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Development of Chemical Vapor Composites, CVC Materials

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Submitted by:

ThermoTrex Corporation
10455 Pacific Center Court
San Diego, CA 92121-4399
(619) 646-5300

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1.0 INTRODUCTION

Industry has a critical need for high-temperature operable ceramic composites that are strong, non-brittle, light weight, and corrosion resistant. Improvements in energy efficiency, reduced emissions and increased productivity can be achieved in many industrial processes with ceramic composites if the reaction temperature and pressure are increased. Ceramic composites offer the potential to meet these material requirements in a variety of industrial applications. However, their use is often restricted by high cost. The Chemical Vapor Composite, CVC¹, process can reduce the high costs and multiple fabrication steps presently required for ceramic fabrication.

Assuming the fabrication cost can be reduced, many new potential applications that were closed ceramic composite materials become open. A low cost ceramic composite material would have a profound effect on the U.S. industrial energy usage and environmental maintenance. DOE estimates that ceramic composites could save 1.1 quads/year of energy and reduce No_x emissions by 0.6 million ton/year.

The traditional processing techniques for fabricating ceramic composites require multiple fabrication steps (woven preforms, multiple densifications and diamond grinding). Current technology is limited by problems of unreliability, multiple production steps and cost.

CVC deposition has the potential to eliminate many difficult processing problems and greatly increase fabrication rates for composites. With CVC, the manufacturing process can control the composites' density, microstructure and composition during growth. The CVC process:

- Can grow or deposit material 100 times faster than conventional techniques;
- Does not require an expensive woven preform to infiltrate;
- Can use high modulus fibers that cannot be woven into a preform;
- Can deposit composites to tolerances of less than 0.025 mm on one surface without further machining.

In CVC a second solid phase is added to the reactant vapor stream of the usual Chemical Vapor Deposition (CVD) system. This solid phase of powder, whisker, and/or fiber is thermochemically stable in the CVD vapor environment and is incorporated into the deposit as a separate species. The ratio of the particulate flux to the vapor flux can be varied over a wide range during deposition, allowing continuous control of the composition during deposition.

The CVC process is inherently flexible because of the large number of matrix/particle combinations possible. Only two restrictions apply; the matrix material must be vapor deposited and the particle must be mixable and thermochemically stable in the deposition.

A schematic of a CVC SiC reactor is shown in Figure 1. This reactor was used to deposit composites with a SiC matrix and particle reinforcements of powder, whiskers and fibers. The reactor controls the mass flow of both the gas reactants and the particles which are mixed with H_2 and combined with CH_3SiCl_3 to form the SiC composites.

Figure 1. Schematic of CVC reactor.

2.0 SIGNIFICANT ACCOMPLISHMENTS

Powder sensor and controller for CVC reactors was successfully designed, fabricated, and tested. A carbon and ceramic fiber feeder and controller for a CVC SiC reactor was also successfully designed, fabricated and tested. SiC composite material was fabricated using SiC powder ranging in diameter from 0.005" to 0.150". SiC was also fabricated using multiple SiC powders of 10, 30 or 90 microns. Still other SiC composite materials were fabricated using SiC platelets of 30 or 40 microns and fibers up to 0.25" long.

A wide variety of particulate compositions were used to fabricate CVC SiC matrix material. They included SiC, B₄C, TiB₂, Si₃N₄, Al₂O₃, BN powder. Fibers of the following composition (Textron SiC, Nicalon SiC, Nextel Al₂O₃ and carbon) were also used to fabricate CVC material. CVC material was deposited on a horizontal 4 1/2" diameter tube reactor and on a vertical plate 7" in diameter reactor. The CVC process was scaled-up to fabricate SiC tubes (8" in diameter x 36" long) with powder and fiber reinforcement. Deposition rates for SiC with 30 μ powder 99% dense were in the 0.030" to 0.040" per hour range. The room temperature flexural strength of CVC SiC ranged from 468 MPa to 170 MPa depending on the geometry and volume percentage of the particulate loading. The flexural strength at 1200°C in air ranged from 380 MPa to 173 MPa. The fracture toughness ranged from 3.0 MPa M^{1/2} to 3.6 MPa M^{1/2}.

3.0 TASK - EQUIPMENT MODIFICATION

The objective of this task is to design and implement particulate feeders and manifolds which can accurately monitor and control the particulate feed rate (grams/hour) into the CVC reactor. This equipment is critical in order to control and reproduce the microstructure and material properties of the deposited composite.

A powder/fiber sensor and controller for CVC reactors was successfully designed, fabricated, and tested. The sensor functions with a laser and detector. Laser light is directed across the flow of gas and particulates in the plumbing to the reactor. The sensor, set at right angles to the laser, detects the amount of light reflected off the particulates. Figure 2 illustrates the design principle, and Figure 3 shows the sensor in the CVC control system. The controller compares the sensor readings to a predetermined setpoint and accordingly regulates the particulate feeder to produce a uniform flow of particulates. Figure 4 is a photo of the sensor and the controller in operation. This design has been successfully used to accurately control a wide range of both powder and carbon fiber sizes, at flow rates varying from 0.01 grams/hour to 100 grams/hour. Five particulate sensors and controllers have been placed in routine CVC operation.

Figure 2. Particulate sensor schematic.

Figure 3. Particulate feeder control system.

Figure 4. Photo of sensor and controller in operation.

A carbon and ceramic fiber feeder and controller for a CVC SiC reactor has been designed, fabricated and tested. It is based on a design similar to an old-fashioned flour sifter. The goal of the fiber feeder is to produce a stream of individual fibers from an agglomerated fiber mass. A motor drives a shaft and flat plate which oscillate a mass of agglomerated fibers. The oscillating fibers rub against a metal screen. The agglomerated fibers are agitated; this agitation forces the individual fibers through a screen into the reactor. The amount of fibers allowed into the reactor can be controlled by the degree of agitation and size of the screen. During operation the fiber controller compares the sensor readings in the gas stream to the set point and regulates the drive motor to the feeder.

The majority of the CVC experiments were performed at 760 torr. This allowed the products of the reaction to exhaust directly to the chemical scrubber. However, a few experiments were conducted at 50 torr. The vacuum deposition required installing a particular filter and a chemical pump between the vertical chamber and the scrubber.

The inlet plumbing for the CVC gas and solid reactants was modified. This was done because EDAX analysis of fracture origins indicated a small percentage of iron and nickel present in the deposited CVC material (see EDAX trace in Figure 5). These impurities may be introduced into the CVC deposit because of abrasion of the SiC powder on the stainless steel tubing, and on the powder auger feeder drive, or because of a chemical reaction between the reactant vapors and the hot inlet line. The first attempted solution was to purify the SiC powder by chemical etching, however this did not reduce the amount of impurities in the CVC deposited material. The following plumbing modifications to the gas reactant and particulate feedline were implemented and successfully reduced the impurities in the deposit.

As an alternative to the original half inch diameter, non-cooled stainless steel inlet manifold, a half inch diameter, water cooled inlet manifold has been constructed from molybdenum. This water cooled injector joins the hot graphite tube in the reaction chamber. The plumbing material between the reactor and the feeder itself has been changed from stainless steel (304SS) to copper (OFHC). Copper was chosen because either it will evaporate in the high heat of the reactor, or it will leave easily detectable traces. After analyzing the CVC SiC material we concluded that most of the impurities originated from the hot noncooled inlet manifold.

Figure 5. EDAX trace of CVC SiC.

The inlet plumbing has been further modified by the addition of several thumpers. The “thumpers” consist of electronic solenoids (2 or 3 in number) connected to a timer, and attached at tees or elbows of the inlet plumbing. The timer causes the solenoids to “thump” or tap the plumbing every 1 or 2 seconds producing a more uniform powder flow into the reactor.

The powder feeder and gas reactant system was successfully scaled up for the 100 Kw horizontal tube reactor. As part of the technology transfer task this reactor was used to fabricate SiC combustion tubes 72” long by 6” in diameter with a 0.10” wall thickness.

4.0 TASK – CVC MATERIAL FABRICATION

The objective of this task is to fabricate SiC CVC material with powders and/or fibers that meet the program goals of high strength and toughness. This CVC SiC material was analyzed in the Material Characterization Task.

4.1 Horizontal Reactor with Powder

CVC materials were fabricated using various sizes and combinations of powder in a SiC matrix. The powder, composition and feedrate used in the CVC process are summarized in Table 1. The sensor and controller described in the previous task were used in the CVC deposition process. Powder and gas reactants were mixed in a single half inch diameter manifold inlet. Both a stainless steel and water cooled molybdenum inlet manifold were utilized. Material was deposited in a 20 KW horizontal graphite tube reactor 4.5 inches in diameter by 24 inches long. A drawing of this reactor is shown in Figure 6 and a photo is shown in Figure 7. The graphite tube was heated by a 20 KW inductive power supply. The reactor’s hot zone produced uniform CVC SiC material 8” long which was characterized in the following Material Characterization Task.

