831-6063	MARTIN MARIETTA ENERGY SYSTEMS, INC. P.O. BOX 2002 OAK RIDGE, TN 37831-6501

Security class (U,C,S,TS) : U
ONR resident rep. is ACO (Y/N): N
Defense priority rating :
supplemental sheet
Equipment title vests with: Sponsor X GIT

Administrative comments -
COMPLETES TRANSFER OF PI/PROJECT AND ALL RECORDS. THIS IS "MAIN" PROJECT.
NOTE: ~~REL~~ DELIVERABLES [redacted] (INPUT UNDER -X09B).

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Closeout Notice Date 10/24/95

Project No. E-18-X09

Center No. 24-6-R9280-000

Project Director STARR T L

School/Lab MSE

Sponsor OAK RIDGE NAT'L LAB/MARTIN MARIETTA

Contract/Grant No. 86X-SL260C

Contract Entity GTRC

Prime Contract No. DEAC05-84OR21400

Title CHARACTERIZATION OF CVI

Effective Completion Date 950831 (Performance) 950831 (Reports)

Closeout Actions Required:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	Y	
Final Report of Inventions and/or Subcontracts	Y	
Government Property Inventory & Related Certificate	Y	
Classified Material Certificate	N	
Release and Assignment	Y	
Other	N	

Comments
NOTE USE SPONSOR FORMS FOR PROPERTY.

Subproject Under Main Project No.

Continues Project No.

Distribution Required:

Project Director	Y
Administrative Network Representative	Y
GTRI Accounting/Grants and Contracts	Y
Procurement/Supply Services	Y
Research Property Managment	Y
Research Security Services	N
Reports Coordinator (OCA)	Y
GTRC	Y
Project File	Y
Other	N
	N

NOTE: Final Patent Questionnaire sent to PDPI.

E-18-X09

MILESTONE SCHEDULE

Task 1. Interrupted CVI (8/1/92 - 2/28/93)

1.1 Reconstruct CVI reactor for interrupted infiltrations (12/31/92)

1.2 Perform interrupted infiltrations for XTM analysis (2/28/93)

Task 2. Model Development (8/1/92 - 7/31/93)

2.1 Extract densification and microstructure data from prior XTM experiments (11/30/92)

2.2 Compare experimental results to model predictions, revise model and develop experimental plan for Task 1.2 (12/31/92)

2.3 Extract densification and microstructure data from Task 1.2 and compare to revised model predictions (7/31/93) [illegible] [illegible]

H 2

CHARACTERIZATION OF CVI DENSIFICATION OF CERAMIC COMPOSITES

T.L. Starr and A.W. Smith
Georgia Tech Research Institute

S.R. Stock, S. Lee and M.D. Butts
School of Materials Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

Subcontract #19X-SL260C

INTRODUCTION

Ceramic matrix composites promise higher operating temperature and better thermodynamic efficiency in many energy conversion systems. In particular, composites fabricated by the chemical vapor infiltration (CVI) process have excellent mechanical properties and, using the forced flow-thermal gradient variation, good processing economics in small scale demonstrations. Scale-up to larger, more complex shapes requires understanding of gas flow through the fiber preform and of the relationship between fiber architecture and densification behavior. This understanding is needed for design of preforms for optimum infiltration.

The objective of this research is to observe the deposition of matrix material in the pores of a ceramic fiber preform at various stages of the chemical vapor infiltration process. These observations will allow us to relate local deposition rates in various regions of the composite to the connectivity of the surrounding network of porosity and to better model the relationship between gas transport and fiber architecture in CVI preforms. We will observe matrix deposition using high resolution X-ray tomographic microscopy (XTM) in collaboration with Dr. John Kinney at Lawrence Livermore National Laboratory by repeated imaging of a small preform specimen after various processing times. Also, we will determine geometry and dimensions of channels between and through layers in cloth lay-up preform during CVI densification and relate these to a transport model.

TECHNICAL PROGRESS

Summary

Image data from an experimental run in February and March 1992 has been reconstructed and examined. For the next synchrotron run in April 1993, we plan to modify our CVI system to increase the size of the preform.

Milestones

1. Perform interrupted CVI experiment with XTM imaging

Progress toward this milestone has been limited to planning for the 1993 experimental effort. It appears that our next access to the Stanford Synchrotron Light Source (SSLS) will be in April 1993. The forced flow-isothermal CVI reactor for this run will be similar to that used in the previous run but will be somewhat larger. The reactor is designed to infiltrate cylindrical preforms and to allow easy removal and re-installation of the preform and holder. We will perform interrupted infiltration runs using this reactor. Each run will be interrupted 3-5 times prior to full densification, the preform and holder shipped to SSLS for XTM imaging, returned and reinstalled for further densification. We will consult with fiber weaving/braiding vendors and with researchers at Oak Ridge National Laboratory prior to selection of the fiber architecture for this set of experiments.

2. Use XTM images to develop gas transport model

Image data from an experimental run in February and March 1992 using a 0°/90° cloth lay-up preform have been reconstructed and examined. Using inclusions in the graphite holder surrounding the preform, registry between preform image and the image after partial infiltration is within one pixel (15 μm). This allows us to use image subtraction to gain a detailed view of matrix deposition. An example of this analysis is shown in Figures 1 and 2 below. These are gray-scale images (we normally use color images on a workstation screen) of the preform and the partially infiltrated composite. Subtracting these two images yields the deposit distribution.

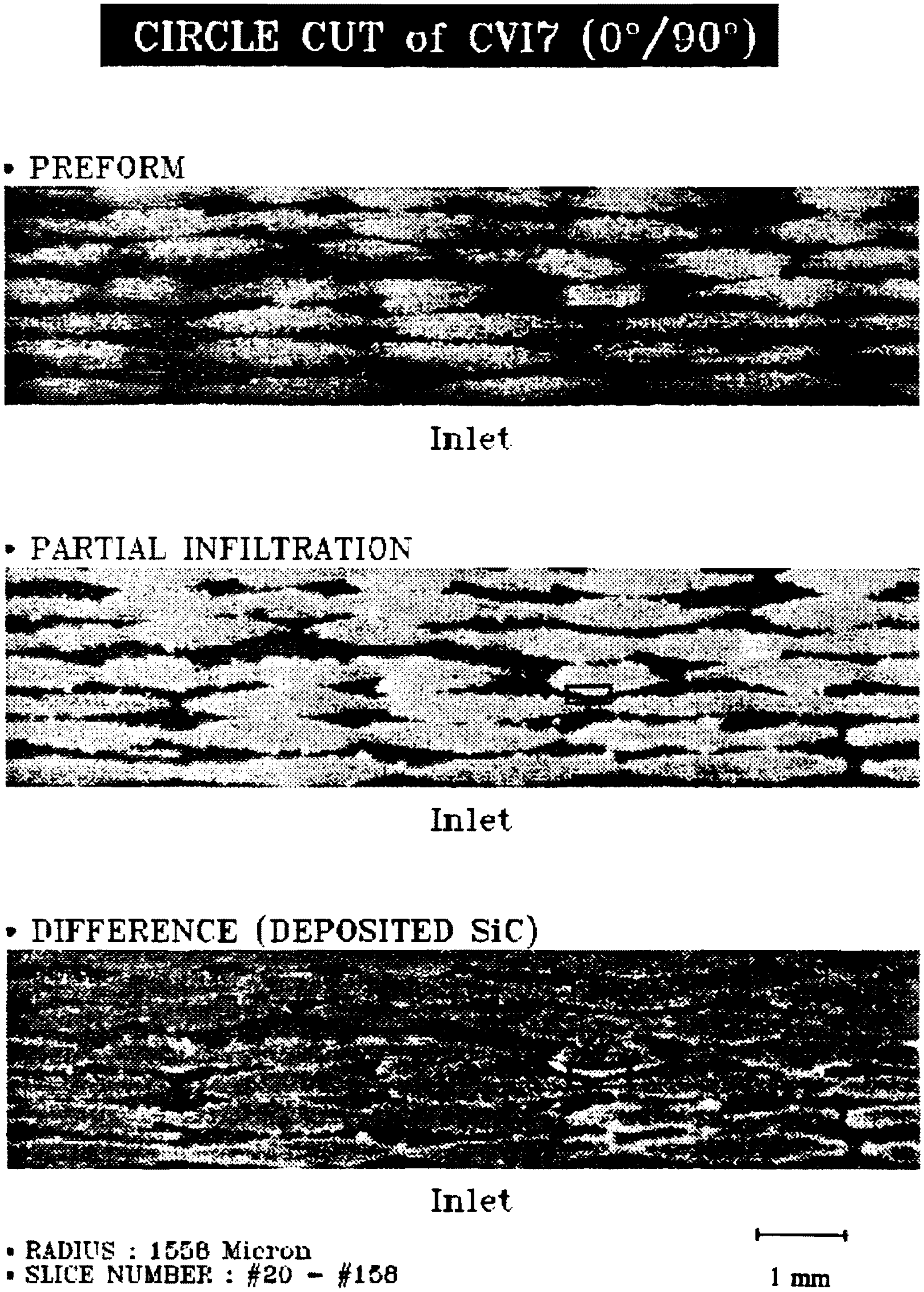


Figure 1. In these grey-scale XTM images lighter areas are higher density. Subtraction of the preform image from the infiltrated yields the distribution of deposited SiC. The area in the box is shown in Figure 2.

