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HERMETIC SIC-SIC COMPOSITE TUBES

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W Kowbel,Y Liu, C Bruce, JC Withers,LE Kolaya, N Lewis

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Hermetic SiC-SiC Composite Tubes

Witold Kowbel,* Yin Liu, Calvin Bruce and James C. Withers, MER Corporation, Tucson, AZ 85706

Lynne E. Kolaya and Nathan Lewis, Lockheed Martin, Schenectady, NY 12301

Abstract:

SiC-SiC composites have good potential for structural applications but are limited by expensive forming techniques. A high purity β-SiC fiber produced by MER, and a polymer derived SiC matrix were used to fabricate small diameter hermetic SiC-SiC tubes. The process was optimized to prevent the formation of a brittle structure while rapidly forming a dense matrix. This tube was made hermetic by first coating the surface of the tube with a silicon carbide particle filled polymer slurry, followed by a Chemical Vapor Infiltration/ Deposition (CVI/CVD) SiC deposition which was performed to close any residual porosity on the composite tube surface. X-ray diffraction and Transmission Electron Microscopy (TEM) examination was performed to determine the fiber and matrix structures. These tubes were found to be impermeable to helium with leak rates below 10^{-9} cc/sec as determined by testing similar to MIL-STD-883D, method 1014.10. This high level of impermeability was sustained following thermal cycling between room temperature and 1520°C.

1. Introduction

High temperature hermetic materials are critical to many engineering applications; e.g., thermocouple wells, coal plants, and fusion power plants. In addition to hermeticity, these high temperature applications usually require reliable materials with high strength, toughness, and thermal-chemical stability. Monolithic ceramic materials have high strength, good hermeticity, and thermal-chemical stability; but suffer from poor toughness and reliability.[1] In contrast, ceramic matrix composites (CMCs) reinforced with ceramic fibers offer high strength and toughness, however, fabricating hermetic CMC materials is technically difficult. For instance, making a CMC with the polymer infiltration and pyrolysis (PIP) method, can take nine or more PIP cycles to reduce the void proportion to < 10%. In addition to voids, shrinkage cracks due to pyrolysis are also potential leakage paths. CMCs made from the chemical vapor infiltration (CVI) method also have voids trapped in the matrix. The architecture of the fiber reinforcements influences the hermeticity of a CMC component. Component shape also affects hermeticity, e.g., a closed end tube where fibers bend close to 90° is difficult to make hermetic.

There are only a few reports of hermetic CMCs. Streckert et al. reported the fabrication of hermetic SiC composite tubes using the CVI method.[2] Nicalon SiC fibers were filament wound on a graphite-rod mandrel at a low bias angle (the fiber tow was almost normal to the mandrel) to minimize large pores due to fiber overlap. Then CVI SiC was applied on the SiC fibers to densify the composites producing hermetic SiC CMC tubes. Several limitations with these hermetic SiC CMC tubes are: (1) no fiber reinforcement along the tube axis direction to increase the strength and toughness; (2) the proportion of fiber reinforcement to the overcoated chemical vapor infiltrated/deposited (CVI/CVD) monolithic SiC was ~1:1, so the mechanical properties are not dominated by composite behavior; and (3) the method does not provide for the fabrication of tubes with one end closed. This paper describes a process for fabrication of a hermetic CMC tube which solves these problems.

2. Experimental Procedure

2.1 Materials

Plain weave SiC fabrics fabricated by the MER chemical vapor reaction (CVR) process were utilized as the reinforcement.[3-6] Ceraset™ inorganic polymer from Du Pont Lanxide Inc. (Newark, DE), was used as a matrix precursor. Toluene (Mallinckrodt Co) and either submicron SiC powders (Superior Graphite Co., Chicago, IL) or MER produced SiC nanoparticles, were mixed with the Ceraset™ polymer to prepare a slurry for coating the composite tube surface.

2.2 Closed End CMC Tube Molding

The as manufactured tube dimensions were 7-8 mm in diameter by 125 mm long with a 0.75-1.5 mm thick wall and one end closed. To fabricate this tube, carbon coated (0.1 µm) SiC fabrics were first impregnated with Ceraset polymer, then the fabrics were wrapped on an aluminum mandrel. One side of the pre-preg was cut into tabs, which were folded over one end of the mandrel to form a closed end as illustrated in Figure 1. Three fabric layers were needed for hermeticity, resulting in walls ~1 mm thick.

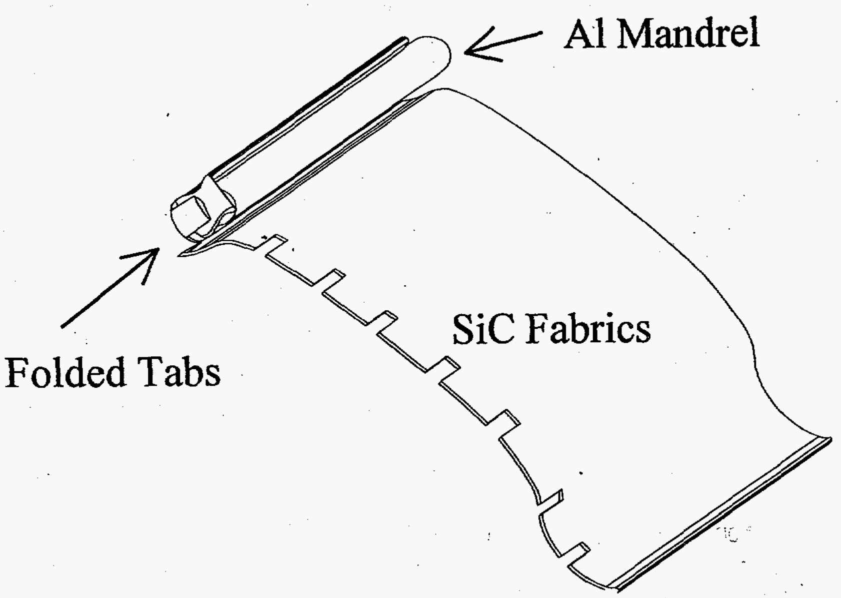


Figure 1. SiC fabric wrapping for one end closed CMC tube

The SiC pre-preg wrapped on an Al mandrel was placed into a flexible rubber mold, and heated to 185°C for 1 hour (Figure 2).

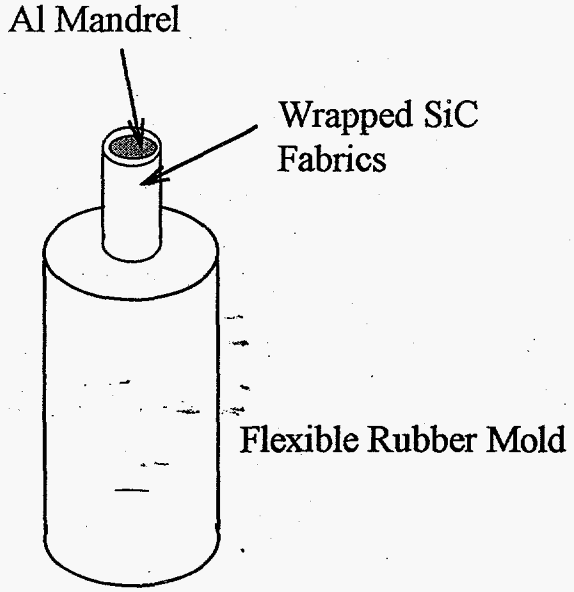


Figure 2. CMC Tube Skeleton formed using Lay-up-Pressure Molding Technique

2.3 CMC Densifications

The tubes were initially pyrolyzed to 1100°C in argon and then were re-infiltrated with Ceraset polymer and thermally treated to 1100°C. There was a third polymer infiltration and pyrolysis (PIP) cycle with the temperature raised to 1400°C. This sequence was repeated for a total of six PIP cycles.