All the gas reactants and powders and fibers were mixed in a single manifold at the center of the horizontal graphite tube. When powder was mixed with the proper gas reactants the deposit was uniform in thickness and powder distribution along the center 8" of the graph tube hot zone. The total flow rate of the H₂ had some control on the powder distribution and thickness profile of the deposit along the tube.

TABLE 1. CVC POWDER REINFORCEMENT.

Composition	Size (microns)	Feed Rate (g/hr.)
SiC	5 to 120	1 - 50
BN	30 - 40	10
Si ₃ N ₄	1 - 3	5
Al ₂ O ₃	0.15" Spheres	50
Al ₂ O ₃	30 - 40	5 - 10
B ₄ C	30 - 40	5 - 10
TiB ₂	30 - 40	5 - 10

Figure 6. Horizontal CVC reactor.

Figure 7. Horizontal CVC reactor.

For example, if the H₂ flow was reduced by 50% the powder would accumulate at the inlet end of the tube. This reduced gas flow would produce a nonuniform and low density deposit at the inlet end of the tube. However, if the H₂ flow rate was increased by 100% the powder would not be co-deposited in the SiC matrix. The majority of the powder would exit out into the exhaust tube and into the scrubber. Whenever the powder composition, density or size was changed significantly the H₂ carrier gas had to be modified and calibrated in order to obtain a uniform powder distribution along the length of the tube substrate.

Once the total gas flow rates and parameters were calibrated the tube reactor consistently produced uniform SiC composites with SiC powder. The deposition rate and material properties were reproducible as determined in the material characterization test. The following CVC parameters were used to deposit 30 μ SiC powder at 0.040" per hour deposition rate.

Temp	1350 – 1375°C
Press	760 Torr
MTS	400 g/hr
H ₂	15 liter/min
SiC powder	10 g/hr

The CVC deposition process usually started with pure CVD SiC. The time for CVD layer was varied from 5 to 30 minutes depending on the application. To start the CVC process the powder feed rate was increased from 0 to the set point in 1 to 2 minutes. To end the CVC deposition the powder feed rate was reduced to zero and pure CVD SiC was deposited for approximately 30 minutes. The CVC deposits usually produced composite material that was uniform in thickness and density without any nodules or dendrites on the last deposited surface.

When codepositing powder greater than 10 μ in diameter for reinforcement in the CVC process, no clogging occurred in the water cooled inlet manifold or in the plumbing. A downward plumbing geometry was always used from the powder feeder to the inlet manifold of the reactor. However, when powder less than 5 to 10 μ was codeposited agglomeration would occur in the plumbing and in the deposited material. This problem occurred with SiC and Si₃N₄ powder in a SiC matrix. The 1-3 μ diameter Si₃N₄ powder would agglomerate on the inside walls of the tubing and sometimes clog the inlet plumbing at the tees and elbows joints. This agglomeration would sometimes cause a sudden increase in line pressure and would always cause a non uniform Si₃N₄ powder distribution in the SiC matrix deposit. No reliable solution was discovered to deagglomerate 1-3μ diameter Si₃N₄ powder.

Some CVC deposits used dual powder feeder and controllers. This allowed two different powder sizes or compositions to be co-deposited with a SiC matrix. The dual feeders could produce laminated CVC deposits by cycling the feed rate of one powder. This cycling of the powder feed rate produced layers in microstructure by changing the powder volume percent and density in the CVC deposit

4.2 Horizontal Reactor with Fibers

The most successful CVC SiC deposits with fibers were with 1/4" to 1/2" long Textron fiber. Smaller diameter fibers such as Nicalon, Hi Nicalon, Nextel and Carbon had clogging and re-agglomeration problems in the feed lines to the hot zone. The Textron fibers produced tubes 8" long, 4 1/2" in diameter with uniform fiber distribution with approximately 1% porosity in the SiC matrix.

Various design modifications to the reactor set-up and plumbing were tested in order to deposit non-agglomerated small diameter (5 μ) fibers in a SiC matrix. The fiber feeder was successfully designed and tested to deliver nonagglomerated fibers 5 μ in diameter by 0.1" long. However, after being discharged from the fiber feeder the nonagglomerated fibers would attach to the fiber controller windows and to the inside surfaces of the plumbing. The electrostatic forces allowed the small fibers to stick to the inside walls of the tubing and controller windows. As the fiber feeding process continued the thickness of the fibers on tubing would increase eventually causing the fibers to break free in an agglomerated mass and flow into the reaction chamber. The agglomerated fibers would deposit in the SiC matrix with less than 100% density.

Purge gas was successfully used to prevent fibers from depositing on the window of the fiber control module. An H_2 gas was directed on the center of the laser window and detector to prevent fiber attachment. However, no permanent and reliable solution was found to prevent the small fibers from electrostatically attaching to the inside surface of the inlet plumbing. The following modifications were tested to reduce fiber re-agglomeration. The gas flow purge rates were varied over a wide range. The diameter of the plumbing and the fitting joints were changed. Vibrators and thumpers were attached to the inlet plumbing. Polished and acid cleaned tubing was used in the inlet plumbing. Only the use of the vibrators and thumpers helped reduce the amount of re-agglomeration of fibers in the inlet plumbing. However, the fiber feed rate of 5 μ diameter fibers into the reactor hot zone was not controlled or reproducible enough to analyze the CVC SiC material.

The CVC material produced with non-agglomeration 5 μ diameter fibers had a low fiber volume percentage in the SiC matrix. When the fiber feed rate was increased agglomeration would occur in the inlet plumbing. The agglomerated fibers would produce a higher fiber volume in the SiC matrix but at a lower density. The agglomerated fibers depositing on the substrate were not fully densified by the MTS vapors. No set of CVC parameters produced a high volume percentage of small diameter fibers with high (99%) density at a high deposition rate. However, the combination of reducing the MTS gas reactant rate by 75% and reducing the fiber feed rate to deliver non agglomerated fibers produced high density SiC deposits. Reducing the MTS gas reactant rate reduced the volume percentage of SiC matrix. When non agglomerated small fibers were added to the SiC matrix a 5% volume percent fiber loading was deposited. Examples of cross sections of 5 μ diameter deposits are shown in Material Characterization Task. Table 2 summaries the results of various combination of 5 μ and MTS feedrates.

It was observed that the amount of fiber agglomeration was reduced in the exhaust end of the horizontal tube reactor. Comparisons of cross-sections of CVC SiC material at the input end versus the exhaust end showed reduced fiber agglomeration in the matrix. It's possible that the

pre-heating of the fibers flowing in the hot zone reduced agglomeration. A dual inlet manifold was fabricated and tested what allowed a small amount of fiber preheating. The dual manifold consisted of an outer concentric ring around the water cooled gas reactants inlet. The outer ring flowed hot H_2 and fibers while the center hole flowed cold MTS and H_2 . The deposits produced fewer agglomerated fibers with preheating in the SiC matrix. However, this dual manifold was very difficult to set-up. Therefore, the majority of the fiber preheating experiments were performed in the vertical reactor which has dual and separate injectors that are less difficult to set-up.

Table 2. CVC SiC DEPOSITS WITH 5 μ DIAMETER FIBERS.

	Low MTS Feedrate	High MTS Feedrate
Low feedrate of 5 μ diameter fibers	Best material	Weak material
	Low deposition rate	High deposition rate
	High density (99 1/2)	Low fibers volume
	2% fiber volume	High density
High feedrate of 5 μ diameter fiber	Weak material	Weak material
	Low density	High deposition rate
	High fiber volume Agglomerated fibers in matrix	Low density

4.3 Vertical Reactor With Powder

SiC material was also deposited in a vertical 30 Kw CVC reactor. The diameter of the CVC SiC deposit on the graphite disk was 7". A drawing of the vertical reactor is shown in Figure 8 and a photo is shown in Figure 9. The reactor could use dual or single injectors for particulate and gas reactants. The position of the injectors from the center line of the rotated graphite disk controls the powder distribution in the matrix and the thickness profile of the deposited SiC.

Figure 8. Dual injector vertical reactor.

Figure 9. Photo of vertical CVC reactor.