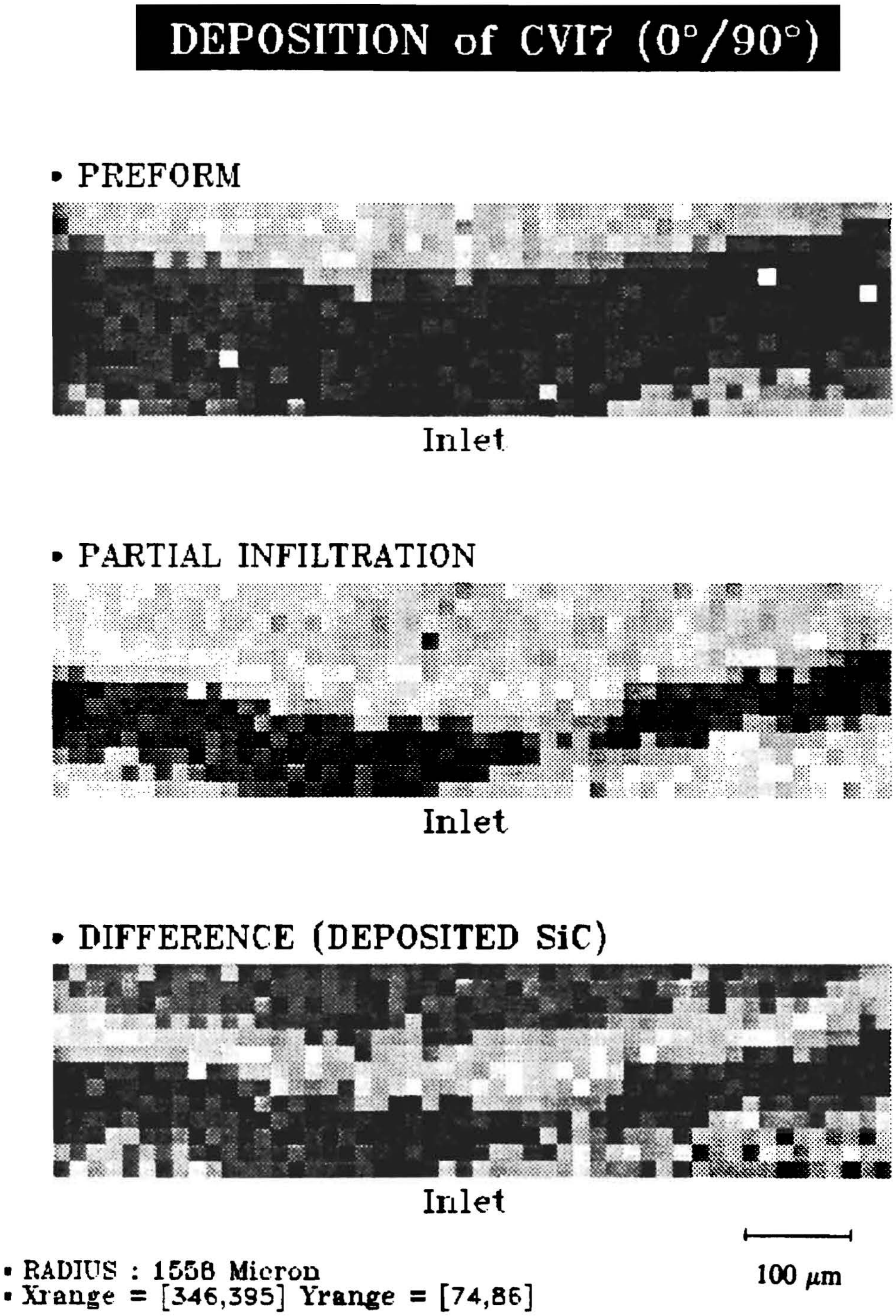


Figure 2. Higher magnification of the pixel images clearly shows an approximately 30μm layer of SiC deposited on the upstream side of one fiber tow.

In addition to this high resolution analysis we are making measurements of coarser features in the preform. Of particular interest is the measurement of the widths of "channels" between cloth layers and the spacial distribution of "holes" through cloth layers. These results will be used to refine CVI process modeling and the relationship between fiber architecture and preform transport properties.

PUBLICATIONS

Journals

1. M.D. Butts, S.R. Stock, J.H. Kinney, T.L. Starr, M.C. Nicols, C.A. Lundgren, T.M. Breunig and A. Guvenilir, "X-ray Tomographic Microscopy of Nicalon Preforms and Chemical Vapor Infiltrated Nicalon/Silicon Carbide Composites," *Mat. Res. Soc. Symp. Proc.* 250, 215-220 (1992).

PRESENTATIONS None

HONORS AND AWARDS None

PATENTS/DISCLOSURES None

LICENSES None

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER None

COST SHARING None

HIGHLIGHTS

High resolution images have been obtained during CVI densification of a cloth lay-up preform. The resolution and registry of the images allows local observation of matrix deposition within fiber tows and within the holes and channels that are formed by the tows.

U.S. DEPARTMENT OF ENERGY
SUMMARY REPORT

DOE F1332.2
(11-84)

FORM APPROVED
OMB NO. 1901-1400

1. IDENTIFICATION NUMBER CEED001

2. PROGRAM/PROJECT TITLE CHARACTERIZATION OF CVI DENSIFICATION OF CERAMIC MATRIX COMPOSITES

3. REPORTING PERIOD AUG. - SEP. 1992

4. PARTICIPANT NAME AND ADDRESS
THOMAS L. STARR
GEORGIA TECH RESEARCH INSTITUTE
GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GA 30332

5. START DATE August 1, 1992

6. COMPLETION DATE July 31, 1992

7. FY 92

8. MONTHS

9. COST STATUS

a. $ Expressed in: Thousands

b. Budget and Reporting No. ED 38 03 00 0

c. Cost Plan Date 8/92

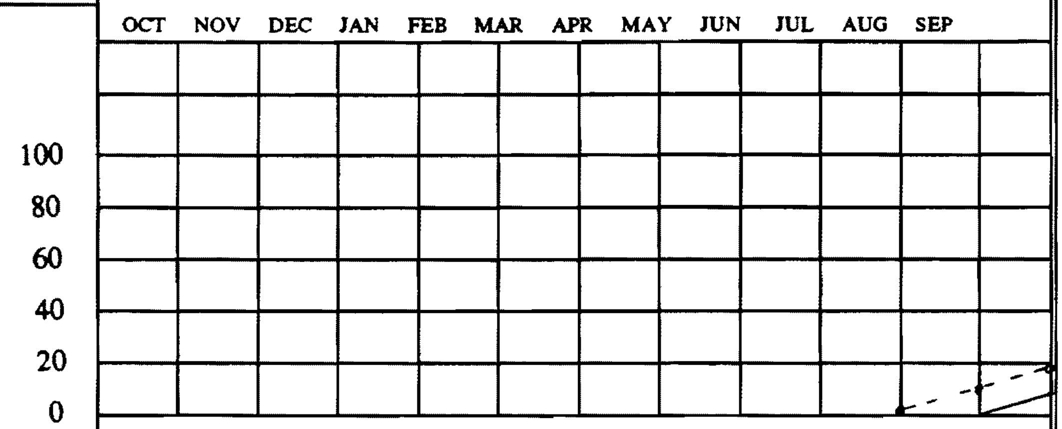
d. Actual Costs Prior Years

e. Planned Costs Prior Years

f. Total Est. Cost for Contract

g. Total Contract Value $110

h. Est. Subsequent Reporting Period



Accrued Costs	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	
g. Planned												9	9
h. Actual												0	8
i. Variance												9	1
j. Cumulative Variance												9	10

10. LABOR STATUS

a. Labor Expressed in: Person Months

b. Labor Plan Date: 8/92

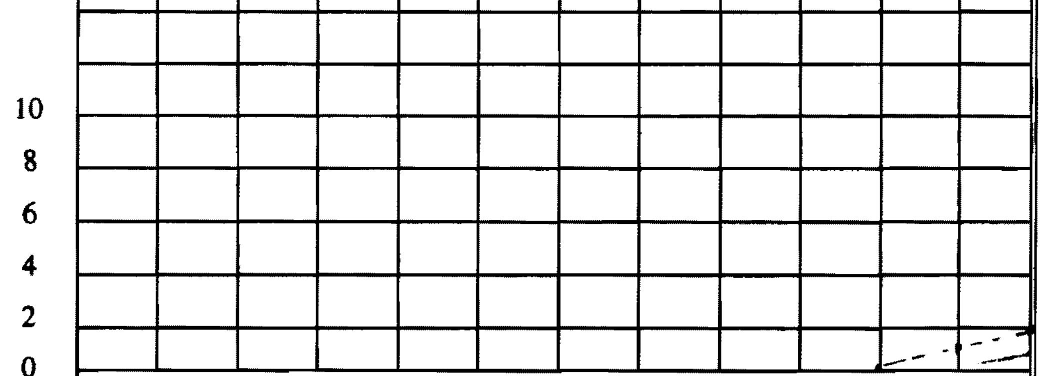
c. Planned Labor Prior Fiscal Months

d. Actual Labor Prior Fiscal Months

e. Total Est.Labor for Contract

f. Total Contract Labor 10.2

LEGEND
Planned (dash)
Actual (solid)
Projected (dots)



Labor	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	
g. Planned												.8	.8
h. Actual												0	.8
i. Variance												.8	0
j. Cumulative Variance												.8	.8