2.4 CMC Tube Sealing

After the sixth PIP cycle, a SiC powder (sub-micron)/Ceraset slurry (2:1 weight ratio) was coated on the outside surface of the composite tubes to seal the large pores. After curing at 150°C/1 hour/air, the tubes were pyrolyzed to 1100°C in Ar to convert the Ceraset polymer into SiC producing a SiC_p/SiC composite layer.

Subsequently, CVI/CVD was used to provide the final seal (Figure 3). Methyltrichlorosilane (MTS) and H_2 were separately passed through capillary tubes to the inside of the composite tube. This processing scheme resulted in a CVI/CVD layer on both the inside and outside of the tube. The CVI/CVD process was carried out at a deposition temperature of 1120°C, and a pressure of 25 Torr.

2.5 CMC Tube Testing

The hermeticity testing of the CVI/CVD sealed CMC tubes was conducted using a Varian Porta-Test Leak Detector (Model 938-41), which has a sensitivity limit of 1×10^{-9} cc/sec helium leak rate. A transmission electronic microscope (TEM) was used to examine the CMC and coating microstructure, and a scanning electronic microscope (SEM) was used to examine the structural integrity. The thermal shock test consisted of cycling from 25°C to 1520°C with a 10°C/min heating/cooling rate in argon (Ar) three times.

3. Results and Discussion

3.1 Hermeticity

During development, the CMC tubes were frequently checked for hermeticity between fabrication steps. Tubes without the CVI/CVD sealing were not hermetic. Studies were

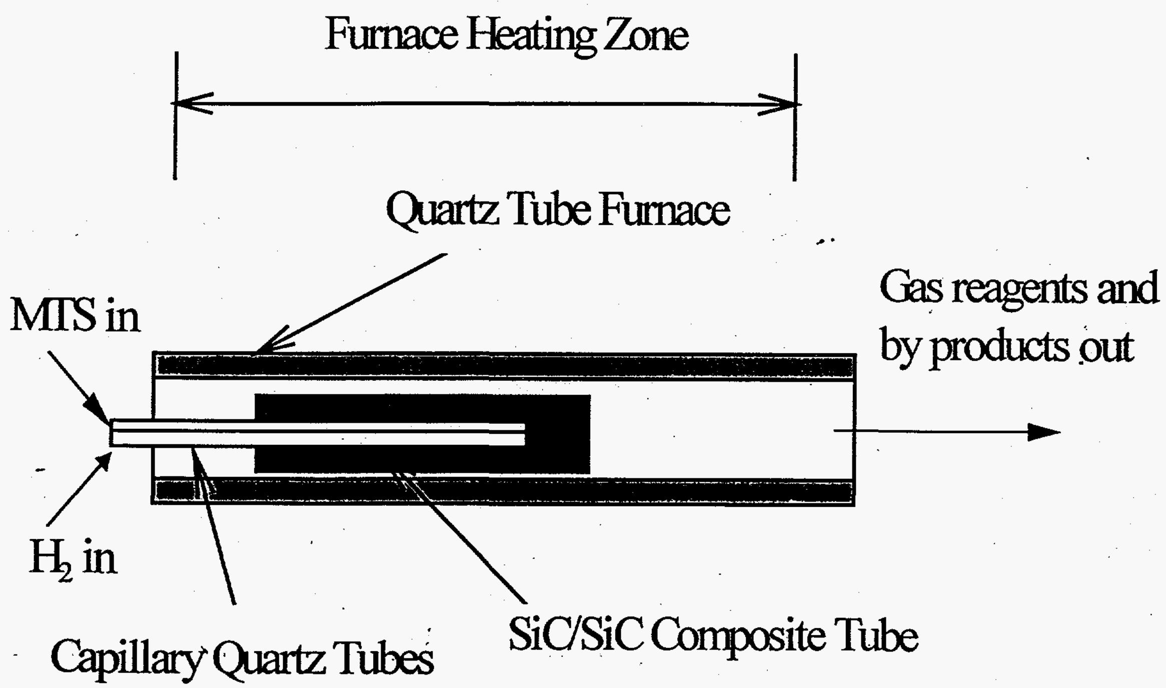


Figure 3. CVI/CVD SiC Deposition on the Inside Surface of a Composite Tube with One End Closed

performed to determine how much PIP densification was needed before CVI/CVD. It was found that only a few PIP cycles were needed yielding tubes which were still quite porous. These tubes only held a vacuum of 500 torr, which is too high a pressure for the leak detector to operate at. After CVI/CVD the hermeticity was measurable, yielding leak rates $< 1 \times 10^{-9}$ cc/sec (the lower limit of the detector). More than five CMC tubes have been fabricated with leak rates $< 1 \times 10^{-9}$ cc/sec. Studies to optimize the thickness of the CVI/CVD layer indicated that a minimum of ~30 μm is needed for helium impermeability. The polymer infiltrations and slurry application provide a uniform surface for the CVI/CVD.

3.2 Thermal shock

Two hermetic CMC tubes with leak rates $< 1 \times 10^{-9}$ cc/sec were thermally shocked three times and retained the same leak rates. SEM inspection of the shocked tubes (Figure 4) revealed no cracks on the outer surface. Thus indicating that residual cracks, either from the polymer conversion or the thermal processing during fabrication, did not propagate a leakage path through the slurry and CVD layers. Also, the lack of surface cracks or spalling indicates good adhesion and matching of thermal properties between the polymer derived CMC and the CVD seal layers.