The majority of the CVC powder experiments were conducted in the horizontal CVC reactor. The successful CVC parameters used in the horizontal reactor were scaled up to the vertical reactor. The majority of the CVC experiments in the vertical reactor were conducted to fabricate a prototype CVC SiC fan with SiC powder and to deposit CVC SiC with fibers. The fan activities are discussed in the Technology Transfer task.

Most of the CVC experiments were conducted at 760 torr which eliminated the cost of maintaining an expensive chemical pump and filters. However, five runs were conducted at 50 torr deposition pressure. The lower pressure reduced the normal deposition rate from 0.040" to 0.020" per hour. No other changes to the CVC deposit were noted.

4.4 Vertical Reactor with Fibers

The vertical reactor was used to conduct experiments with 5 μ diameter fibers in order to reduce agglomeration of fibers in the SiC matrix. Similar CVC deposits were observed when using 5 μ diameter fibers in both the vertical and horizontal reactor. When delivering the 5 μ fibers at a low feeder rate the deposit had a low fiber volume ($\approx 2\%$) in the SiC matrix. Increasing the fiber delivery rate caused the fibers to reagglomerate in the inlet plumbing and co-deposit as clumps in the SiC matrix. The mixture of agglomerated fibers in the SiC matrix increased the fiber volume percent but decreased the density and therefore, the strength of the composite. Two techniques were attempted to decrease the agglomerated fibers in the SiC matrix while maintaining 99% density.

The dual injector vertical reactor was set-up to preheat the fibers and H₂ purge gas in one of the inlet manifolds. The water cooled injector was replaced with a graphite tube threaded into the graphite chamber cover. The graphite chamber cover is heated to 1,300°C during deposition. This graphite cover heated the graphite inlet tubing up to 1,200°C which preheated the flowing H₂ and fibers. The gas reactants of MTS and H₂ were delivered on a separate water cooled injector.

This preheat set-up produced less agglomeration preheated fibers in the deposit; however, the MTS reactants also mixed and diffused up the end of the graphite tube. This MTS mixture caused SiC to deposit on the inside of the graphite tube rapidly blocking the flow of fibers. After one hour of deposition the experiments had to be aborted because of fibers clogging the graphite inlet tube. Various graphite nozzle geometrics and H₂ flow rates and preheating temperature were tested but all caused SiC deposits on the graphite tube restricting the fiber flow.

Vacuum depositions at 50 torr were conducted in order to reduce agglomeration of fibers in the matrix. The result of these experiments showed no fibers in the SiC matrix. Apparently all the fibers were exhausted out of the chamber into the exhaust filter. Increasing the fiber feed rate to the chamber didn't allow any fibers to co-deposit in the SiC matrix.

5.0 TASK – MATERIAL CHARACTERIZATION

5.1 Introduction

The objective of this task is to analyze the microstructure of CVC materials reinforced with powder and fibers to determine porosity, impurities, powder and fiber distribution, and fiber matrix interaction. Selected CVC samples were machined into bend bars to determine RT and high temperature strength and toughness in the air.

Silicon carbide (SiC) owns numerous advantages including high melting point (2,500-2,700°C), low density (3.21 g/cm³), wide energy gap (2.2 eV at 25°C), good resistance to oxidation, creep, and thermal shock, high strength and stiffness, high abrasion resistance, excellent thermal and chemical stability, low coefficient of thermal expansion, large thermal conductivity (1.25 W/cm°C at 25°C), and excellent polishability. Most of its mechanical, physical, and chemical properties are highly dependent on the morphology, structure, microstructure, and composition of the material, which in turn depend upon the physical-chemical characteristics of the material at a microscopic scale, as well as the processing technique used.

Composite materials for applications in severe conditions (high temperature, high loading, and long duration) require second-phase reinforcements with excellent mechanical properties, high chemical and structural stability, and good oxidation resistance at high temperatures. CVC SiC containing high-performance particles and fibers is an ideal material for these applications. The CVC SiC is especially useful when the ceramic composite is applied to surfaces with complex geometry and to internal cavities.

The properties of CVD SiC-based ceramic composites are highly dependent on the nucleation growth process and various process parameters employed. This report documents the growth behavior, morphology, microstructure, mechanical properties, and thermal properties of CVC SiC composites (Run #3455 to #4013) processed from CH_3SiCl_3 (MTS)- H_2 mixtures using a wide range of process conditions, from 1994 to 1998. The emphasis of the present study is focused on the microstructure and mechanical behavior of the CVC SiC materials. The relationship between the deposition process parameters and the material microstructure/properties is also discussed.

5.2 Process Conditions

Additives

In the present study, various powders and fibers were used as the additives to the CVC SiC composites, as summarized in Master Table 3. Figures 10A to 10D are micrographs to show the morphologies of some typical powders and fibers used in the present study.

The majority of the powders used in the CVC SiC composites are SiC micro-particles with a nominal size of 30 μm (Figure 10). SiC particles with larger or smaller sizes, as well as diamond particles, were also used.

Three types of tubular fibers were used in the CVC SiC composites. The first one is Panex carbon fiber (Figure 10B), with an outer diameter (O.D.) of approximately 10 μm . Carbon fibers exhibit high stiffness, high fracture strength, and good creep resistance at high temperatures under an inert atmosphere, but they are highly sensitive to oxidation at temperatures above 450°C. The second one is Hi-Nicalon SiC fiber (Figure 10C), with an O.D. of approximately 30 μm . Hi-Nicalon fibers are mainly composed of SiC nanocrystals (~ 76 vol.%) with an average crystal size closed to 5 nm. They are basically oxygen-free Si-C fibers, containing very little of the amorphous SiO_xC_y phase, and as a consequence, they have a much better creep resistance than the Si-C-O fibers. The last one is Textron carbon fiber coated with SiC on the outer surface (Figure 10C). The O.D. of the Textron fibers is approximately 100 μm .

Process Parameters

The CVC SiC composites examined in the present study were processed from MTS- H_2 mixtures. It is well known that the microstructure and properties of CVD/CVC SiC are strongly related to the CVD process parameters employed. The properties of deposits can be controlled by adjusting process parameters such as substrate material and temperature, chamber pressure, reactant gas concentration, gas flow rate, deposition geometry, etc. (Pickering 1992). The most important parameter which controls the microstructure and properties of the deposited material in a CVD reactor is the deposition temperature .

MASTER TABLE 3 – ADDITIVES IN CVC SiC

Test No.	Run No.	Temp. (°C)	Powder Type	Powder Size (μm)	Powder Feed (g/hr)	Fiber Type	Fiber Feed (g/Hr)	Growth (mil/hr)
1	3455	1340	Norton SiC	30	4.50	1/8" Panex Carbon	0.20	-
2	3459	1350	-	-	-	1/8" Panex Carbon	0.20	12.5
3	3462	1350	-	-	-	1/8" Panex Carbon	0.20	12.5
4	3465	1350	-	-	-	-	-	10.0
5	3471	1350	-	-	-	-	-	-
6	3473	1350	Norton SiC	30	9.00	-	-	15.0
7	3477	1350	Norton SiC	30	9.00	1/8" Panex Carbon	-	16.5
8	3483	1350	SiC platelet	40	9.00	-	-	18.0
9	3484	1340	SiC platelet	40	8.40	-	-	12.0
10	3486	1350	SiC platelet	30	8.30	-	-	15.0
11	3488	1340	SiC platelet	40	8.20	-	-	20.0
12	3507	1350	Norton SiC	30	8.40	-	-	19.5
13	3508	1350	Norton SiC	30	9.00	-	-	18.0
14	3511	1350	SiC platelet	40	5.00	-	-	-
15	3512	1350	SiC platelet	40	5.00	-	-	18.0
16	3514	1350	SiC platelet	40	9.00	-	-	15.0
17	3517	1350	Diamond:SiC=1:1	20 diamond+30 SiC	9.00	-	-	20.0
18	3519	1300	Norton SiC	30	8.50	-	-	23.0
19	3521	1300	Norton SiC	17:30:72=1:1:1	8.30	-	-	-
20	3526	1300	Norton SiC	17:30:72=1:1:1	28.70	-	-	20.0
21	3527	1350	-	-	-	-	-	17.0
22	3530	1350	Norton SiC	30	8.90	-	-	13.0
23	3536	1200	Norton SiC	30	18.50	-	-	-
24	3539	1350	Norton SiC	17:30:72=1:1:2	29.50	-	-	25.0
25	3542	1330	Norton SiC	17:30:72=1:1:2	40.60	-	-	24.5
26	3544	1370	Norton SiC	17:30:72=1:1:2	40.00	-	-	26.0
27	3548	1200	Norton SiC	30	10.00	-	-	-
28	3549	1334	Norton SiC	17:30:72=1:1:2	-	-	-	-
29	3550	1200	Norton SiC	30	12.20	-	-	23.0
30	3555	1200	Norton SiC	30	12.30	-	-	-
31	3560	1190	Norton SiC	30	7.20	-	-	35.6
32	3564	1100	Norton SiC	30	6.40	-	-	33.3
33	3565	1350	Norton SiC	30	7.30	-	-	-
34	3566	1150	Norton SiC	30	6.00	-	-	33.8