11. MILESTONES	COMMENTS	STATUS
a.		
b.		
c.		
d.		
e.		
f.		
g.		

12. SIGNATURE OF PARTICIPANTS' PROJECT MANAGER AND DATE 12/22/92

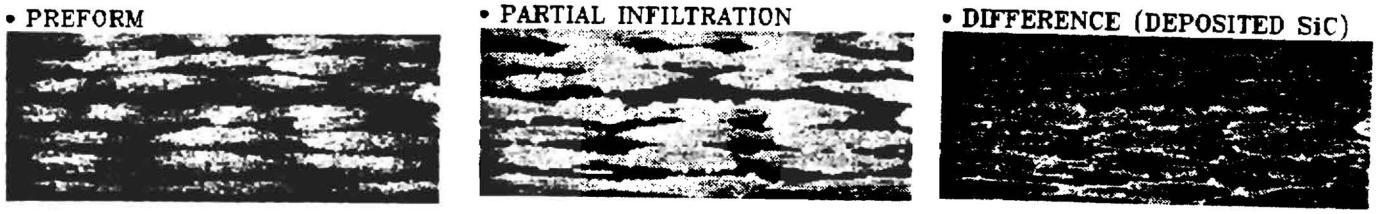
NON-INVASIVE IMAGING TECHNIQUE PROVIDES DETAILED VIEW OF CHEMICAL VAPOR INFILTRATION PROCESS

Problem:

The densification of ceramic composites using chemical vapor infiltration (CVI) is a complex process that is critically dependent on gas transport through the network of fibers that reinforce the composite. Previous methods of investigating the relationships between the fiber architecture and the densification process have been limited to destructive, post-process sectioning of a composite. Better understanding would be gained by continuous observation of the progress of densification from preform to dense composite.

Results:

High resolution images have been obtained during CVI densification of a cloth lay-up preform. The resolution and registry of the images allows local observation of matrix deposition within fiber tows and within the holes and channels that are formed by the tows. Future efforts will seek to correlate these local deposition rates with pathways for gas transport within the composite.



• PREFORM • PARTIAL INFILTRATION • DIFFERENCE (DEPOSITED SiC)

Image subtraction shows local deposition of matrix material

Significance - For Energy Conservation:

Ceramic matrix composites allow higher operating temperatures and better thermodynamic efficiency for many energy conversion systems.

Significance - For Materials Technology:

Better understanding of the CVI process will improve the properties and lower the cost of ceramic composite materials fabricated using this process. Advancement in the science of structure-transport relationships will benefit other composite fabrication processes and application of these materials, such as hot gas filtration, that involve fluid transport.

(R&D performed at the Georgia Institute of Technology under subcontract #19X-SL260C with Martin Marietta Energy Systems under their contract #DEAC05-840R21400)

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT TITLE: Characterization of CVI Densification of Ceramic Composites

FISCAL YEAR: 1992 **COMPLETION DATE:** 7/31/93

PERFORMING ORGANIZATION: Georgia Institute of Technology

PRINCIPAL INVESTIGATORS: Thomas L. Starr, (404) 853-0579
Stuart R. Stock, (404) 894-6882

PHASE OBJECTIVE: Determine geometry and dimensions of channels between and through layers in cloth lay-up preform during CVI densification and relate to transport model.

ULTIMATE OBJECTIVE: Develop understanding of relationship between preform fiber architecture and densification behavior, and use to design preform for optimum infiltration.

TECHNICAL APPROACH: In collaboration with Dr. John Kinney at Lawrence Livermore National Laboratory we will use high resolution X-ray tomographic microscopy (XTM) to repeatedly image a small preform specimen after various processing times. The objective of this research is to observe the deposition of matrix material in the pores of a ceramic fiber preform at various stages of the chemical vapor infiltration (CVI) process. These observations will allow us to relate local deposition rates in various regions of the composite to the connectivity of the surrounding network of porosity and to better model the relationship between gas transport and fiber architecture in CVI preforms.

PROGRESS: Image data from an experimental run in February and March 1992 has been reconstructed and examined. Using inclusions in the graphite holder surrounding the preform, registry between preform image and the image after partial infiltration can be insured within one pixel (15 μm). This allows us to use image subtraction to gain a detailed view of matrix deposition.

Patents: - **Publications:** 1 **Proceedings:** -

ACCOMPLISHMENTS:

Licenses: -

Known Follow-on Product: None

Industry Workshop: None

Technology Transfer or Industrial Interaction: None

PROJECT TITLE: Characterization of CVI Densification of Ceramic Composites

CRITICAL ISSUES: Preform architectures for experiments in 1993 must be selected to maximize results since only two architectures can be examined. These likely will include at least one 3-D weave or braid and also may include a different fiber type.

FUTURE PLANS: Analysis of image data from 1992 run will continue, extracting structure data that is critical to testing of the microstructure-transport property model. We will contact weaving/braiding vendors and researchers at Oak Ridge National Laboratory to identify candicate preform architectures for the 1993 run.

POTENTIAL PAYOFF:

ESTIMATED ENERGY SAVINGS:

FUNDING HISTORY: FY 1992
Amt. $7.8K

Cum. Total to Date $7.8K

OTHER SOURCES: None

CHARACTERIZATION OF CVI DENSIFICATION OF CERAMIC COMPOSITES

T.L. Starr and A.W. Smith
Georgia Tech Research Institute

S.R. Stock, S. Lee and M.D. Butts
School of Materials Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

Subcontract #19X-SL260C

INTRODUCTION

The objective of this research is to observe the deposition of matrix material in the pores of a ceramic fiber preform at various stages of the chemical vapor infiltration (CVI) process. These observations will allow us to relate local deposition rates in various regions of the composite to the connectivity of the surrounding network of porosity and to better model the relationship between gas transport and fiber architecture in CVI preforms. We will observe matrix deposition using high resolution X-ray tomographic microscopy (XTM) in collaboration with Dr. John Kinney at Lawrence Livermore National Laboratory by repeated imaging of a small preform specimen after various processing times. Also, we will determine geometry and dimensions of channels between and through layers in cloth lay-up preform during CVI densification and relate these to a transport model.

TECHNICAL PROGRESS

Summary

Channel width (the distance between successive cloth layers) has been measured for the 0/90 cloth layup preform at various positions and after one, two and three infiltration cycles. For the next synchrotron run we plan to use larger, 1 cm diameter preform specimens and 3-5 different fiber architectures. Also we hope to include specimens of commercial composites fabricated by the isothermal CVI process.

Milestones

1. Perform interrupted CVI experiment with XTM imaging

We continue planning for the 1993 experimental effort which is scheduled for April 1993. The forced flow-isothermal CVI reactor for this run will be similar to that used in the previous run but will be somewhat larger to accommodate a 1 cm diameter specimen. This larger size will allow us to prepare specimens of various preform architectures while avoiding surface effects resulting from the edge. In addition to repeating the 0/90 and 0/45 cloth layup preforms, we plan to include a 0/30/60 cloth layup and an orthogonal 3-D weave. Other candidates include braid, polar weave, filament wound and chopped fiber architectures. The final selection will depend both on potential for commercial interest and on ability to prepare a suitable specimen. In initial discussions duPont has indicated an interest in supplying specimens of their commercial CVI composite at various degrees of infiltration. While we will not be able to follow the densification process in the same way as with our interrupted CVI experiment, we will be able to compare the morphology of the developing porosity.

2. Use XTM images to develop gas transport model

Image data from the previous experimental run using a 0/90 cloth lay-up preform have been examined. We have measured the widths of "channels" between cloth layers and the cross-sectional area of "holes" through cloth layers. Average measured channel widths range from 100 to 130 μm for different pairs of cloth layers through the preform. This value is somewhat larger than the 60 μm used in the densification model but includes many large values near holes. By examining these channels during densification we will measure the more important "effective" channel width, i.e. the width of deposit that closes off transport parallel to the cloth.

PUBLICATIONS

None

HONORS AND AWARDS

None

PATENTS/DISCLOSURES

None

LICENSES

None

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

We have had some discussion with duPont toward including their material in the next XTM experiment.

COST SHARING

None

HIGHLIGHTS

None

PERMISSION TO PUBLISH

TITLE CHARACTERIZATION OF CVI DENSIFICATION OF CERAMIC COMPOSITES -

AUTHOR T.L. Starr, A.W. Smith, S.R. Stock, S. Lee and M.D. Butts

PUBLICATION Advanced Industrial Concepts (AIC) Annual Progress Report, Project Summary and Significant Accomplishment

CIRCLE ONE

You [✓ have], do not have, permission to use the above information.

1/26/93
Date

Signature

A-9289
#4

Georgia Tech
RESEARCH INSTITUTE

Georgia Tech Research Institute
Georgia Institute of Technology
Atlanta, Georgia 30332-0800

April 29, 1993

Dr. Peter Angelini, Manager
Advanced Industrial Concepts Material Program
Oak Ridge National Laboratory
Building 4515, MS-6065
P. O. Box 2008
Oak Ridge, TN 37831-6065

Dear Peter:

Enclosed is the quarterly report for the Georgia Tech part of our collaborative effort with Dr. John Kinney at LLNL.

As always I appreciate your support of this research and look forward to working with you in the future.