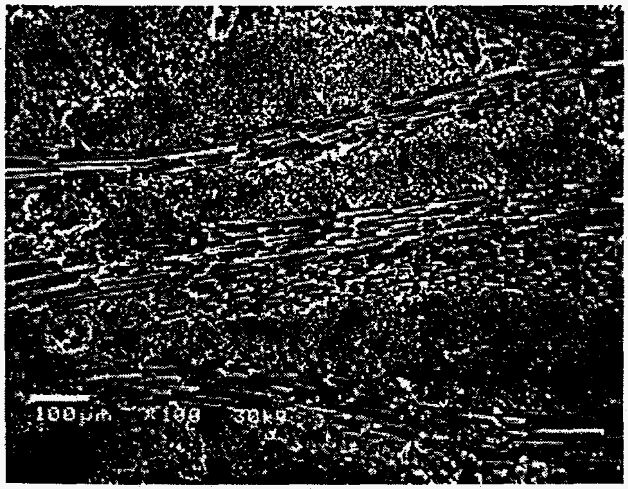
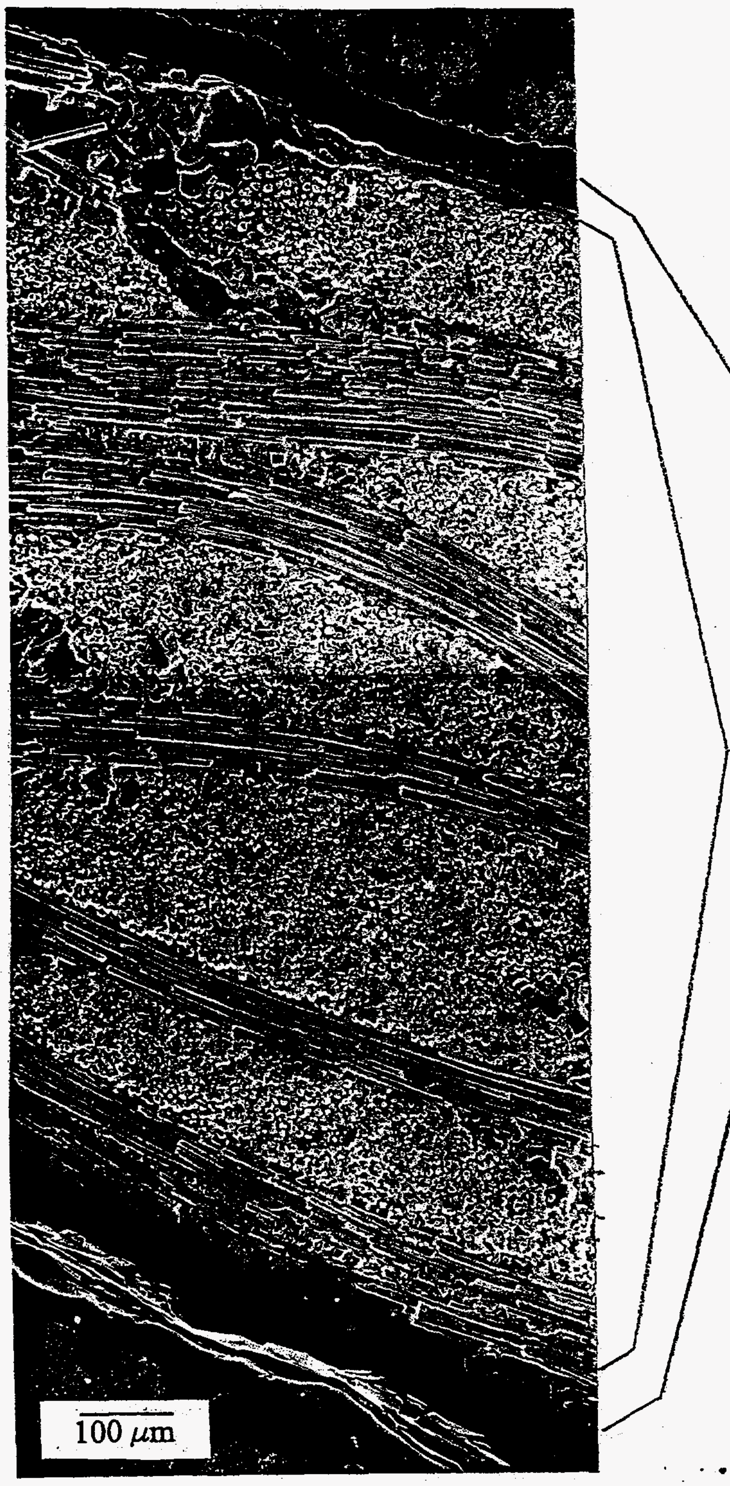


Figure 4. CMC after thermal shock for three times

3.3 CMC Tube Microstructure

The overall hermetic behavior of the CMCs depends on several factors: (1) type of SiC fiber, (2) type of SiC matrix, and (3) type and quality of the seal. In order to elucidate the influence of these factors on the overall CMC tube hermeticity, a thorough microstructural analysis of all these factors was conducted. Figure 5 shows a cross section of a CMC tube. The coefficient of thermal expansion (CTE) mismatch between the CVR-SiC fibers and the PIP matrix appears to be minimized; thus resulting in no transverse cracking. In addition, no gross defects such as large pores or voids are observed. The adherence between the outer CVD layer and the CMC tube appears to be good.



CVD layer on the outer diameter of the tube. Between this and the fibers is the SiC layer derived from a slurry of polymer and and powder.

MER fibers and Ceraset derived SiC.

CVD layer on the inner diameter of the tube.

Figure 5. Cross section of a CMC tube

Figure 6 shows TEM images of the CVR-SiC fiber. The outer shell of the fiber consists of fine grain β-SiC (10-20 nm), while the interior has regions of turbostratic carbon. This indicates that the CVR conversion proceeds from the fiber surface to the fiber center. The fine β-SiC grains may have resulted from the fine grains of the initial T-300 PAN based carbon fibers which acted as nuclei for the CVR process.

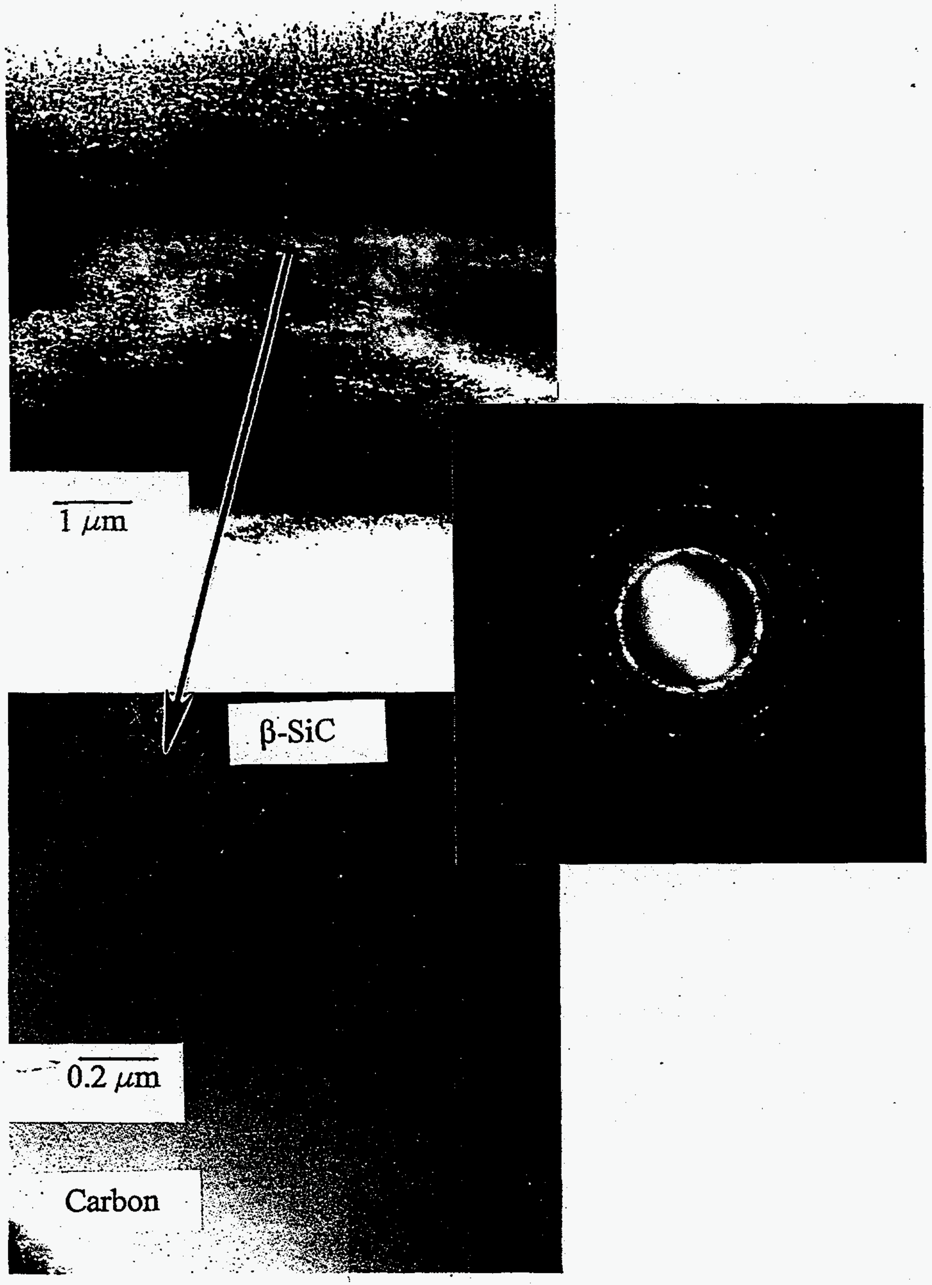


Figure 6. TEM of CVR-SiC fibers (longitudinal section)