MASTER TABLE 3 – ADDITIVES IN CVC SiC (continued)

Test No.	Run No.	Temp. (°C)	Powder Type	Powder Size (µm)	Powder Feed (g/hr)	Fiber Type	Fiber Feed (g/Hr)	Growth (mil/hr)
35	3570	1310	Norton SiC	30	5.40	-	-	36.2
36	3574	1310	Norton SiC	30	6.90	-	-	38.4
37	3577	1350	-	-	-	1/8" Panex Carbon	-	30.9
38	3579	1310	-	-	-	1/8" Panex Carbon	-	27.5
39	3583	1350	-	-	-	1/8" Panex Carbon	-	16.7
40	3587	1350	Norton SiC	30	-	-	-	34.3
41	3595	1350	-	-	-	1/8" Panex Carbon	-	47.5
42	3598	1345	-	-	-	1/8" Panex Carbon	-	18.0
43	3604	1300	Norton SiC	30	4.62	1/8" Panex Carbon	-	28.0
44	3608	1350	-	-	-	Hi-Nicalon SiC	-	19.3
45	3611	1300	-	-	3.56	Hi-Nicalon SiC	0.82	50.0
46	3613	1287	Norton SiC	30	14.80	-	-	22.0
47	3615	1348	-	-	3.66	Hi-Nicalon SiC	0.23	29.0
48	3616	1345	Norton SiC	30	13.40	-	-	-
49	3617	1300	Norton SiC	30	3.29	Hi-Nicalon SiC	0.75	66.0
50	3618	1343	-	-	4.15	Hi-Nicalon SiC	0.37	30.0
51	3622	1342	Norton SiC	30	26.20	-	-	65.0
52	3627	1358	Norton SiC	30	49.20	-	-	91.0
53	3629	1300	-	-	4.52	Hi-Nicalon SiC	0.26	29.0
54	3630	1337	Norton SiC	30	17.10	-	-	14.2
55	3636	1300	-	-	3.74	Hi-Nicalon SiC	0.17	20.0
56	3637	1315	Norton SiC	30	7.10	-	-	27.5
57	3640	1315	Norton SiC	30	3.11	Hi-Nicalon SiC	0.46	15.0
58	3648	1340	Norton SiC	30	2.44	Hi-Nicalon SiC	0.66	31.0
59	3653	1350	Norton SiC	30	3.92	Hi-Nicalon SiC	-	-
60	3657	1301	Norton SiC	30	4.30	Hi-Nicalon SiC	-	26.7
61	3660	1345	Norton SiC	30	3.90	Hi-Nicalon SiC	1.26	18.0
62	3662	1340	Norton SiC	17	7.72	Hi-Nicalon SiC	2.24	-
63	3665	1278	Norton SiC	30	4.60	-	-	18.3
64	3666	1340	Norton SiC	17	11.10	C coated Hi-Nicalon	0.68	51.7
65	3674	1340	Norton SiC	17	6.30	C coated Hi-Nicalon	0.44	22.0
66	3675	1300	Norton SiC	17	3.60	C coated Hi-Nicalon	0.30	18.0
67	3677	1300	Norton SiC	30	5.70	-	-	45.9
68	3683	1305	Norton SiC	17	4.78	C coated Hi-Nicalon	0.33	39.0

MASTER TABLE 3 – ADDITIVES IN CVC SiC (continued)

Test No.	Run No.	Temp. (°C)	Powder Type	Powder Size (μm)	Powder Feed (g/hr)	Fiber Type	Fiber Feed (g/Hr)	Growth (mil/hr)
69	3685	1255	Norton SiC	17	4.60	C coated Hi-Nicalon	1.04	30.3
70	3688	1300	Norton SiC	30	4.78	Hi-Nicalon SiC	0.14	30.0
71	3691	1300	Norton SiC	30	8.60	-	-	53.6
72	3694	1315	Norton SiC	30	3.00	-	-	-
73	3697	1360	Norton SiC	30	11.50	Chopped Hi-Nicalon	-	22.5
74	3698	1300	Norton SiC	30	4.40	-	-	34.8
75	3700	1300	Norton SiC	9	4.00	Hi-Nicalon SiC	0.32	36.0
76	3714	1300	Norton SiC	9	5.35	C coated Hi-Nicalon	0.85	65.5
77	3716	1310	Norton SiC	9	4.30	C coated Hi-Nicalon	0.79	42.1
78	3718	1300	Norton SiC	30	4.10	-	0.00	30.4
79	3723	1300	Norton SiC	9	2.70	C coated Hi-Nicalon	0.40	32.6
80	3727	1295	Norton SiC	30	3.70	-	0.00	29.0
81	3730	1300	Norton SiC	9	2.60	C coated Hi-Nicalon	0.92	64.6
82	3732	1300	Norton SiC	9	2.30	C coated Hi-Nicalon	0.75	64.5
83	3737	1280	Norton SiC	9	3.20	C coated Hi-Nicalon	0.91	64.3
84	3754	1290	Norton SiC	-	3.34	Hi Nicalon SiC	0.32	25.0
85	3779	1295	-	-	-	-	-	-
86	3788	1350	Norton SiC	30	3.42	-	-	-
87	3789	1350	Norton SiC	30	2.89	Hi-Nicalon SiC	1.36	-
88	3793	1350	Norton SiC	30	3.20	-	-	-
89	3853	1325	Norton SiC	30	-	Hi-Nicalon SiC	-	-
90	3855	1377	Norton SiC	30	3.52	-	-	13.0
91	3857	1370	Norton SiC	30	-	Nical/Texttr/Carbon	-	13.0
92	3860	1320	-	-	-	-	-	29.0
93	3870	1330	Norton SiC	30	3.20	-	-	112.0
94	3874	1335	Norton SiC	30	1.20	-	-	67.2
95	3876	1300	Norton SiC	30	8.00	-	-	-
96	3877	1370	Norton SiC	30 & 70	4.9 for 30μ	-	-	27.0
97	3878	1300	Norton SiC	30	2.60	-	-	30.0
98	3880	1375	Norton SiC	30 & 70	3.8 for 30μ	-	-	12.0
99	3881	1370	Norton SiC	30 & 70	6.0 for 30μ	-	-	32.0
100	3884	1345	Norton SiC	30	4.90	-	-	20.0
101	3885	1350	Norton SiC	30 & 70	4.5 for 30μ	-	-	-
102	3888	1370	Norton SiC	30 & 70	6.5 for 30μ	-	-	-

MASTER TABLE 3 – ADDITIVES IN CVC SiC (continued)

Test No.	Run No.	Temp. (°C)	Powder Type	Powder Size (μm)	Powder Feed (g/hr)	Fiber Type	Fiber Feed (g/Hr)	Growth (mil/hr)
103	3889	1343	Norton SiC	30	5.40	-	-	35.0
104	3890	1340	Norton SiC	30	4.90	-	-	47.0
105	3893	1370	Norton SiC	30	4.30	1/8" Textron SiC	10.00	-
106	3894	1370	Norton SiC	30	4.80	1/8" Textron SiC	-	12.0
107	3896	1350	Norton SiC	30	5.50	-	-	33.0
108	3898	1344	-	-	5.20	-	-	27.0
109	3902	1355	Norton SiC	30	5.20	-	-	-
110	3904	1340	Norton SiC	30	5.30	-	-	29.0
111	3905	1370	Norton SiC	30	4.50	-	-	60.0
112	3907	1350	Norton SiC	30	5.30	-	-	33.0
113	3910	1340	Norton SiC	30	-	-	-	25.0
114	3913	1370	Norton SiC	30	8.00	-	-	-
115	3916	1370	Norton SiC	30	4.00	-	-	11.0
116	3918	1370	Norton SiC	30	4.00	-	-	17.0
117	3920	1340	Norton SiC	30	8.00	-	-	27.0
118	3922	1374	-	-	9.10	-	-	42.0
119	3923	1370	Norton SiC	30	4.00	-	-	10.0
120	3928	1345	Norton SiC	30	7.00	-	-	11.8
121	3929	1340	Norton SiC	30	4.40	-	-	35
122	3930	1340	Norton SiC	30	5.00	-	-	20
123	3932	1370	Norton SiC	30	7.00	-	-	13.9
124	3933	1370	Norton SiC	30	5.40	-	-	23.0
125	3935	1345	Norton SiC	30	4.00	-	-	9.5
126	3936	1373	Norton SiC	30	8.00	-	-	28.3
127	3938	1345	Norton SiC	30	8.00	-	-	19.6
128	3940	1345	Norton SiC	30	7.00	-	-	10.7
129	3941	1370	Norton SiC	30	4.00	-	-	10.2
130	3942	1372	Norton SiC	30	8.60	-	-	28.3
131	3943	1342	Norton SiC	30	8.2	-	-	17.0
132	3944	1345	Norton SiC	30	4.00	-	-	11.0
133	3945	1376	Norton SiC	30	5.00	-	-	17.8
134	3946	1370	Norton SiC	30	7.00	-	-	8.9
135	3964	1240	Norton SiC	30	-	-	-	5.4
136	3969	1370	SiC particles	30	-	Hi-Nicalon SiC	-	-