Sincerely,

Thomas L. Starr
Materials Science and
Technology Laboratory

Enclosure

CHARACTERIZATION OF CVI DENSIFICATION OF CERAMIC COMPOSITES

T.L. Starr and A.W. Smith
Georgia Tech Research Institute

S.R. Stock, S. Lee and M.D. Butts
School of Materials Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

Subcontract #19X-SL260C

INTRODUCTION

Ceramic matrix composites promise higher operating temperature and better thermodynamic efficiency in many energy conversion systems. In particular, composites fabricated by the chemical vapor infiltration (CVI) process have excellent mechanical properties and, using the forced flow-thermal gradient variation, good processing economics in small scale demonstrations. Scale-up to larger, more complex shapes requires understanding of gas flow through the fiber preform and of the relationship between fiber architecture and densification behavior. This understanding is needed for design of preforms for optimum infiltration.

The objective of this research is to observe the deposition of matrix material in the pores of a ceramic fiber preform at various stages of the chemical vapor infiltration process. These observations will allow us to relate local deposition rates in various regions of the composite to the connectivity of the surrounding network of pores and to better model the relationship between gas transport and fiber architecture in CVI preforms. We will observe matrix deposition using high resolution X-ray tomographic microscopy (XTM) in collaboration with Dr. John Kinney at Lawrence Livermore National Laboratory, by repeated imaging of a small preform specimen after various processing times. Using these images we will determine the morphology and dimensions of channels between and through layers in cloth lay-up preform during CVI densification and relate these to a transport model.

TECHNICAL PROGRESS

Summary

Image data for the 0/90° lay-up preform has been used to measure changes in the size and morphology of the channels between cloth layers during densification. The overall changes in channel width are qualitatively consistent with our understanding of transport and deposition in CVI but suggest some refinement the associated model parameters. Our analysis of the channel morphology has produced a new and interesting result. For this simple cloth lay-up architecture where the fiber tows of two adjoining cloths are parallel, the relative alignment of holes can produce strikingly different gas paths for transport through the cloth layers and lead to different ultimate densities during infiltration.

Milestones

1. Perform interrupted CVI experiment with XTM imaging

Ten graphite CVI reactors for the next XTM run have been obtained. These are similar to those used in the previous run but accept a specimen 8 mm diameter (compared to the 6 mm used previously). Eight preform architectures will be used. These include 0/30/60° lay-ups using square-weave Nicalon and Tyranno cloths, with and without controlled hole alignment; 0/90° and 0/45° lay-ups with the Tyranno cloth; and two specimens of a 3-D weave Nicalon preform.

2. Use XTM images to develop gas transport model

We have completed measurement of the widths of "channels" between cloth layers. These results offer a detailed measure of deposition rate at various positions. Measurements indicate a significant transport resistance parallel to the cloth layers which is contrary to the "uniform deposition" assumption made in previous microstructure development models.

Our analysis of the effect of hole alignment from layer to layer has produced an unexpected and important finding. For holes offset diagonal (45°) to the principal tow directions, the gas passageway from hole to hole is tortuous and is "sealed off" relatively early in the densification process. In contrast, for holes offset along one of the principal tow directions (0° or 90°) a well defined, relatively open passageway is created which remains open until very late in the densification process. Systematic control of cloth lay-up alignment to develop this channel morphology could improve the ultimate density achieved during CVI.

PUBLICATIONS None

PRESENTATIONS

J.H. Kinney, T.M. Breunig, M.C. Nicols, T.L. Starr, S.R. Stock and M.D. Butts, "Time Evolution of Microstructure During Forced Flow Chemical Vapor Infiltration of a Continuous Fiber Ceramic Matrix Composite" at the American Ceramic Society 17th Annual Conference on Composites and Advanced Ceramics, January 10-15, 1993

S.B. Lee, S.R. Stock, T.L. Starr, M.D. Butts, T.M. Breunig, M.C. Nicols and J.H. Kinney, "Influence of Tow Geometry on Microstructure Evolution of CVI Composites" at the American Ceramic Society 17th Annual Conference on Composites and Advanced Ceramics, January 10-15, 1993

HONORS AND AWARDS None

PATENTS/DISCLOSURES None

LICENSES None

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER None

COST SHARING None

HIGHLIGHTS

Channel width measurements indicate a significant transport resistance parallel to the cloth layers which is contrary to the "uniform deposition" assumption made in previous microstructure development models. Our analysis of the effect of hole alignment from layer to layer suggests that systematic control during cloth lay-up could produce a channel morphology that would improve the ultimate density achieved during CVI.

N/A

CHARACTERIZATION OF CVI DENSIFICATION OF CERAMIC COMPOSITES

S.R. Stock, S.B. Lee and M.D. Butts
School of Materials Science and Engineering

T.L. Starr and A.W. Smith
Georgia Tech Research Institute
Georgia Institute of Technology
Atlanta, Georgia 30332

ORNL Subcontract #19X-SL260C

INTRODUCTION

Ceramic matrix composites promise higher operating temperature and better thermodynamic efficiency in many energy conversion systems. Ceramic composites fabricated by the chemical vapor infiltration (CVI) process have demonstrated excellent mechanical properties and good processing economies in small scale demonstrations. Preserving these attributes in scale-up, however, requires improved understanding of gas flow through the fiber preform and of the relationship between fiber architecture and densification behavior. This understanding is needed for design of preforms for optimum infiltration.

The objective of the research is to observe the deposition of matrix material in a ceramic fiber preform at various stages of CVI, to relate local deposition rates in various regions of the composite to the connectivity of the surrounding network of porosity and to apply these observations to improved modeling of the relationship between gas transport and fiber architecture in CVI preforms. Matrix deposition is observed using x-ray tomographic microscopy (XTM) in collaboration with Dr. John Kinney at Lawrence Livermore National Laboratory by repeatedly imaging a small preform sample after various processing times. Analysis focuses on the geometry and dimensions of the channels between and the holes through layers in cloth lay-up preforms and the incorporation of this data into a transport model.

TECHNICAL PROGRESS

A set of several samples was prepared and partially infiltrated; theses samples where sent to Kinney's group for tomographic imaging. Included were samples with 0°/45° and 0°/30°/60° lay-ups. The cloths were of Tyranno and Nicalon fibers. Infiltration and imaging was partially completed on some of the samples, but limited beam time prevented completion of the experiments.

Analysis centered on a 0°/90° cloth lay-up SiC/Nicalon composite that was densified under isothermal/forced-flow condition by methyltrichlorosilane (MTS) and imaged by high resolution XTM at four times during densification, i.e., before infiltration and after three, six, and nine hours of infiltration. The volume fraction of SiC deposited within the tows of the cloth layers was studied as a function of infiltration time and position relative to the gas inlet; this was used as a comparison with the work going on in Kinney's group. The widths of the channels and holes in the composite were studied in detail: these are particularly important because they are the main route of gas flow during the final stages of densification. From the measurement of channel width as a function of position, several other quantities were obtained as a function of time and distance from the gas inlet: total channel volume, preform channel structure, average channel width, the relationship between channel width and displacement between holes in the cloths on either side of the channel, and the thickness of SiC deposited on the wall of the channels. The number of moles of SiC deposited within the sampling volume (i.e., the channel and the tows on either side of the channel) and surface area per unit volume are also quantified.

Perhaps the most important observation made on the 0°/90° layup sample was the first observation of the dependence of channel structure on the relative displacements of the bordering cloths: patterns of channel widths were found for the nineteen different channels of the sample. Figure 1 maps channel width across the cross-section of the sample for three channels; darker pixels represent positions where the channel is wider. Figure 1 a, b and c (channels 1, 10 and 11, respectively) show the three patterns of channel openings observed: two-dimensional networks of "pipes", one-dimensional arrays of "pipes" and relatively structure-free channels. As shown in Figure 2 a, b and c, these patterns correspond to situations where the holes in the cloths on either side of the channel are well-aligned, displaced along the axis of a tow or displaced along a direction bisecting the two orthogonal tows, respectively.

The periodicity would be expected to be manifest in the densification of the sample. The data showed that densification of SiC strongly depends on the distance from the gas inlet, i.e., on the concentration of MTS and HCl, both inside microporosity (tows) and on the walls of macroporosity (channel and holes) but does not seem to relate significantly to cloth lay-up geometry. The rate of SiC deposition on the surface of tows is most rapid on the walls of channel near the gas inlet, and particularly at the tips of tows (i.e., the boundaries of the holes). Holes in the cloth layers near the gas inlet are almost clogged after three hours of infiltration, and after three hours, the MTS gas flowed around these cloths, mostly along the wall of the reaction chamber. Loose fibers or small bundles of fibers within open sections of channels may also play significant role in limiting the final density which the composite can reach.

Hole alignment or the direction of displacement of the holes does not, however, appear to have an effect on the local deposition rates. In other words, the macroscopic gradients seem to render insignificant any local variations. Use of the displacement of the holes as a measure of local structure is, however, an oversimplification of the actual three-dimensional nature of the cloths. As is indicated in the two-dimensional section perpendicular to two cloths (Figure 3), well-aligned holes can correspond to two very different channel structures. The two structures can be termed anti-coincident and coincident for the situation where the parallel tows on either side of the channel are the nearest-neighbors across the channel and where the orthogonal tows are nearest-neighbors, respectively. The channels formed by anti-coincident and coincident well-aligned cloth layers would have very different channel volumes, etc. It may be that looking for differences in local deposition based on only hole position is inaccurate and that the weave structure must be taken into account. This is currently under investigation.