Figure 7 shows TEM images of the Ceraset derived β-SiC microstructure. Very fine (2-5 nm) and fine (10-20 nm) β-SiC grains were observed suggesting that the 1400°C heat treatment employed during the CMC processing resulted in the crystallization of the Ceraset derived matrix.

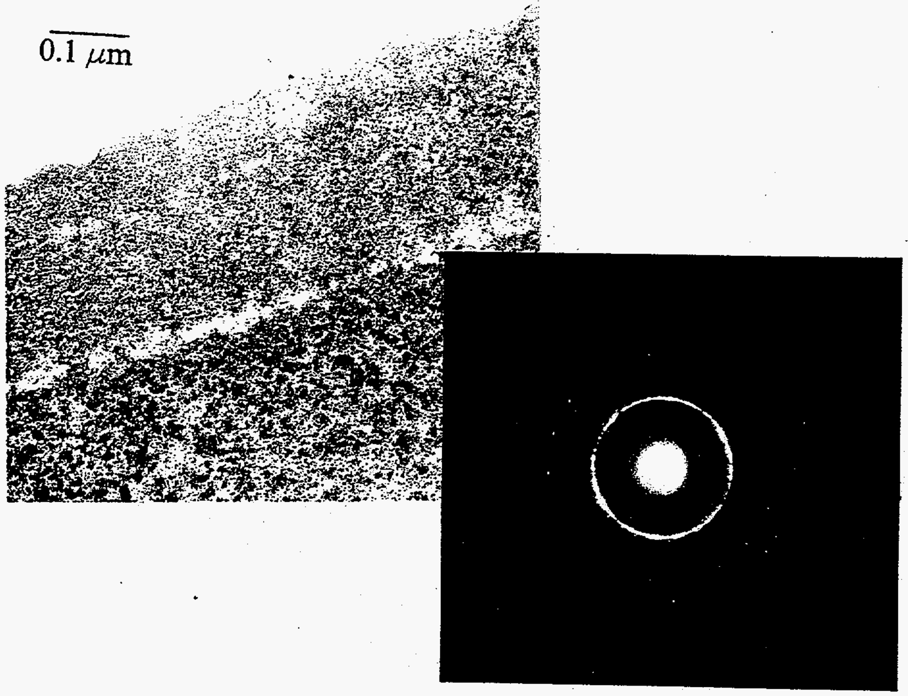


Figure 7. TEM of Ceraset-derived SiC matrix

The PIP processing studies for this material combination show that a higher heat treatment temperature has a stronger influence on the final product toughness. The 1100°C pyrolysis produces a brittle composite, which has no fiber pull out during crack propagation, as shown in Figure 8a. The ≥1400°C pyrolysis offers a tough fracture structure, which has good fiber pull out, as shown in Figure 8b.

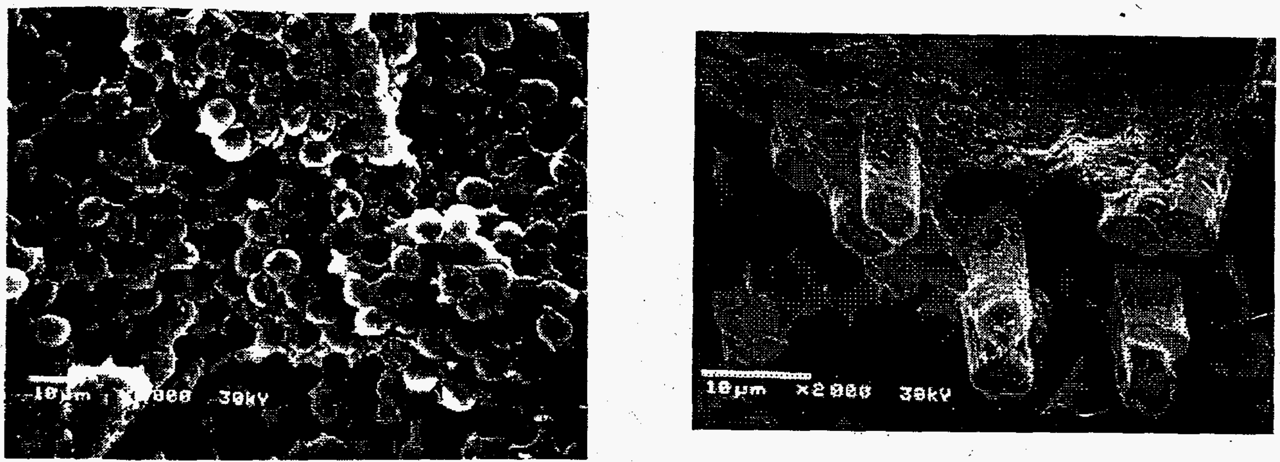


Figure 8. a) Is an SEM micrograph of the brittle structure resulting from the 1100°C pyrolysis. b) Shows an SEM image of the tough fracture structure (with fiber-pull-out) after pyrolysis at 1400°C/Ar/1h.

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3.2 Microstructure of the PIP/CVD Sealant

Figures 9a and 9b are SEM micrographs of the SiC slurry derived coating as applied to the SiC CMC tube. As a result of the volume change during the Ceraset pyrolysis, voids (about 100 μm) are formed within the slurry coating. However, no cracks due to thermal processing are observed on the slurry coating surface. The absence of the thermal processing cracks is the key factor enabling the subsequent pore infiltration with CVI to form a hermetic seal because thermal processing cracks open and close with thermal exposure, so they usually cannot be sealed.

Figure 10 shows TEM micrographs corresponding to the slurry coating. It reveals large β-SiC grains embedded in a Ceraset derived fine β-SiC crystallites. Subsequent to the slurry coating application, a CVI/CVD overcoating was applied to yield a hermetic seal.

Figure 11 shows SEM micrographs corresponding to the CVD SiC overcoat after thermal shock testing. No surface cracks or pores are observed. The CVI/CVD conditions employed provided for the full infiltration of the pores in the slurry coating.