MASTER TABLE 3 – ADDITIVES IN CVC SiC (continued)

Test No.	Run No.	Temp. (°C)	Powder Type	Powder Size (µm)	Powder Feed (g/hr)	Fiber Type	Fiber Feed (g/Hr)	Growth (mil/hr)
137	3972	1370	SiC particles	30	4.00	1/8" Textron SiC	10.00	8.0
138	3973	1370	SiC particles	-	4.40	1/8" Textron SiC	20.00	10.0
139	3977	1360	SiC particles	30	5.00	1/8" Textron SiC	8.00	35.5
140	3978	1370	SiC particles	30	5.00	1/8" Textron SiC	8.00	35.5
141	3985	1370	SiC particles	30	5.00	1/8" Textron SiC	15.00	35.5
142	3986	1360	SiC particles	30	5.00	1/8" Textron SiC	10.17	32.0
143	3987	1370	SiC particles	30	5.00	1/8" Textron SiC	11.37	36.0
144	3991	1370	SiC particles	30	5.00	1/8" Textron SiC	10.00	35.7
145	3992	1365	SiC particles	30	5.00	1/8" Textron SiC	7.65	30.0
146	4001	1360	SiC particles	30	5.00	1/8" Textron SiC	6.75	34.0
147	4002	1360	SiC particles	30	5.00	1/8" Textron SiC	12.00	34.0
148	4006	1360	SiC particles	30	5.00	1/8" Textron SiC	12.00	-
149	4010	1120	-	-	-	-	-	4.5
150	4013	1360	SiC particles	30	5.00	Chopped Textron	16.00	10.0

* Dense: 0-4% porosity. Semi-porous: 5-10% porosity. Porous: 11-20% porosity. Very porous: >20% porosity.

(A) SiC micro-particles

(B) Carbon fibers

Figure 10. SEM views of the powders and fibers added to CVC SiC.

(C) Hi-Nicalon SiC fibers

(D) SiC coated Textron carbon fibers

Figure 10 (cont'd). SEM views of the powders and fibers added to CVC SiC.

A wide range of CVD/CVC process parameters were employed in the present study. The process parameters vary as follows:

Deposition Temperature:	1,100 - 1,377°C
Deposition Pressure:	760 Torr
H ₂ /MTS Molar Ratio:	0.2 - 28
Powder Feed Rate:	1 - 50 g/hr
Fiber Feed Rate:	0.1 - 20 g/hr
H ₂ -MTS Flow Rate:	1.5 - 20 LPM
Substrate:	Graphite, etc.

The process parameters for some selective runs are summarized in Master Table 4.

Material Characterization

The CVC SiC composites obtained were subjected to optical microscopy, Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDX), hardness testing, flexural testing, fracture toughness testing, and thermal measurement.

The material characterization was conducted as follows:

1. Preparation of micrographic samples through sectioning, cold/hot mounting, polishing, and etching.
2. Optical microscopy for deposit thickness, general microstructure, and examination of the bonding between the matrix and the second-phase particles and fibers.
3. SEM for deposit surface morphology, deposit/substrate interface, and fractography.
4. Computer image analysis for grain size, porosity, and fiber/powder distribution.
5. EDS for chemical composition analysis of the deposits.
6. Mechanical/physical testing per corresponding ASTM standards and specifications.

5.3 Growth Rate

The deposition rate of SiC from MTS-H₂ system is a direct function of temperature, pressure, total flow rate, and reactant depletion. The growth rate varies linearly with the input concentration and by about the square root of the input velocity of the gas. It is also noted that the deposition rate is strongly suppressed by the generation of by-product HCl during the CVD process (Besmann 1992). For CVC SiC composites, furthermore, the deposition rate is also related to the powder and fiber feed rate.

MASTER TABLE 4 – PROCESS PARAMETERS OF CVC SiC

Test No.	Run No.	Temp (°C)	MTS Feed (Lb/hr)	H2 Feed (LPM)	H2-MTS Feed (LPM)	H2/MTS Molar Ratio	Powder Feed (g/hr)	Fiber Feed (g/hr)	Growth (mil/hr)
1	3455	1340	1.19	1.5	5.0	1.1	4.50	0.20	-
2	3459	1350	-	-	-	-	-	0.20	12.5
3	3462	1350	-	-	-	-	-	0.20	12.5
4	3465	1350	-	-	-	-	-	-	10.0
5	3471	1350	-	-	-	-	-	-	-
6	3473	1350	-	-	-	-	9.00	-	15.0
7	3477	1350	-	-	-	-	9.00	-	16.5
8	3483	1350	-	-	-	-	9.00	-	18.0
9	3484	1340	-	-	-	-	8.40	-	12.0
10	3486	1350	-	-	-	-	8.30	-	15.0
11	3488	1340	-	-	-	-	8.20	-	20.0
12	3507	1350	-	-	-	-	8.40	-	19.5
13	3508	1350	-	-	-	-	9.00	-	18.0
14	3511	1350	-	-	-	-	5.00	-	-
15	3512	1350	-	-	-	-	5.00	-	18.0
16	3514	1350	-	-	-	-	9.00	-	15.0
17	3517	1350	-	-	-	-	9.00	-	20.0
18	3519	1300	-	-	-	-	8.50	-	23.0
19	3521	1300	-	-	-	-	8.30	-	-
20	3526	1300	-	-	-	-	28.70	-	20.0
21	3527	1350	-	-	-	-	-	-	17.0
22	3530	1350	1.35	1.5	2.0	1.0	8.90	-	13.0
23	3536	1200	1.47	1.5	5.0	0.9	18.50	-	-
24	3539	1350	2.14	9.0	16.2	3.7	29.50	-	25.0
25	3542	1330	1.90	9.0	14.4	4.2	40.60	-	24.5
26	3544	1370	2.18	9.0	-	3.6	40.00	-	26.0
27	3548	1200	-	-	-	-	10.00	-	-
28	3549	1334	-	3.0	-	-	-	-	-
29	3550	1200	1.58	1.5	5.0	0.8	12.20	-	23.0
30	3555	1200	2.00	1.5	5.0	0.7	12.30	-	-
31	3560	1190	1.74	1.5	5.0	0.8	7.20	-	35.6
32	3564	1100	1.20	1.5	5.0	1.1	6.40	-	33.3
33	3565	1350	3.87	1.0	5.0	0.2	7.30	-	-
34	3566	1150	1.63	1.5	5.0	0.8	6.00	-	33.8
35	3570	1310	1.60	1.5	5.0	0.8	5.40	-	36.2
36	3574	1310	-	-	-	-	6.90	-	38.4
37	3577	1360	1.53	2.0	7.0	1.1	-	-	30.9
38	3579	1310	1.26	2.0	35	1.4	-	-	27.5

MASTER TABLE 4 – PROCESS PARAMETERS OF CVC SiC (continued)