PUBLICATIONS

1. J.H. Kinney, T.M. Breunig, T.L. Starr, D. Haupt, M.C. Nichols, S.R. Stock, M.D. Butts and R.A. Saroyan, "X-ray Tomographic Study of Chemical Vapor Infiltration Processing of Ceramic Composites," Science, **260**, pp. 789-792, 1993.
2. M.D. Butts, "Nondestructive Examination of Nicalon Fiber Composite Preforms Using X-ray Tomographic Microscopy," MS Thesis, Georgia Institute of Technology, June 1993, (supervised by S.R. Stock).
3. S.B. Lee, "Nondestructive Examination of Chemical Vapor Infiltration of 0°/90° SiC/Nicalon Composites," PhD Thesis, Georgia Institute of Technology, December 1993, (supervised by S.R. Stock).

PRESENTATIONS

1. S.B. Lee, S.R. Stock, T.L. Starr, M.D. Butts, T.M. Breunig, M.C. Nichols and J.H. Kinney, "Influence of Tow Geometry on Microstructure Evolution of CVI Composites," 17th Annual Conference and Exposition on Composites and Advanced Ceramics,

American Ceramic Society, Cocoa Beach, Florida, January 14, 1993.

2. T.L. Starr, S.R. Stock, M.D. Butts and S.B. Lee, "Constriction of Flow Paths During Forced Flow CVI," Ninety-fifth Annual Meeting, American Ceramic Society, Cincinnati, Ohio, April 20, 1994.

HONORS AND AWARDS

None.

PATENTS/DISCLOSURES

None.

LICENSES

None.

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

None.

COST SHARING

None.

HIGHLIGHTS

An illustration from publication 1 above, which was produced by our collaborators on the joint work described in this report appeared on the cover of Science.

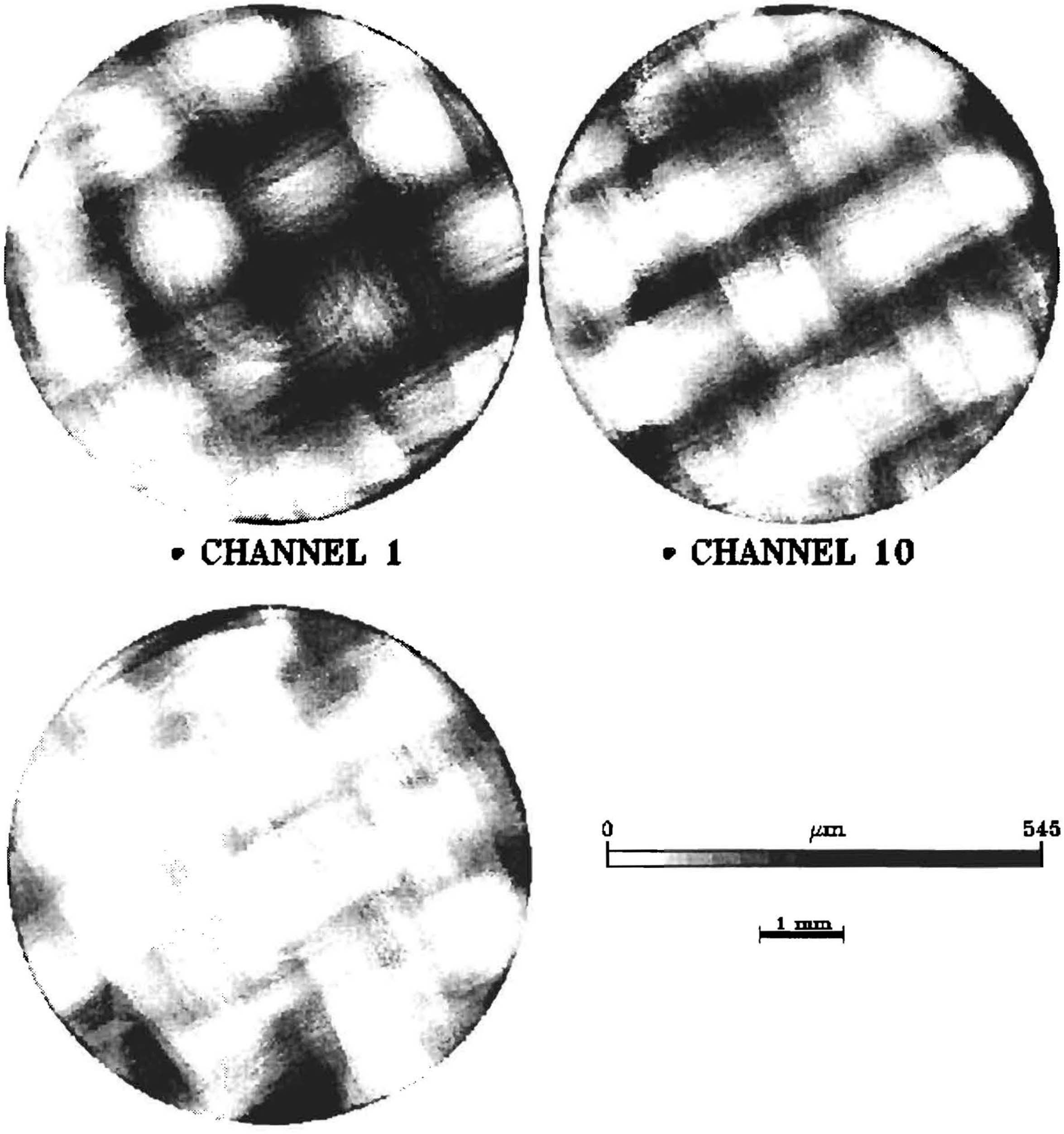
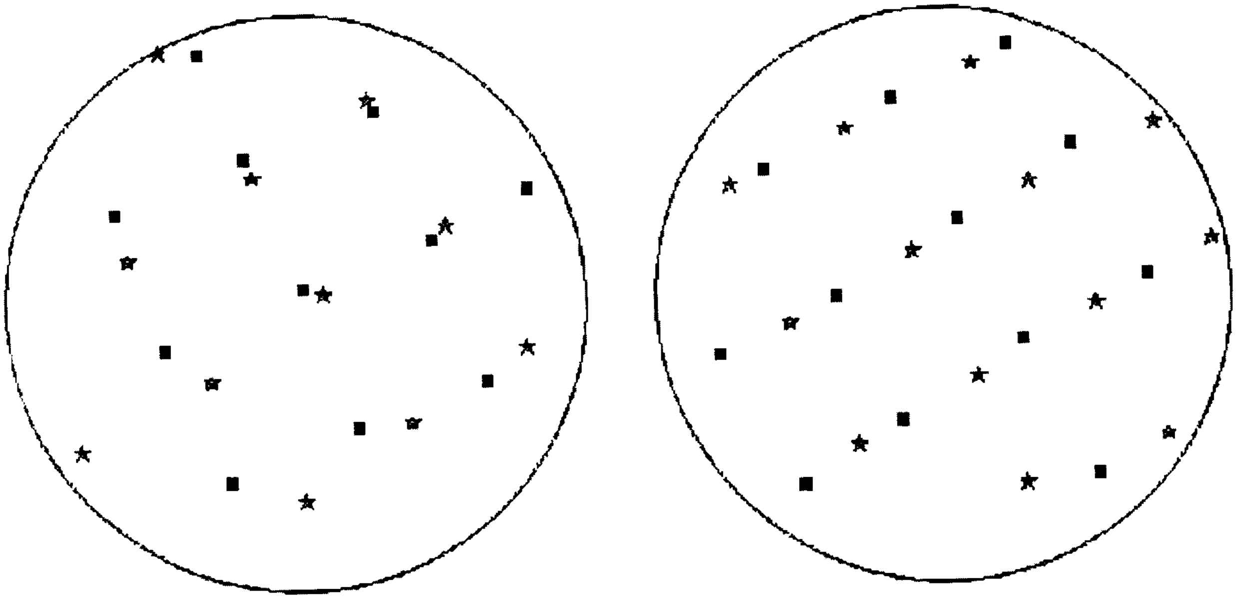
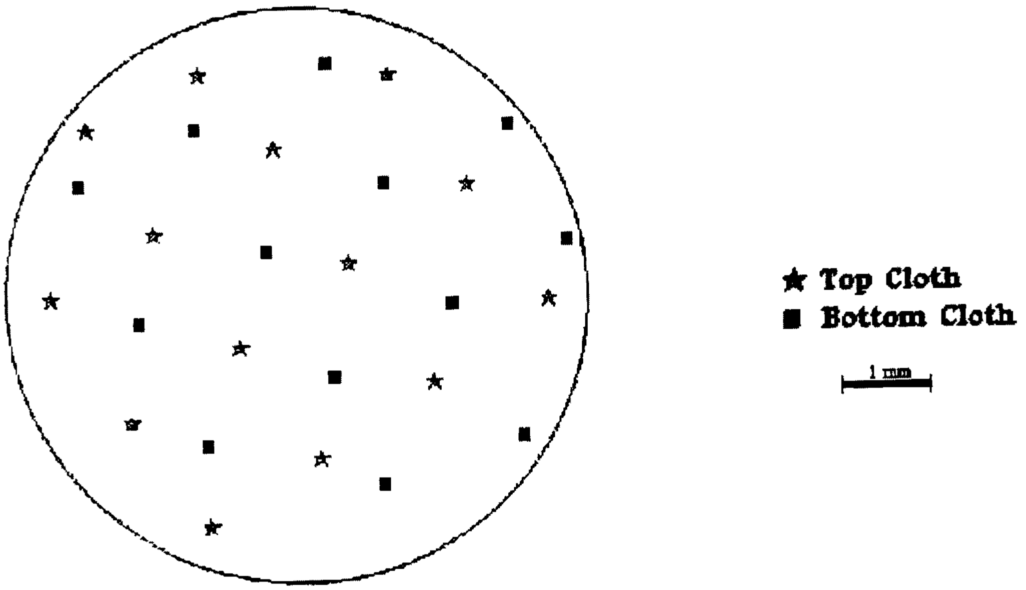


Figure 1. Channel width as a function of position.