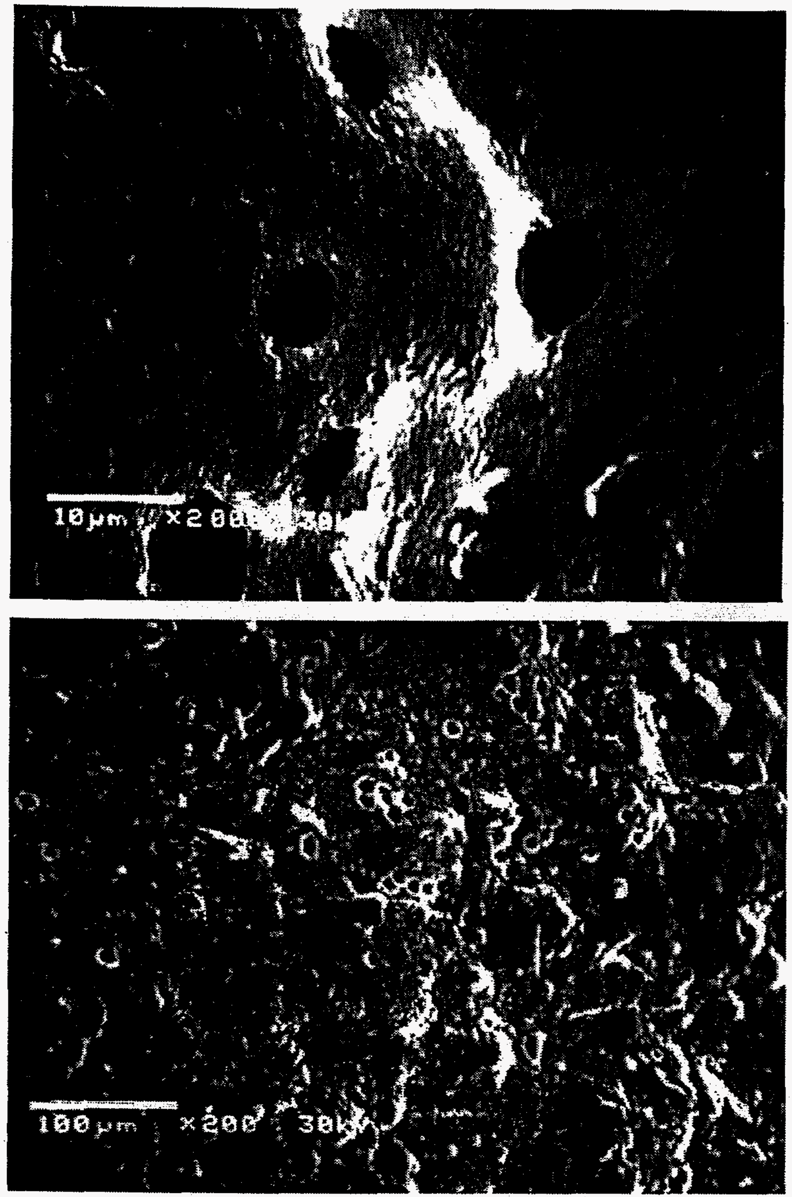


Figure 9 a and b. SEM of slurry coating

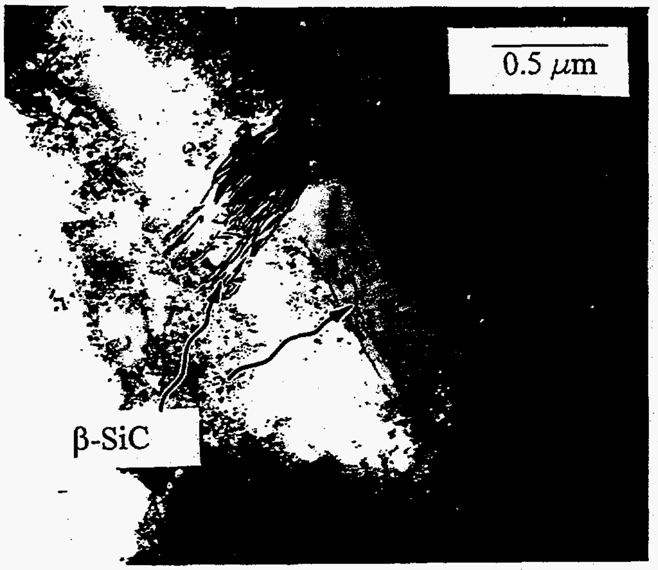


Figure 10. TEM of slurry coating

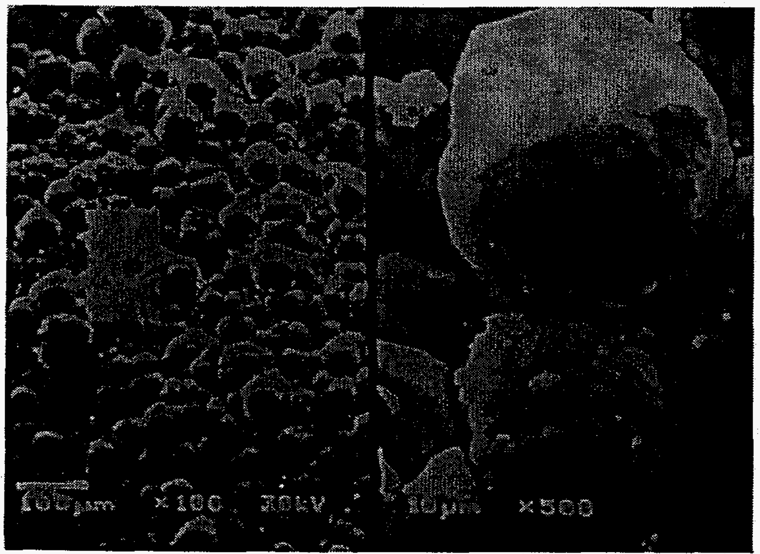


Figure 11. SEM of CVD overcoat

Figure 12 shows TEM micrographs of the CVD SiC overcoat. A columnar growth is observed.

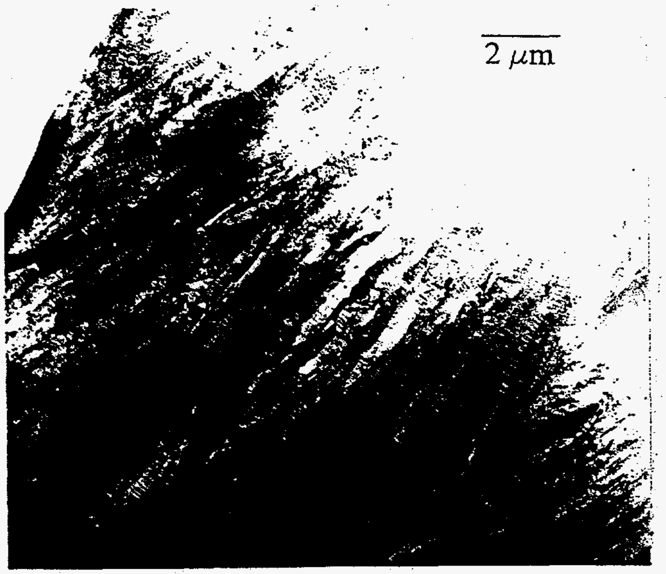


Figure 12. TEM of CVD overcoat

4. Conclusions

1. Small diameter, thin walled SiC composite tubes can be fabricated using a PIP matrix, a polymer slurry coating, and a CVI/CVD overcoat.
2. About a 30μm thick CVI/CVD coating yields an impermeable seal.
3. No transverse cracks are observed within CVR-SiC/PIP SiC composites.
4. The hermetic CMC tubes exhibit thermal shock resistance.

References:

[1] Y. Liu, "Fiber Processing for Composite Applications," Ph.D dissertation, Department of Material Science and Engineering, University of Michigan, 1997.

[2] H. Streckert, K. Norton and C. Wong, "Hermetic SiC Composite Tubes," *ACers Bulletin*, 75 [12] 61-64 (1996).