Test No.	Run No.	Temp (°C)	MTS Feed (Lb/hr)	H2 Feed (LPM)	H2-MTS Feed (LPM)	H2/MTS Molar Ratio	Powder Feed (g/hr)	Fiber Feed (g/hr)	Growth (mil/hr)
39	3583	1350	1.05	2.0	3.5	1.7	-	-	16.7
40	3587	1350	1.72	5.0	3.0	2.6	-	-	34.3
41	3595	1350	0.61	1.0	2.0	1.4	-	-	47.5
42	3598	1345	0.72	0.5	2.0	0.6	-	-	18.0
43	3604	1300	0.73	1.5	2.0	1.8	4.62	-	28.0
44	3608	1350	0.80	1.0	2.0	1.1	-	-	19.3
45	3611	1300	1.55	1.5	5.0	0.9	3.56	0.82	50.0
46	3613	1287	1.98	1.0	9.0	0.4	14.80	-	22.0
47	3615	1348	1.56	1.5	5.0	0.8	3.66	0.23	29.0
48	3616	1345	1.80	1.0	9.0	0.5	13.40	-	-
49	3617	1300	1.60	1.5	5.0	0.8	3.29	0.75	66.0
50	3618	1343	1.58	1.5	5.0	0.8	4.15	0.37	30.0
51	3622	1342	2.00	1.0	9.0	0.4	26.20	-	65.0
52	3627	1358	2.06	1.0	9.0	0.4	49.20	-	91.0
53	3629	1300	1.68	1.5	5.0	0.8	4.52	0.26	29.0
54	3630	1337	-	-	-	-	17.10	-	14.2
55	3636	1300	0.66	1.5	2.5	2.0	3.74	0.17	20.0
56	3637	1315	2.27	1.0	9.0	0.4	7.10	-	27.5
57	3640	1315	0.86	1.5	3.0	1.5	3.11	0.46	15.0
58	3648	1340	1.55	1.5	5.0	0.9	2.44	0.66	31.0
59	3653	1350	-	-	-	-	3.92	-	-
60	3657	1301	-	-	-	-	4.30	-	26.7
61	3660	1345	0.62	1.5	3.9	2.1	3.90	1.26	18.0
62	3662	1340	0.55	1.5	7.7	2.4	7.72	2.24	-
63	3665	1278	1.52	1.5	5.0	0.9	4.60	-	18.3
64	3666	1340	0.43	0.8	2.0	1.5	11.10	0.68	51.7
65	3674	1340	0.45	1.5	2.0	2.9	6.30	0.44	22.0
66	3675	1300	0.55	1.5	2.5	2.4	3.60	0.30	18.0
67	3677	1300	1.28	1.5	5.0	1.0	5.70	-	45.9
68	3683	1305	0.40	1.5	1.5	3.3	4.78	0.33	39.0
69	3685	1255	1.60	1.5	6.0	0.8	4.60	1.04	30.3
70	3688	1300	0.65	1.5	3.5	2.0	4.78	0.14	30.0
71	3691	1300	1.60	1.5	5.0	0.8	8.60	-	53.6
72	3694	1315	1.30	1.5	5.0	1.0	3.00	-	-
73	3697	1360	2.04	1.0	9.0	0.4	11.50	-	22.5
74	3698	1300	1.30	1.5	5.0	1.0	4.40	-	34.8
75	3700	1300	1.05	1.5	3.5	1.3	4.00	0.32	36.0

MASTER TABLE 4 – PROCESS PARAMETERS OF CVC SiC (continued)

Test No.	Run No.	Temp (°C)	MTS Feed (Lb/hr)	H2 Feed (LPM)	H2-MTS Feed (LPM)	H2/MTS Molar Ratio	Powder Feed (g/hr)	Fiber Feed (g/hr)	Growth (mil/hr)
76	3714	1300	0.94	1.0	3.5	0.9	5.35	0.85	65.5
77	3716	1310	1.65	1.5	6.0	0.8	4.30	0.79	42.1
78	3718	1300	1.03	1.5	5.0	1.3	4.10	0.00	30.4
79	3723	1300	1.43	1.5	6.0	0.9	2.70	0.40	32.6
80	3727	1295	1.32	1.5	5.0	1.0	3.70	0.00	29.0
81	3730	1300	1.56	1.5	6.0	0.8	2.60	0.92	64.6
82	3732	1300	1.31	1.5	6.0	1.0	2.30	0.75	64.5
83	3737	1280	1.67	1.0	6.0	0.5	3.20	0.91	64.3
84	3754	1290	1.88	1.5	6.0	0.7	3.34	0.32	25.0
85	3779	1295	0.80	3.0	5.0	3.3	-	-	-
86	3788	1350	2.20	1.0	9.0	0.4	3.42	-	-
87	3789	1350	2.04	1.5	5.0	0.6	2.89	1.36	-
88	3793	1350	2.00	5.0	9.0	2.2	3.20	-	-
89	3853	1325	-	3.0	6.0	-	-	-	-
90	3855	1377	2.04	17.00	6.00	7.3	3.52	-	13.0
91	3857	1370	-	-	-	-	-	-	13.0
92	3860	1320	1.00	9.0	5.0	7.9	-	-	29.0
93	3870	1330	1.20	10.5	5.0	7.7	3.20	-	112.0
94	3874	1335	1.90	10.5	5.0	4.9	1.20	-	67.2
95	3876	1300	-	30.0	20.0	-	8.00	-	-
96	3877	1370	1.80	17.0	-	8.3	4.9 for 30μ	-	27.0
97	3878	1300	1.10	30.0	20.0	24.0	2.60	-	30.0
98	3880	1375	1.50	17.0	6.0	10.0	3.8 for 30μ	-	12.0
99	3881	1370	1.40	17.0	6.0	10.7	6.0 for 30μ	-	32.0
100	3884	1345	0.93	30.0	20.0	28.4	4.90	-	20.0
101	3885	1350	1.80	17.0	6.0	8.3	4.5 for 30μ	-	-
102	3888	1370	2.80	21.0	10.0	6.6	6.5 for 30μ	-	-
103	3889	1343	1.30	6.0	9.5	4.1	5.40	-	35.0
104	3890	1340	1.47	9.5	6.0	5.7	4.90	-	47.0
105	3893	1370	-	-	-	-	4.30	10.00	-
106	3894	1370	2.05	17.0	6.0	7.3	4.80	-	12.0
107	3896	1350	1.50	9.5	6.0	5.6	5.50	-	33.0
108	3898	1344	1.40	9.5	6.0	6.0	5.20	-	27.0
109	3902	1355	1.50	9.5	6.0	5.6	5.20	-	-
110	3904	1340	1.30	9.5	6.0	6.4	5.30	-	29.0
111	3905	1370	2.00	17.0	6.0	7.5	4.50	-	60.0
112	3907	1350	1.30	9.5	6.0	6.4	5.30	-	33.0

MASTER TABLE 4 – PROCESS PARAMETERS OF CVC SiC (continued)

Test No.	Run No.	Temp (°C)	MTS Feed (Lb/hr)	H2 Feed (LPM)	H2-MTS Feed (LPM)	H2/MTS Molar Ratio	Powder Feed (g/hr)	Fiber Feed (g/hr)	Growth (mil/hr)
113	3910	1340	1.50	9.5	6.0	5.6	-	-	25.0
114	3913	1370	1.08	17.0	6.0	13.8	8.00	-	-
115	3916	1370	1.80	17.0	6.0	8.3	4.00	-	11.0
116	3918	1370	1.80	-	-	-	4.00	-	17.0
117	3920	1340	1.73	15.0	10.0	7.6	8.00	-	27.0
118	3922	1374	1.40	9.5	6.0	6.0	9.10	-	42.0
119	3923	1370	1.50	17.0	6.0	10.0	4.00		10.0
120	3928	1345	2.00	16.0	6.0	7.0	7.00	-	11.8
121	3929	1340	1.50	9.5	6.0	5.6	4.40	-	35
122	3930	1340	1.35	17.0	9.0	11.1	5.00	-	20
123	3932	1370	2.00	21.0	8.0	9.2	7.00	-	13.9
124	3933	1370	1.03	12.0	6.0	10.2	5.40	-	23.0
125	3935	1345	1.50	2.0	8.0	1.2	4.00	-	9.5
126	3936	1373	1.33	11.5	6.0	7.6	8.00	-	28.3
127	3938	1345	0.97	12.5	9.0	11.3	8.00	-	19.6
128	3940	1345	1.50	19.0	6.0	11.1	7.00	-	10.7
129	3941	1370	2.00	20.0	8.0	8.8	4.00	-	10.2
130	3942	1372	1.40	15.0	9.0	9.4	8.60	-	28.3
131	3943	1342	1.10	14.0	6.0	11.2	8.2	-	17.0
132	3944	1345	2.00	19.0	8.0	8.4	4.00	-	11.0
133	3945	1376	-	14.5	9.0	-	5.00	-	17.8
134	3946	1370	1.50	18.0	8.0	10.5	7.00	-	8.9
135	3964	1240	0.30	6.0	6.0	17.6	-	-	5.4
136	3969	1370	1.40	11.0	6.0	6.9	-	-	-
137	3972	1370	1.50	17.0	6.0	10.0	4.00	10.00	8.0
138	3973	1370	1.50	17.0	6.0	10.0	4.40	20.00	10.0
139	3977	1360	1.40	11.0	6.0	6.9	5.00	8.00	35.5
140	3978	1370	1.40	11.0	6.0	6.9	5.00	8.00	35.5
141	3985	1370	1.40	11.0	6.0	6.9	5.00	15.00	35.5
142	3986	1360	1.40	12.0	6.0	7.5	5.00	10.17	32.0
143	3987	1370	1.40	12.0	6.0	7.5	5.00	11.37	36.0
144	3991	1370	1.40	1.4	12.0	6.0	5.00	10.00	35.7
145	3992	1365	1.40	1.4	12.0	6.0	5.00	7.65	30.0
146	4001	1360	1.40	12.0	6.0	7.5	5.00	6.75	34.0
147	4002	1360	1.40	12.0	6.0	7.5	5.00	12.00	34.0
148	4006	1360	1.40	12.0	6.0	7.5	5.00	12.00	-
149	4010	1120	0.30	7.0	6.0	20.5	-	-	4.5
150	4013	1360	1.60	12.0	6.0	6.6	5.00	16.00	10.0

* Dense: 0-4% porosity. Semi-porous: 5-10% porosity. Porous: 11-20% porosity. Very porous: >20% porosity.