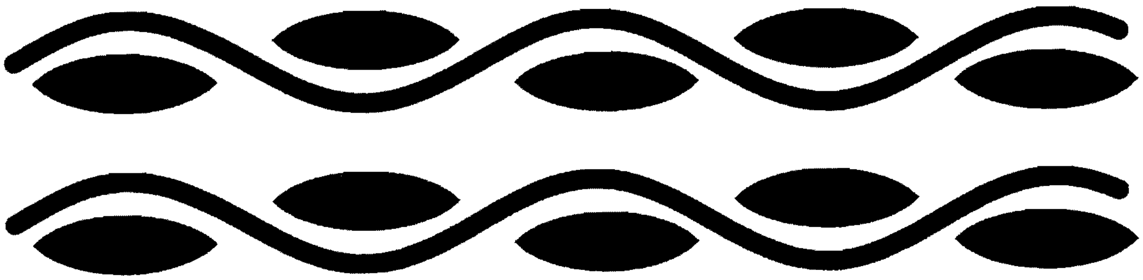
(A) CHANNEL 1 **(B) CHANNEL 10**



(C) CHANNEL 11

Figure 2. Hole positions on either side of the channels shown in Figure 1.

Coincident Cloth Alignment



Anti-Coincident Cloth Alignment

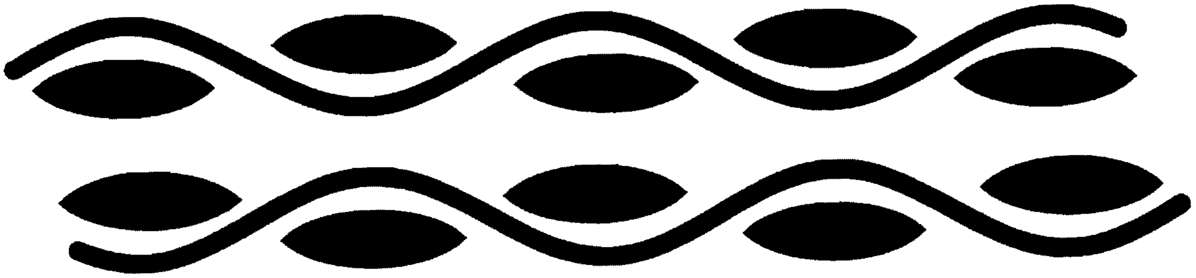
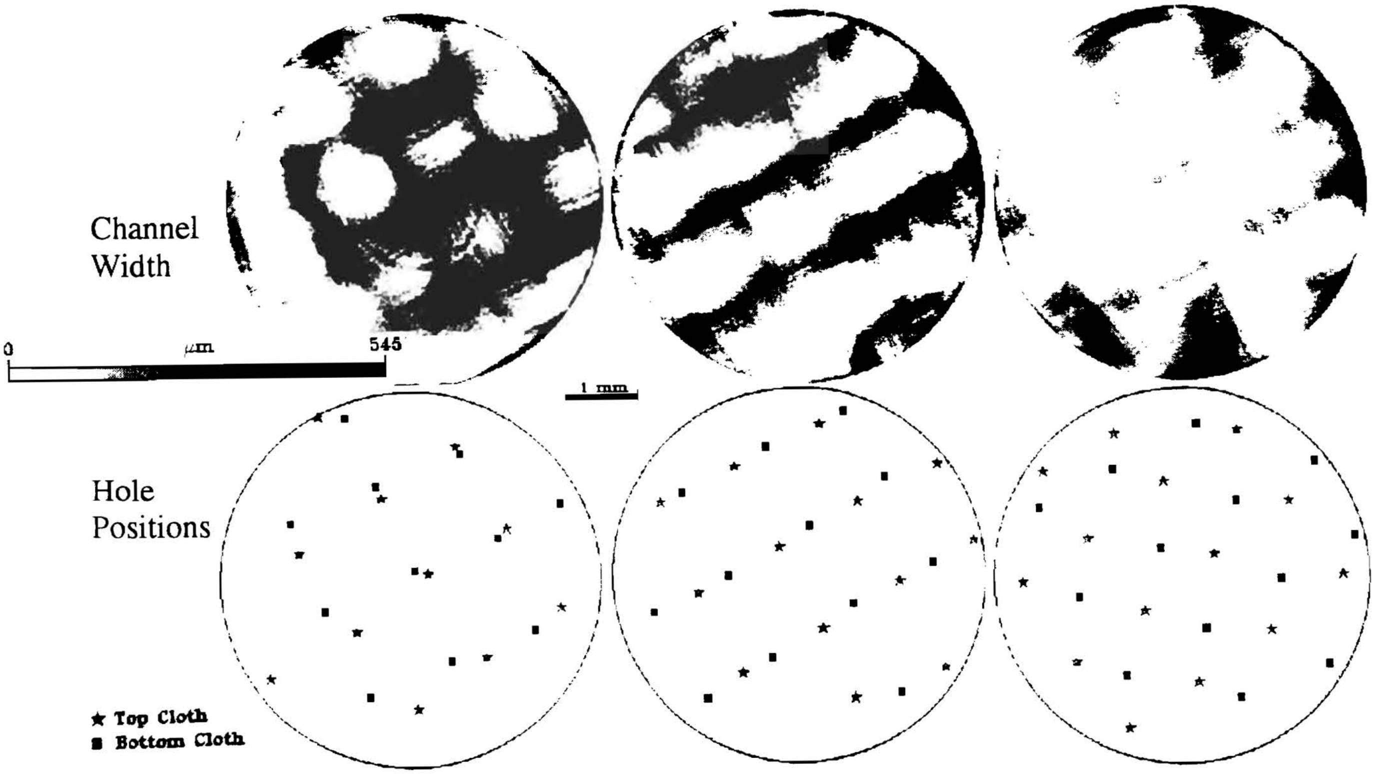


Figure 3. Cross-section schematically showing the arrangement of cloths on either side of a channel in the coincident (top) and anti-coincident (bottom) alignments. This shows that well-aligned holes can have one of two very different structures.

CHEMICAL VAPOR INFILTRATION AND THE ROLE OF THE WIDTH OF CHANNELS BETWEEN CLOTH LAYERS

Problem: The densification of ceramic composites using chemical infiltration (CVI) is a complex process that is critically dependent on gas transport through the network of fibers that reinforce the composite. Previous methods of investigating the relationship between fiber architecture and the densification process have been limited to destructive, post-process sectioning. Nondestructive observation at several stages from preform to dense composite would produce better understanding of CVI.

Results: Channel width as a function of position in a 0°/90° sample was found to belong to one of three types of patterns: two-dimensional networks of pipes, arrays of parallel pipes or relatively pattern-free (upper row of the Figure). These patterns correspond to channels with holes on either side of the channel being well-aligned, being displaced along fiber tow directions or being unaligned, respectively (lower row of the Figure).



Significance - For Energy Conservation: Ceramic matrix composites allow higher operating temperatures and better thermodynamic efficiency for many energy conversion systems.

Significance - For Materials Technology: Better understanding of the CVI process will improve the properties and lower the cost of ceramic composite materials fabricated using this process. Improving knowledge of structure-transport relationships will benefit other composite fabrication processes, leading to more widespread application of composites.

(R&D performed at Georgia Institute of Technology under subcontract #19-SL260C with Martin Marietta Energy Systems under their contract #DEAC05-840R21400).

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT SUMMARY: CHARACTERIZATION OF CVI DENSIFICATION OF CERAMIC COMPOSITES

PHASE: FY 1993

PERFORMING ORGANIZATION: Georgia Institute of Technology

PRINCIPAL INVESTIGATORS: T.L. Starr 404/853-0579 and S.R. Stock 404/894-6882

PHASE OBJECTIVE: Relate geometry and dimensions of channel between and of holes through layers in cloth lay-up preforms during CVI densification and relate to transport model.

ULTIMATE OBJECTIVE: Develop understanding of relationship between preform fiber architecture and densification behavior, and use to design preform for optimum infiltration.

TECHNICAL APPROACH: In collaboration with Dr. J.H. Kinney at Lawrence Livermore National Laboratory we will use very high resolution X-ray computed tomography to repeatedly image small preform samples after various processing times. Different cloth lay-ups will be examined. The objective of this research is to observe the deposition of matrix material in the pores of a ceramic fiber preform at various stages of the chemical infiltration (CVI) process. These observations will allow us to relate local deposition rates in various regions of the composite to the surrounding network of porosity and to better model the relationship between gas transport and fiber architecture in CVI preforms.

PROGRESS: A second imaging run was begun during Spring 1993. The influence of cloth positioning on channel geometry and the spatial variation of channel widths was studied in detail for a 0°/90° Nicalon/SiC composite as a function of infiltration time. Two-dimensional arrays of pipes were found when the holes in adjacent cloths were well-aligned, a single set of parallel pipes were found when the holes were shifted along one of the tow directions and little structure was seen when the translation was not along between the tow directions. The change in surface area of macroporosity per unit volume was found to be in good agreement with model predictions.