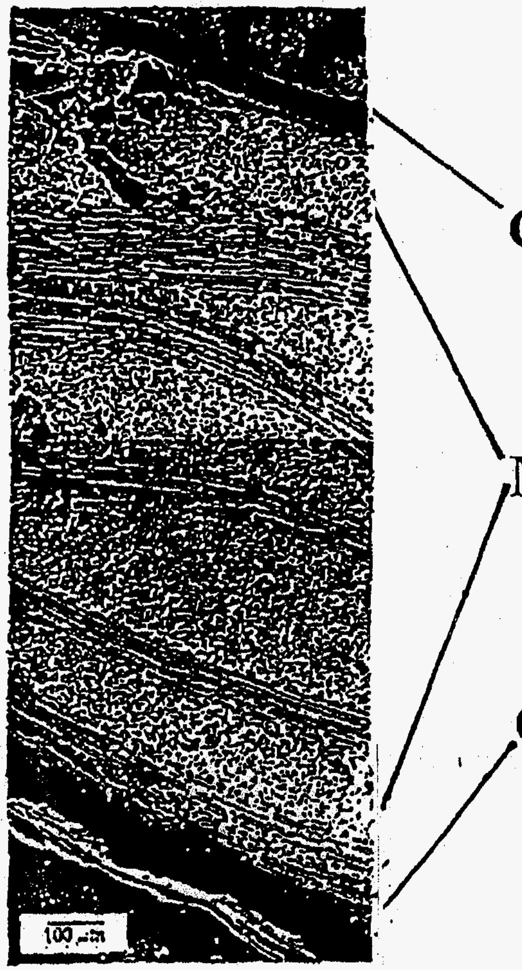
[3] W. Kowbel, J.C. Withers, R.O. Loutfy, C. Bruce, and C. Kyriacou, "Silicon Carbide Fibers and Composites from Graphite Precursors for Fusion Energy Applications", *J. Nuc. Mat.*, Vol. 219, 15 (1995).

[4] W. Kowbel et al., MRS 365 (1995), p197

[5] W. Kowbel et al., MRS 410 (1996) p417

[6] W. Kowbel, et al., 2 IEA, Workshop on SiC-SiC, Sepdai, Japan, to be published.

Cross Section of CMC Tube

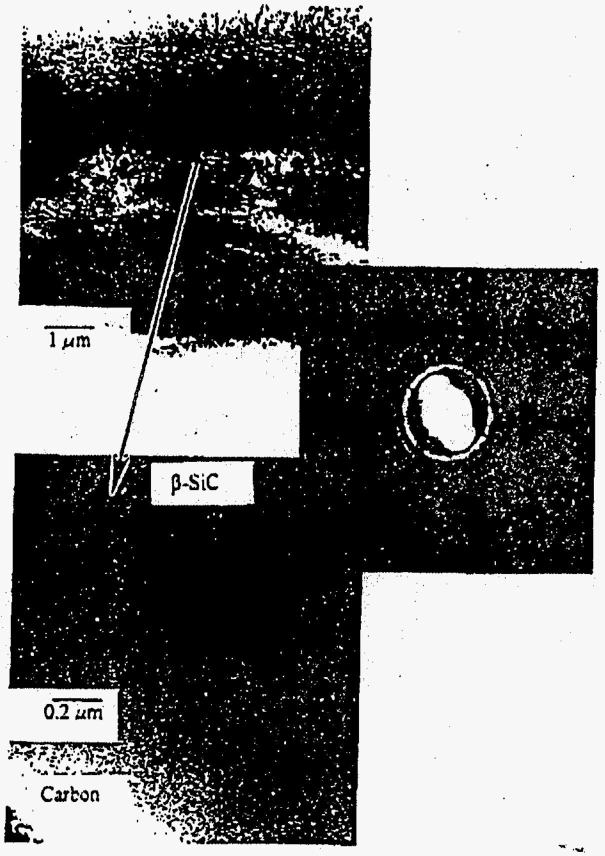


CVD layer on the outer diameter of the tube

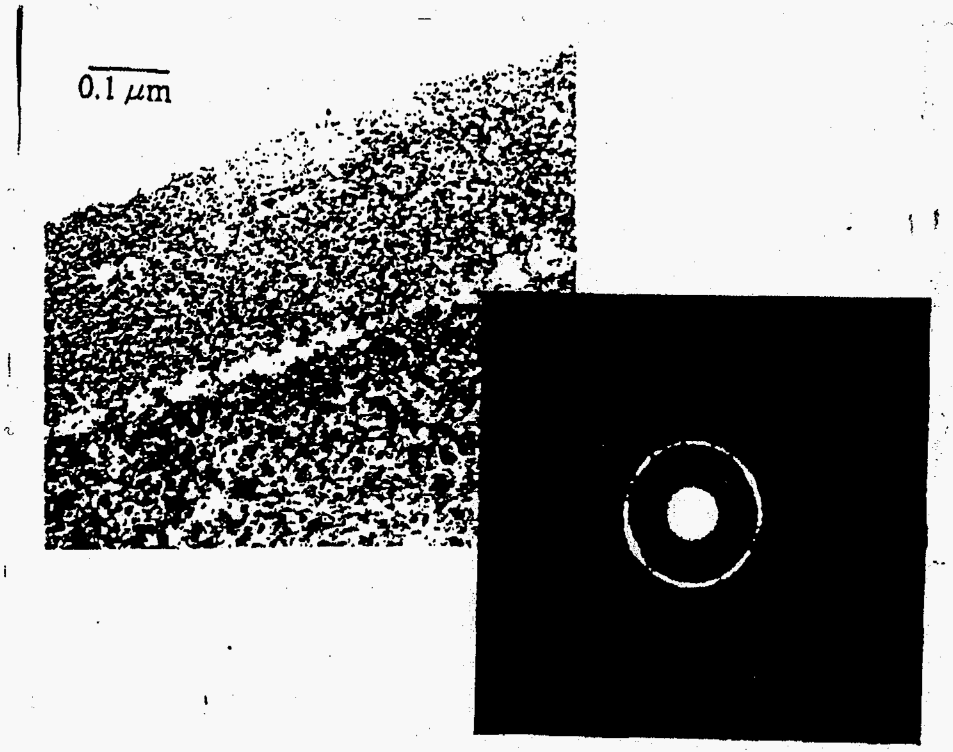
MER fibers and Ceraset derived SiC

CVD layer on the inner diameter of the tube

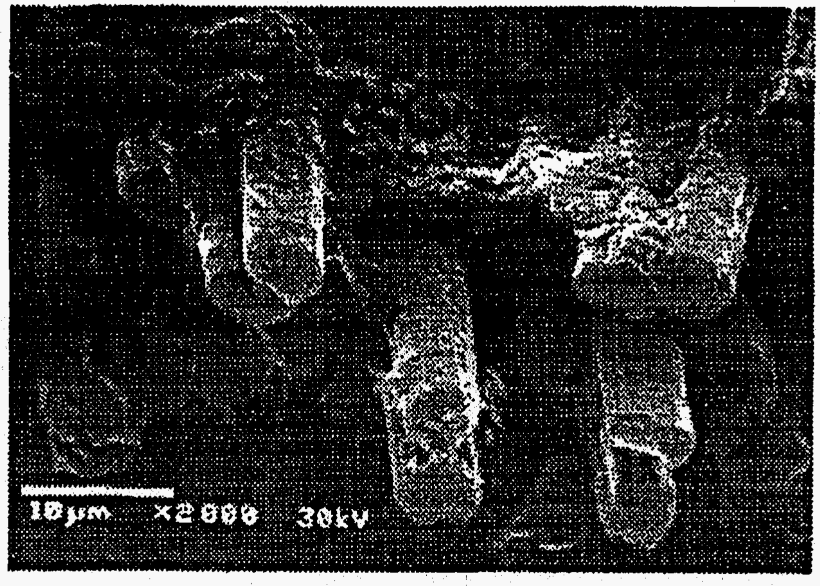
TEM of CVR-SiC Fiber
(longitudinal section)