The effects of deposition temperature, H_2 /MTS molar ratio, powder feed rate, fiber feed rate, and H_2 -MTS total flow rate on the growth rate of CVC SiC composites are given in Figures 2 to 6. It should be pointed out that although hundreds of runs had been conducted in the present study, majority of them were performed at very different conditions. However, in order to examine the effect of each individual process parameter on the deposit growth rate, it is required to adjust only one parameter with all the other parameters fixed. An examination of Master Table 4 indicates that there are not many runs falling into this category. Therefore, only limited data points are presented in Figures 11 to 15.

As can be seen in Figure 11, the growth rate of CVC SiC composites increases with increased substrate temperature, which is consistent with the growth behavior of most other CVD materials. For a surface-control process, with increasing substrate temperature, the reactivity at the growing surface increases, resulting in higher deposit growth rate. Also, it is noted that the influence of the substrate temperature is significant on the growth rate. With a temperature increase by approximately 80°C ($\sim 6\%$), the growth rate increases by approximately 450%.

H_2 /MTS molar ratio is a measure of the input reactant concentration. The smaller the ratio, the higher the reactant concentration in the input gas. Figure 12 illustrates the effect of the H_2 /MTS molar ratio on the deposit growth rate, at a constant deposition temperature. When the H_2 /MTS molar ratio increases from 0.8 to 2.4, the deposit growth rate decreases from approximately 60 mil/hr to 20 mil/hr, suggesting that the deposit growth rate has an inversely linear relationship with respect to the H_2 /MTS molar ratio of the input gases, i.e., the growth rate doubles when the H_2 /MTS molar ratio reduces by one half.

As expected, the growth rate of the CVC SiC is proportional to the feed rate of either powders or fibers (Figures 13 and 14). As a ceramic composite, the CVC SiC consists of CVD SiC matrix and second-phase powders and fibers. Therefore, the overall growth rate of the deposit is determined by the growth rate of the matrix and the feed rate of the second-phase particles/fibers. With increased amount of the powders or fibers getting into the deposition chamber, the growth rate of the CVC SiC deposit should increase.

Finally, it is found that the growth rate of CVC SiC increases with increased H_2 -MTS total flow rate (Figure 13). However, the growth rate is not a strong function of the total flow rate. When the total flow rate increases from 2 to 7 LPM (350% increase), for example, the growth rate of the deposit only increases by approximately 50% (from 20 mil/hr to approximately 30 mil/hr).

In reviewing Figures 11 to 15, it is confirmed that the substrate temperature is the most important process parameter controlling the growth rate of the CVC SiC composites, as having been found in many other CVD materials.

Figure 11. Effect of SiC powder feed rate on the growth rate of CVC SiC, at constant deposition temperature and H₂/MTS molar ratio.

Figure 12. Effect of fiber feed rate on the growth rate of CVC SiC, at constant deposition temperature, H₂/MTS molar ratio, and powder feed rate.

Figure 13. Effect of substrate temperature on the growth rate of CVC SiC.

Figure 14. Effect of H₂/MTS molar ratio on the growth rate of CVC SiC, at constant deposition temperature.

Figure 15. Effect of H₂/MTS total flow rate on the growth rate of CVD SiC.

5.4 Microstructure

Surface Morphology

The surface morphology of SiC deposits is a function of the deposition temperature and degree of supersaturation (Loumagne 1995). Deposits which are prepared from the MTS-H₂ gas precursor can have a rough, a smooth, or an angular surface morphology. More generally speaking, these features are characteristics of vapor-deposited materials from any chemical system (Besmann 1992, Ning 1991, Singh 1994, Fischbach 1990).

Smooth deposits with rounded features are generally formed at low temperature, low H₂/MTS ratios and high pressures. At high temperatures, high H₂/MTS ratios and low pressures, large-grained, snap-faceted structures were attained (Chin 1977). An increase in the deposition temperature improves the crystallization state of the deposits and therefore induces a smooth to rough to angular transition on the surface morphology (Fischbach 1990). Surface morphology of the deposits is also highly dependent on the gas phase supersaturation. The roughness increases as the supersaturation decreases. When the MTS molar fraction is high (low H₂/MTS molar ratio), the deposit surface morphology is smooth, i.e., the roughness decreases with increased supersaturation. Low H₂ partial pressure will induce an angular morphology, whereas a hydrogen-rich composition gives a rough morphology (Pickering 1992).

Figures 16A and 16B show typical CVC SiC deposit surface morphology. The material was deposited at 1,360°C at 760 Torr with a H₂/MTS molar ratio of 7.5, which is considered to be a low H₂/MTS ratio (high reactant gas concentration). The deposit surface is dense and relatively smooth (Figure 7A), featuring a rounded surface morphology (Figure 16B). This is consistent with the results obtained by other researchers.

Microstructure

In general, for CVD SiC from MTS-H₂ mixtures, the density increases with increased temperature and MTS concentration. The two most important parameters which control the microstructure, morphology and grain size of the deposited material is the deposition temperature and reactant gas concentration. The low temperature deposits usually have fine grains and low density while the materials deposited at higher temperatures have larger grain sizes. For bulk CVD SiC materials, a fine-grained structure is generally preferred because good material uniformity and high strength are obtained with this structure at a relatively high deposition rate.

The general microstructure of the CVC SiC composites is shown in Figures 17A and 17B. Uniformly distributed powders and fibers are seen in a SiC matrix. The microstructure is characterized by a laminated growth of CVD SiC around the second-phase powders and fibers, with an inter-layer spacing of approximately 4-7 μm . The matrix shows good bonding with the SiC powders (Figures 18A and 18B). No sign of delamination is observed at the interface. Satisfactory bonding is also identified at the matrix/fiber interface (Figure 19).

(A) Low-magnification view

(B) High magnification view

Figure 16. SEM micrographs to show the typical surface morphology of CVC SiC composite. Run #4001.

(A) Low-magnification view. Run #3964.

(B) Carbon fibers in a SiC matrix. Run #3604.

Figure 17. Micrographs of the CVC SiC composites, revealing uniform distribution of the second-phase particles and fibers.

(A) Run #3629.

(B) Run #4001.

Figure 18. Micrographs of the CVC SiC composites, revealing satisfactory bonding between the CVD SiC matrix and the SiC particles.

Figure 19. Micrograph to show interface of the SiC matrix and the SiC fibers in the CVC SiC composite. Run #3986.

A decrease in concentration of C and Si in the gas-phase will decrease deposition rate and increase grain size at constant temperature (Weiss 1973). At the lower deposition temperature, the crystallite size is sufficiently small that the surface morphology and microstructure are determined by surface inhomogeneities and the appearance is similar to pyrolytic graphite. As the temperature is increased, the crystallite size will attain dimensions similar to those of the growth cones caused by surface inhomogeneities. At this temperature or any higher temperature, the microstructure and surface morphology depend on the crystallite size.