Patents: none **Publications:** three **Proceedings:** none **Presentations:** two

ACCOMPLISHMENTS:

Licenses: none

Known Follow-on Product: None

Industry Workshop: None

Technology Transfer or Industrial Interaction: None

PROJECT TITLE: Characterization of CVI Densification of Ceramic Composites

CRITICAL ISSUES: Continuation of the second set of densification experiments is key to determining the effect of such variables as lay-up geometry and fiber type.

FUTURE PLANS: Analysis of image data for a 0°/45° sample will continue. Experiments with different layup variations will be continued.

POTENTIAL PAYOFFS:

ESTIMATED ENERGY SAVINGS:

Georgia Tech
School of Materials Science and Engineering

Georgia Institute of Technology
Atlanta, Georgia 30332-0245
USA
FAX: 404•853•9140

July 21, 1994

Dr. Peter Angelini, Manager
Advanced Industrial Materials Program
Oak Ridge National Laboratory
Building 4515, MS-6065
P. O. Box 2008
Oak Ridge, TN 37831-6065

Dear Peter:

Enclosed is the quarterly report for the Georgia Tech part of our collaborative effort with Dr. John Kinney at LLNL.

Please note that I have transferred to the School of Materials Science and Engineering here at Georgia Tech. My phone number will remain the same, however my fax number and mailing address are different. Please change these in your records.

Sincerely,

Thomas L. Starr

Enclosure

CHARACTERIZATION OF CVI DENSIFICATION OF CERAMIC COMPOSITES

T.L. Starr and S.R. Stock
School of Materials Science and Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332-0245

Subcontract #19X-SL260C

INTRODUCTION

Composites fabricated by the chemical vapor infiltration (CVI) process have excellent mechanical properties and, using the forced flow-thermal gradient variation, good processing economics in small scale demonstrations. Scale-up to larger, more complex shapes requires better understanding of gas flow dynamics in the fiber preform and of the relationship between fiber architecture and densification behavior. The objective of this research is to observe the deposition of matrix material in the pores of a ceramic fiber preform at various stages of the chemical vapor infiltration process. These observations allow us to relate local deposition rates in various regions of the composite to the connectivity of the surrounding network of pores and to better model the relationship between gas transport and fiber architecture in CVI preforms.

We characterize the matrix deposition process using high resolution X-ray tomographic microscopy (XTM) in collaboration with Dr. John Kinney at Lawrence Livermore National Laboratory, by repeated imaging of a small preform specimen after various processing times. Using these images we determine the morphology and dimensions of channels between and through layers in cloth lay-up preform during CVI densification and relate these to a transport model. Previous work has focus on the simple 0/90° cloth lay-up preform, making measurements of local density variations and the dimensions of the macropores between cloth layers.

TECHNICAL PROGRESS

Summary

Our primary effort this quarter has involved preparation and transmittal of specimens for XTM imaging by Dr. John Kinney's group at LLNL. A large block of beam time was available in June 1994 at the Stanford synchrotron facility. Data has been collected for several specimens but only a small amount of this data has been analyzed. In addition we completed measurements of surface area for previously imaged cloth lay-up specimens and compared these results to model estimates.

Milestones

1. Imaging CVI Samples with Density Gradients

Nine of the larger diameter graphite CVI reactors were packed with cloth lay-up preforms. These reactors have 175% of the volume of the earlier reactor design which reduces the possibility of "edge effects" in our results. Fiber architecture variations include 0/30/60° lay-up using square-weave Nicalon and Tyranno cloths with and without controlled hole alignment, and 0/90° and 0/45° lay-ups with Tyranno cloth. Three of these specimens were returned after imaging, partially infiltrated and imaged again. A second infiltration was completed but these could not be imaged since test period at Stanford had expired. In addition to these specially fabricated specimens, we machined and sent XTM specimens from larger samples of CVI composite. These included 3-D weave, 3-D braid and filament wound Nicalon preforms.

2. Model Development

Detailed calculation of surface area available for deposition has been completed for the 0/90 cloth lay-up preform previously imaged. The calculation involves identifying the boundary between the tow and channel regions in the image, fitting triangular elements to this boundary and summing the areas of these elements. When plotted against the local fractional density these results show reasonably good agreement with a simple, semi-empirical model.

PUBLICATIONS

J.H. Kinney, D.L. Haupt, T.M. Breunig, M.C. Nichols, T.L. Starr and S.R. Stock, "Time Evolution of Microstructure During Forced Flow Chemical Vapor Infiltration of a Continuous-Fiber Ceramic Matrix Composite," Ceramic Engineering & Science Proceedings 14(9-10) 1028-1037 (1993)

PRESENTATIONS

T.L. Starr, S.R. Stock and S. Lee, "Microstructure Evolution During CVI Densification," at the American Ceramic Society 18th Annual Conference on Composites and Advanced Ceramics, January 9-14, 1994

HONORS AND AWARDS None

PATENTS/DISCLOSURES None

LICENSES None

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

Application of XTM to CVI carbon composites was discussed with BP Chemicals (Hitco) Inc. during the AIM meeting in June and in a follow-up telephone conversation. A meeting is scheduled with Amercom in Atlanta in July and a visit to 3M in St. Paul is planned for later in the summer.

COST SHARING None

HIGHLIGHTS

Detailed measurement of surface area available for matrix deposition shows good agreement with semi-empirical model over a range of composite densities. Additional image data has been acquired for an additional fiber (Tyranno) and three new fiber architectures. Use of a larger specimen will reduce possibility of "surface effects" in future measurements.

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CHARACTERIZATION OF CVI DENSIFICATION OF CERAMIC COMPOSITES

T.L. Starr, S.R. Stock and S. Lee
School of Materials Science and Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332-0245

Subcontract #19X-SL260C

INTRODUCTION

Ceramic matrix composites promise higher operating temperature and better thermodynamic efficiency in many energy conversion systems. In particular, composites fabricated by the chemical vapor infiltration (CVI) process have excellent mechanical properties and, using the forced flow-thermal gradient variation, good processing economics in small scale demonstrations. Scale-up to larger, more complex shapes requires understanding of gas flow through the fiber preform and of the relationship between fiber architecture and densification behavior. This understanding is needed for design of preforms for optimum infiltration.

The objective of this research is to observe the deposition of matrix material in the pores of a ceramic fiber preform at various stages of the CVI process. These observations allow us to relate local deposition rates in various regions of the composite to the connectivity of the surrounding network of porosity and to better model the relationship between gas transport and fiber architecture in CVI preforms. Our observation of the CVI process utilizes high resolution X-ray tomographic microscopy (XTM) in collaboration with Dr. John Kinney at Lawrence Livermore National Laboratory with repeated imaging of a small preform specimens after various processing times. We use these images to determine geometry and dimensions of channels between and through layers in cloth lay-up preform during CVI densification and relate these to a transport model.

TECHNICAL PROGRESS-FY 1994

Summary

Our progress in FY 1994 includes both additional CVI/XTM experiments and further analysis of previously obtained data. New experimental efforts investigate the effects of cloth orientation and fiber diameter on densification. In addition, permeability measurements at different densification times will guide development of a gas transport model. The analysis effort has produced quantitative measurements of pore surface area during the final stages of densification. This information - not obtainable by any other technique - is critical to design of fiber architectures for rapid, complete densification.

1. Imaging CVI Samples with Density Gradients

In order to reduce the possibility of "edge effects" in our experiments we now use larger graphite CVI reactors - 8.0 mm in diameter versus the previous 6.0 mm. These reactors have 175% of the volume of the earlier reactor design. Nine of these reactors were prepared with fiber architecture variations include 0/30/60° lay-up using square-weave Nicalon and Tyranno cloths with and without controlled hole alignment, and 0/90° and 0/45° lay-ups with Tyranno cloth.

XTM characterization was begun during a June test period at the Stanford Synchrotron Radiation Laboratory (SSRL) and will be completed during the next available test period in January 1995. Three of these specimens were returned after imaging, partially infiltrated and imaged again.

Gas permeability of these specimens was measured at two levels of densification. These results will be compared to pore structure measurements developed from the XTM images. Such correlations will provide a quantitative understanding of gas flow during CVI.

In addition to these specially fabricated specimens, we machined specimens from larger samples of CVI composite and sent these for XTM imaging. These included 3-D weave, 3-D braid and filament wound Nicalon preforms.

2. Model Development

Detailed calculation of pore surface area has been completed for the 0/90 cloth lay-up preform previously imaged. The calculation involves identifying the boundary between the tow and channel regions in the image, fitting triangular elements to this boundary and summing the areas of these elements. The local fractional density also is calculated from the image data including material both within and between the fiber tows.

These results are plotted in Figure 1 and represent the only known experimental measurement of pore surface area in CVI composites. This property controls the densification process, particularly as the composite approaches full density. These measurements and analyses of image data from other preform architectures will be used to develop a preform microstructure model that allows design of fiber architecture for rapid, complete CVI densification.