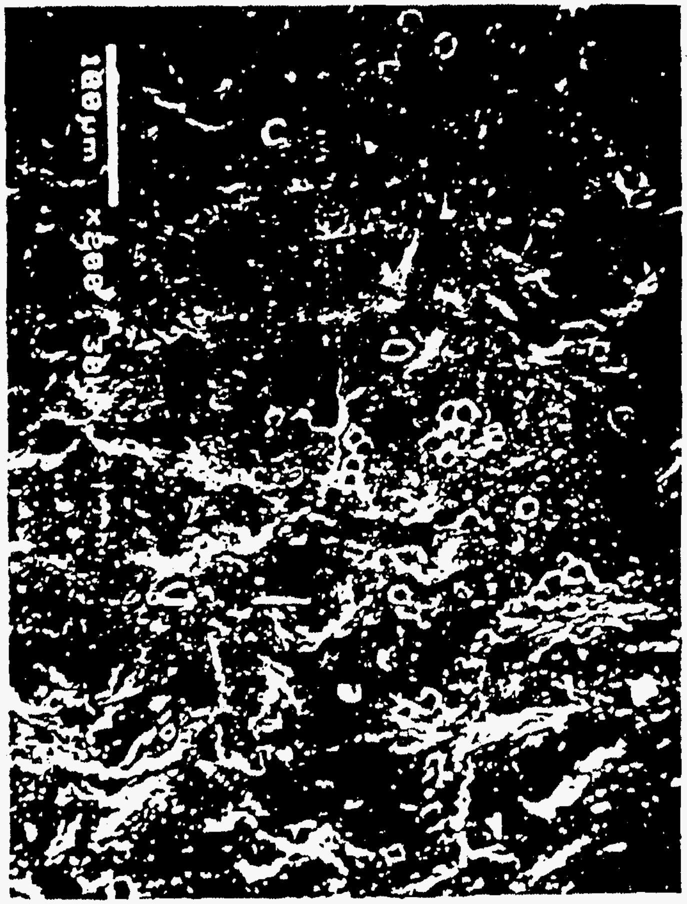
TEM of Ceraset-Derived SiC Matrix



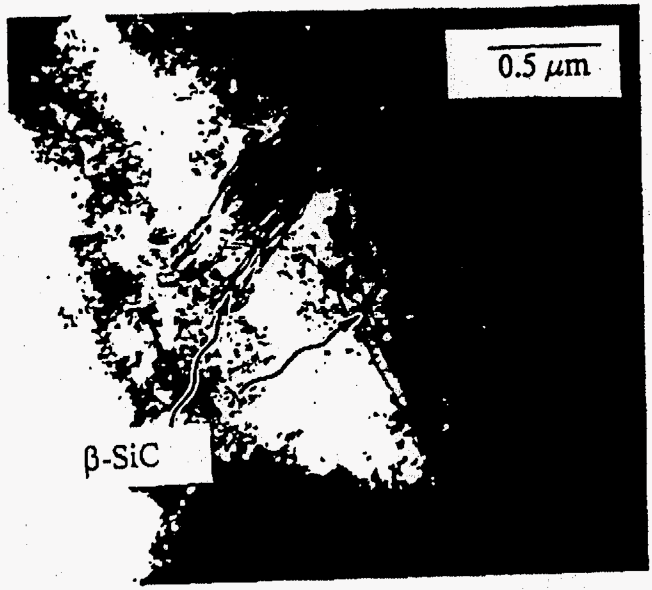
Fracture Surface of SiC-SiC Composite



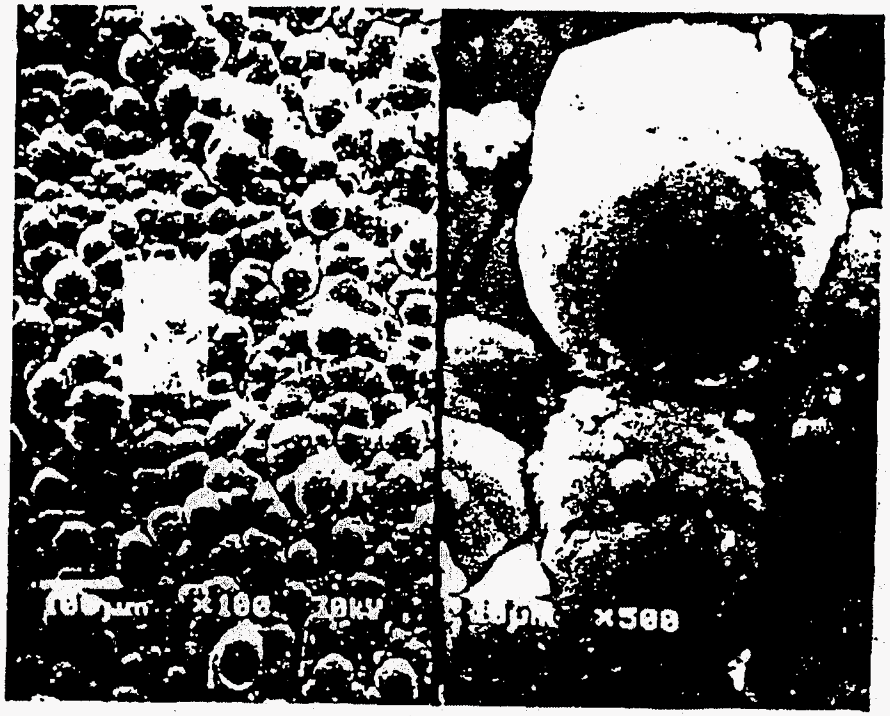
SEM of Slurry Coating



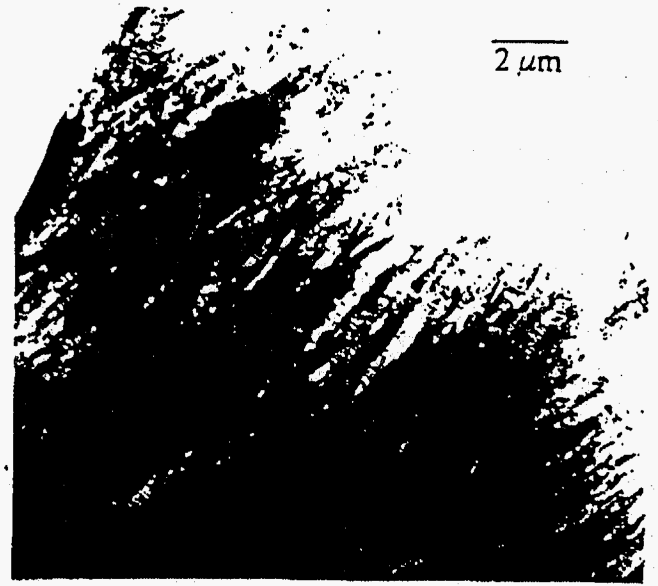
TEM of Slurry Coating



SEM of CVD Overcoat



TEM of CVD Overcoat



CONCLUSIONS

- Hermetic SiC tubes were fabricated
- A 30 μm CVD coating yields an impermeable seal
- No transverse cracks were observed
- The tubes exhibit thermal shock resistance