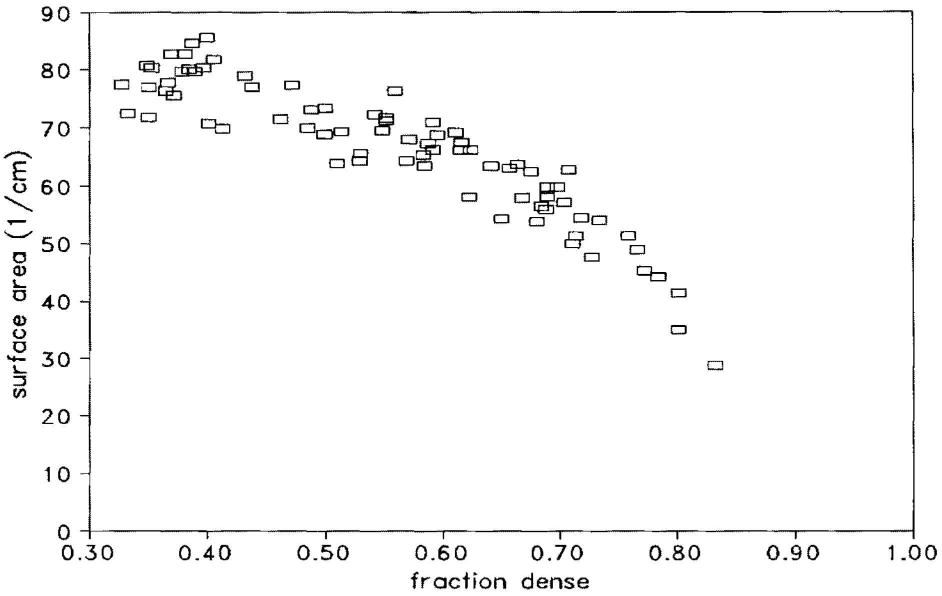


Figure 1. Pore surface area measured from XTM images decreases as density increases. Solid line is the estimate used previously in CVI process modeling.

MILESTONES DURING FY 1994

Progress was made toward completion of milestones, (1) Imaging CVI Samples with Density Gradients and (2) Model Development. These milestones will be completed in FY 95.

PUBLICATIONS

1. J.H. Kinney, D.L. Haupt, T.M. Breunig, M.C. Nichols, T.L. Starr and S.R. Stock, "Time Evolution of Microstructure During Forced Flow Chemical Vapor Infiltration of a Continuous-Fiber Ceramic Matrix Composite," Ceramic Engineering & Science Proceedings 14(9-10) 1028-1037 (1993)

PRESENTATIONS

1. T.L. Starr, S.R. Stock and S. Lee, "Microstructure Evolution During CVI Densification," at the American Ceramic Society 18th Annual Conference on Composites and Advanced Ceramics, January 9-14, 1994

2. S.R. Stock, T.L. Starr and S-B. Lee, "Microstructure Evolution During CVI Densification," Materials Research Society Fall Meeting, Nov. 28-Dec. 2, 1994

HONORS AND AWARDS

None

PATENTS/DISCLOSURES

None

LICENSES

None

INDUSTRIAL INPUT AND TECHNOLOGY TRANSFER

The 3M Company has a strong interest in CVI and is using the process for pilot-scale fabrication of prototype hot gas filters. A visit by 3M personnel to Georgia Tech planned for the end of CY 1994 was postponed until CY 1995 due to prototype production deadlines at 3M. CVI process and preform structure models developed at Georgia Tech could help 3M design future full-scale processing systems.

We had a couple of discussions with BP/Hitco concerning their use of the CVI process for aircraft brake pads. They currently use the isothermal CVI process for this product. While there is interest in better understanding of their process, ongoing corporate reorganization of their parent company inhibited specific actions.

COST SHARING

None

ESTIMATED ENERGY SAVINGS

The development of low-cost, ceramic matrix composites will enable their incorporation into systems for energy conversion and use. Hot gas filters and high temperature heat exchangers are key components in advanced energy conversion systems, such as combined cycle power generation, that offer significant energy savings over current systems. Radiant heaters and burner tubes made of ceramic matrix composites offer significant energy savings in a wide range of industrial processes that involve heating or drying.

HIGHLIGHTS

Pore surface area was calculated from the image data over a range of fractional density. These results represent the only known experimental measurement of pore surface area in CVI composites. This property controls the densification process, particularly as the composite approaches full density. These measurements and analyses of image data from other preform architectures will allow development of a preform microstructure model for use in design of fiber architecture for rapid, complete CVI densification.

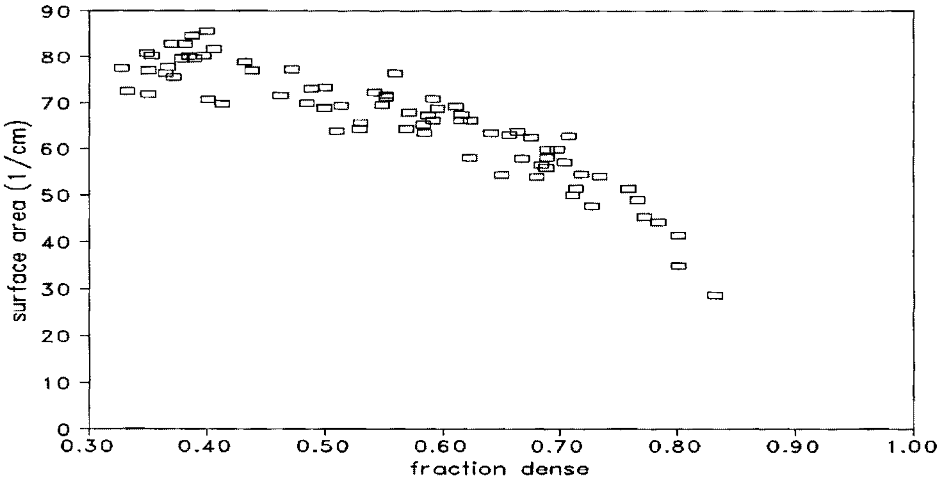
HIGH RESOLUTION X-RAY TOMOGRAPHY PROVIDES CRITICAL DATA FOR CERAMIC COMPOSITE PROCESSING

Problem:

The fabrication of ceramic composites using chemical vapor infiltration (CVI) involves progressive densification by deposition of matrix material on internal pore surfaces. As the composite approaches full density this densification process slows significantly. It is believed that reduction in pore surface area is an important factor in this decrease in densification rate. Previously there has been no method capable of measuring this surface area. Improvements in the CVI process would result from measurement of surface area during CVI densification from preform to final composite and design of preforms and processing to maximize this property.

Results:

High resolution X-ray tomography images obtained during CVI densification of a cloth lay-up preform have been analyzed to produce pore surface area measurements over a range of density. Plotted below these results show a rapid reduction in surface area as density increases. Future measurements with different fiber architectures will identify preform design factors that relate to optimum processing.



Significance - For Energy Conservation:

Ceramic matrix composites allow higher operating temperatures and better thermodynamic efficiency for many energy conversion systems. This research will improve processing efficiency and lower cost of these materials.

(R&D performed at the Georgia Institute of Technology under subcontract #19X-SL260C with Martin Marietta Energy Systems under their contract #DEAC05-840R21400)

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#6

PROJECT SUMMARY

ADVANCED INDUSTRIAL CONCEPTS (AIC) MATERIALS PROGRAM

PROJECT TITLE: Characterization of CVI Densification of Ceramic Composites

FISCAL YEAR: 1994 **COMPLETION DATE:** 5/31/1995

PERFORMING ORGANIZATION: Georgia Institute of Technology

PRINCIPAL INVESTIGATORS: Thomas L. Starr, (404) 853-0579
Stuart R. Stock, (404) 894-6882

PHASE OBJECTIVE: Determine geometry and dimensions of porosity in cloth lay-up preform during CVI densification and relate to gas transport and matrix deposition rate.

ULTIMATE OBJECTIVE: Develop understanding of relationship between preform fiber architecture and densification behavior, and use to design preform for optimum infiltration.

TECHNICAL APPROACH: In collaboration with Dr. John Kinney at Lawrence Livermore National Laboratory we will use high resolution X-ray tomographic microscopy (XTM) to repeatedly image a small preform specimen after various processing times. The objective of this research is to observe the deposition of matrix material in the pores of a ceramic fiber preform at various stages of the chemical vapor infiltration (CVI) process. These observations will allow us to relate local deposition rates in various regions of the composite to the structure of the surrounding pore network and to better model the relationship between matrix deposition and fiber architecture in CVI preforms.

PROGRESS: Image data from have been reconstructed and analyzed. Pore surface area measurements over a range of density have been obtained. These results show a rapid reduction in surface area as density increases. Future measurements with different fiber architectures will identify preform design factors that relate to optimum processing.

Patents:_________ **Publications:** 1 **Proceedings:**_________

Books:___________ **Presentations:** 2

ACCOMPLISHMENTS:

Licenses: None

Known Follow-on Product: None
(This work is relevant to ongoing licensing and technology transfer activities at Oak Ridge National Laboratory)

PROJECT TITLE: Characterization of CVI Densification of Ceramic Composites

CRITICAL ISSUES: Examination of a wider range of preform architectures. Differentiation between "open" and "closed" porosity. Development of relationship between microstructure and processing.

FUTURE PLANS: Analysis of image data from 1994-5 runs will continue. These runs include cloth layups with two fibers and three orientations, 3-D weave and 3-D braid materials. This analysis will extract structure data that is critical to development of a microstructure-processing model.

POTENTIAL PAYOFF: The development of low-cost, ceramic matrix composites will enable their incorporation into systems for energy conversion and use. Hot gas filters and high temperature heat exchangers are key components in advanced energy conversion systems, such as combined cycle power generation, that offer significant energy savings over current systems. Radiant heaters and burner tubes made of ceramic matrix composites offer significant energy savings in a wide range of industrial processes that involve heating or drying.