Hermetic SiC-SiC Tubes

W. Kowbel, Y. Liu, C. Bruce and J.C. Withers
MER Corp.

L.E. Kolaya and N. Lewis
Lockheed Martin

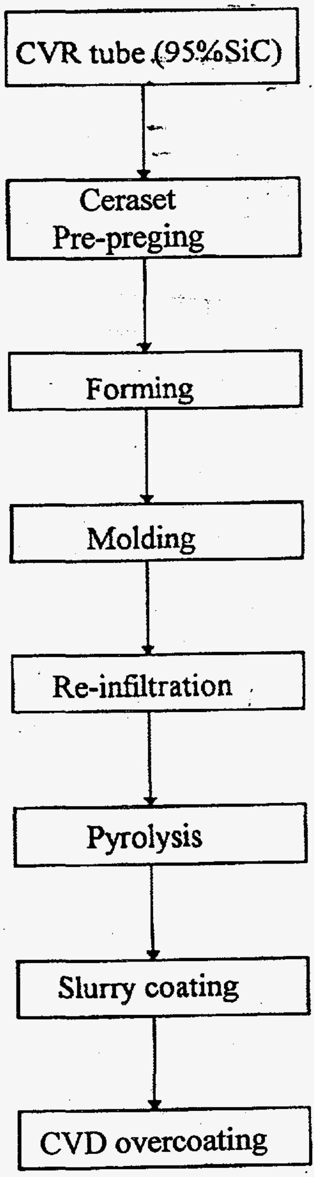
APPROACH

- CVR-SiC Fabric
- PIP-SiC Matrix
- Slurry Coating
- CVD Overcoating

RATIONALE

- CVR-SiC fibers are chemically stable, virtually pure β-SiC
- PIP process easily penetrates fiberous preforms
- Slurry coating helps match the thermo-mechanical property differences
- CVD overcoating fills small pores

Fabrication of Hermetic CMC Tubes



CVR tube (95%SiC)

Ceraset Pre-preging

Forming

Molding

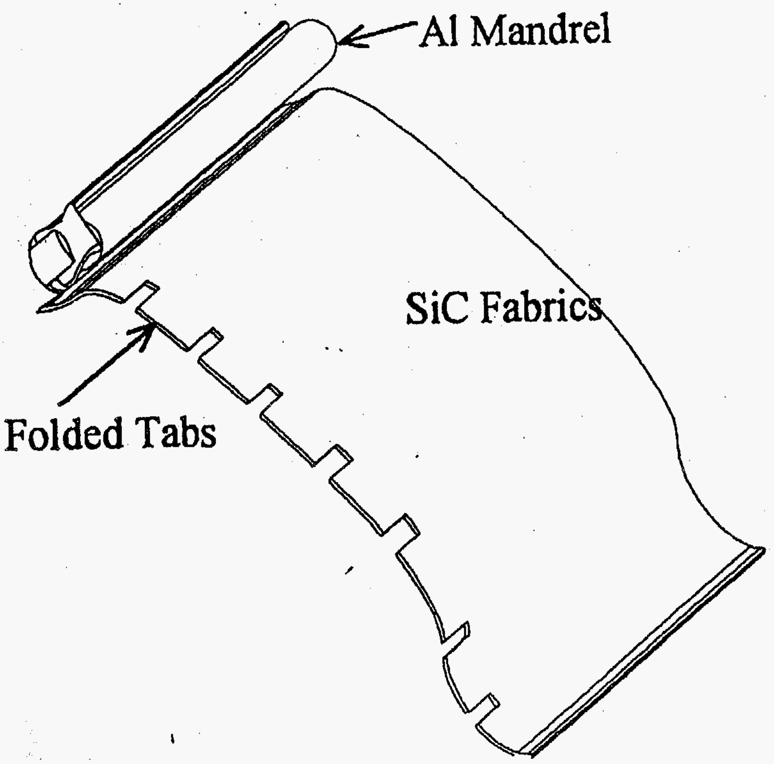
Re-infiltration

Pyrolysis

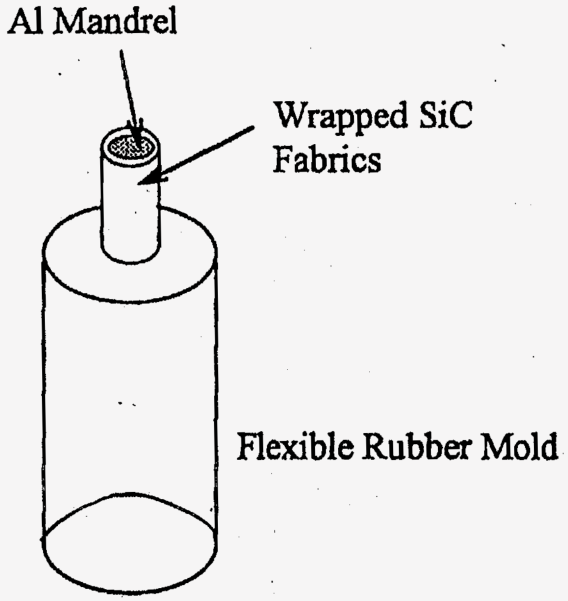
Slurry coating

CVD overcoating

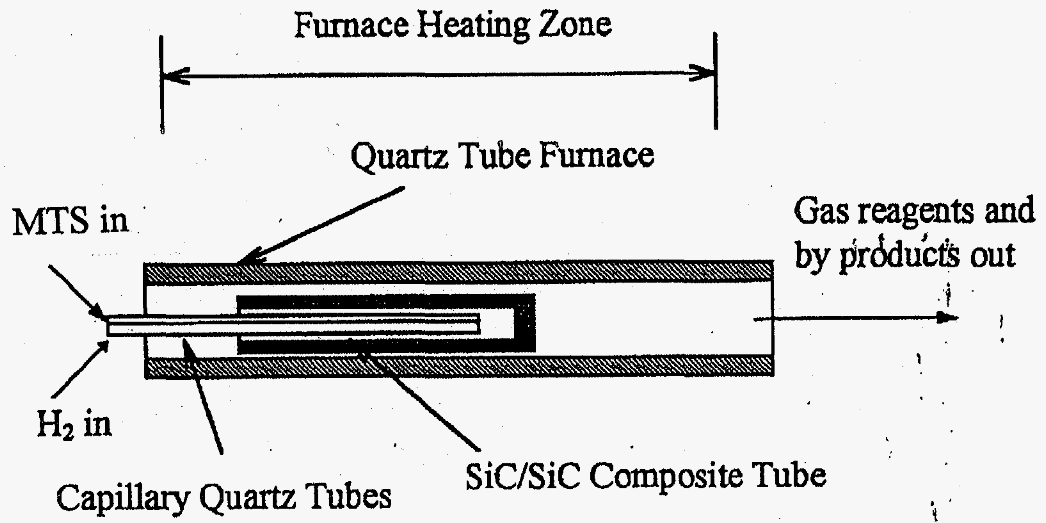
Forming of CMC Closed-end Tube



Molding of CMC Tube



CVI/CVD Overcoat



CHARACTERIZATION

- TEM
- SEM
- XRD

EVALUATION

- Leak Testing
- Thermal Shock