The SiC matrix was found to be fine-grain structure. As can be seen from Figures 17 to 19, a laminated fine-grain microstructure is the dominant structure in the CVD/CVC SiC composites obtained in the present study. This type of microstructure has been observed by a number of researchers in CVD SiC (Weiss 1973, Moeller 1987, Grathwohl 1992). It is well known that the microstructure of CVD deposits primarily depends upon deposition temperature, while carrier gas and reactant flow rate have a secondary effect (Gulden 1968). It has been demonstrated that the Terrace-ledge-link (TLK) transport mechanism or the Twin-plane re-entrant edge (TRRE) mechanism plays major roles in CVD SiC crystal growth (Cheng 1986, Chu 1991), depending upon the deposition temperature. The laminated growth of a faceted crystal from solid surface in an adsorption-desorption equilibrium of gaseous species, is generally understood by the TLK transport mechanism. For a deposition pressure of 760 Torr, the basic growth shape of SiC is lamellar with the plane of the lamella perpendicular to [001] crystalline direction. This growth behavior can be found exaggerated in the semi-dendritic growth of lamellae, especially over a temperature range of 1,300 to 1,500°C (Cabrera 1963), which was employed in the present study. This process is characterized by a layered growth from the tip on spherulites of a sphalerite structure. The laminations, also called "primary bands", are often associated with bands of very fine pores (Walker 1971).

For CVC SiC deposits, it appears that SiC nucleated on the surfaces of the solid additives (powders or fibers). The orientation of the CVD SiC layers was controlled by the curvature of the nucleation surface. Therefore, the CVD SiC has either an onion-like shape or a tubular shape. The nucleation of CVD SiC occurred simultaneously at numerous nucleation sites, due to continuous feeding of the powders and the fibers, forming isolated 'islands'. Each 'island' continued to grow by addition of newly formed SiC layers on the growing surface until the inter-particle gaps were completely filled, or until the supply of the source material was blocked out due to overlapping of the multiple 'islands'.

Excessive porosity levels are seen in a high percentage of CVC SiC deposits obtained, as shown in Figures 20A and 20B. CVD SiC containing no powders or fibers, on the other hand, is essentially porosity-free, suggesting that the porosity is induced by the powder/fiber additives. In general, the porosity level increases with increased volume fraction of the powders or fibers added. The majority of the pores were present at areas near the fibers (Figure 20B). No pores were found at areas near the matrix/particle interface. The root cause for the porosity is attributed to the block out of the source gas during the CVD processing, i.e., the block out of the paths through which the source gas could reach the growing surface of the CVD SiC in the gap regions.

(A) Run #3889.

(B) Run #3986. Voids are seen at areas near the SiC fibers.

Figure 20. Porosity observed in the CVC SiC composites.

Fiber-Matrix Structure

In the present study, it is noted that the CVC SiC composite containing carbon fibers have less porosity than those containing SiC fibers (see Figures 17B and 20B). On the other hand, the CVC SiC composites containing carbon fibers showed microcracks while no microcrack is observed on the CVC SiC composites containing SiC fibers. These phenomena can be explained by the fiber-matrix structure in different composites.

The different porosity level observed in the carbon-fiber-containing and SiC-fiber-containing composites might be due to the fact that the carbon fiber diameter (10 - 20 μm) is much less than the SiC fiber diameter (70 to 110 μm), as can be seen from Figures 10C to 10D, which leads to a higher packing factor of the carbon fibers, resulting in a lower porosity of the composite. Consequently, a complete matrix layer around a fiber is easier to form in the carbon-fiber reinforced composites than in the SiC-fiber composite.

In studying the chemical vapor infiltration (CVI) SiC composites (Grathwohl 1992), two fiber-reinforced SiC matrix with SiC powders materials containing SiC (Textron and Hi Nicalon) and Carbon (Panex) fibers, respectively, were characterized by evaluation of their microstructures and interfaces between the fiber and the matrix. It was also found that the interfaces between fiber and matrix showed a layered structure consisting of carbon layers and an intermediate SiO_2 -layer in the both of the carbon-fiber and SiC-fiber reinforced ceramics. Surface oxidation on SiC fibers releases carbon and silicon oxide, thus being responsible for the formation of the interlayers in the composites.

The microcracks observed in the carbon fiber-containing CVC SiC composites is most likely due to the thermal mismatch of the CVC components when cooling the composite. The coefficient of thermal expansion of the carbon fiber in the axial direction (0.4 $\text{ppm}/^\circ\text{C}$) is much less and in the radial direction (7 $\text{ppm}/^\circ\text{C}$) is much higher than that of the SiC matrix (3 $\text{ppm}/^\circ\text{C}$), resulting cracking of the composites containing carbon fibers, when cooling the material from the deposition temperature.

Deposit/Substrate Adherence

The adherence of a deposit to the substrate is critical for many applications. The quality of the bonding depends upon the deposit and substrate physical property matching and the substrate surface preparation. In the present study, most CVC SiC deposits were formed on graphite substrate. The adherence between the CVC SiC composite and the substrate is therefore mainly controlled by the substrate surface preparation. The adherence of the deposits to the substrate, for some runs, is given in the comment section in the Master Tables 3 and 4.

Figures 21A and 21B illustrate a strong bond and a weak bond at the interfaces of deposit and substrate, respectively. In Figure 21A, the CVC SiC shows satisfactory adherence to the substrate. No interface gaps or sign of delamination are observed, whereas in Figure 21B, there is a 25 μm gap between the deposit and the substrate. It is noted that a rough substrate surface is beneficial to the interface adherence, as can be seen in Figure 21A. A relatively smooth substrate surface, as in Figure 21B, makes it rather difficult to have a good bonding.

(A) Low-magnification view. Run #3964.

(B) Carbon fibers in a SiC matrix. Run #3604.

Figure 21. Interface between the CVC SiC deposits and the graphite substrate.

Composition Analysis

In order to obtain a particular composition (SiC or SiC+C or SiC+Si), the suitable deposition conditions can be chosen from the results of the investigations on the thermodynamic aspects of the process. In the high temperature region ($T > 1,100^{\circ}\text{C}$), decreasing the temperature increases the Si to SiC ratio. For a given temperature, an increase in pressure or MTS molar fraction also favors SiC+Si co-deposition (Pickering 1992). SiC+C co-deposition is only obtained under low pressure and high temperature conditions for an MTS rich gas phase (Sasaki 1988).

Table 5 summarizes the EDX analysis results from selected composites. The CVC SiC was determined to be slightly silicon rich, due to the intermediate deposition temperature region and atmosphere pressure employed in the present study. Some deposits processed in the earlier runs show small amounts of oxides and other contaminants within the voids. The fracture origin of these materials is found to be correlated with a region of high iron contamination. This contamination problem was found to result from the exhaust gas corrosion of a stainless steel rotation shaft located near the exhaust. Use of a molybdenum shaft had eliminated the contamination problem. Currently, most of the deposits show high purity of SiC, containing virtually no other elements except silicon and carbon.

TABLE 5. EDS ANALYSIS OF CVC SiC.

Run Number	Elements Identified	Quantitative Analysis
3465	Si, C	N/A
3483	Si, C	N/A
3486	Si, C, O, Cl, W, Fe, Sn inside crack origin	N/A
3521	Si, C	N/A
3539	Si, C	N/A
3560	Si, C	N/A
3561	Si, C	N/A
3614	Si, C, O	N/A
3617	Si, C, O	N/A
3680	Si, C in bulk; Si, C, O, Fe, Cl inside crack origin	N/A
3610*	Si, C	51.9% Si + 48.1% C

*Analyzed at TTC.

5.5 Mechanical Properties

Hardness

A Vicker microhardness tester was used to determine the hardness of the CVD SiC matrix, with a load of 300 to 1,000g. The hardness of CVD SiC matrix is determined to be 3,200 to 3,260 kg/mm^2 and is fairly constant, as illustrated in Figures 22A and 22B. The hardness of the CVD SiC is substantially higher than the typical value (2,800 kg/mm^2) found in P/M and sintered SiC (Pierson 1992), due to the higher material density achieved by the CVD process.

Figure 22. Vicker indentations (arrows) on the polished CVC SiC matrix. $P = 1,000$ g. The hardness is found to be 3,200 to 3,260 kg/mm² and is fairly constant.

Flexural Strength

The mechanical properties and their relation with microstructures of CVD materials have been a subject of extensive investigation. It was found that the fracture strength of dense, CVD SiC remains approximately constant between room temperature and 900°C, and then decreases above 1,000°C. The fracture mode is transgranular cleavage at all temperatures (Sasaki 1988). This is attributed to the characteristic microstructure of CVD SiC. A high density of planar growth faults exist in CVD SiC, which are identified as extrinsic stacking faults on the {111} crystalline planes (Gulden 1971).

The flexural strength of selected CVC SiC composites were determined by standard four-point bend testing, per ASTM C1161 specification. "B" specimen configuration (4.0 mm x 3.0 mm x 45 mm) was used. The tests were conducted at room temperature and at 1,200°C, respectively, using a 0.5 mm/min loading rate, per ASTM C1161. The inner and the outer spans are 20 mm and 40 mm, respectively.

The flexural strength (S) is calculated using the formula

$$S = \frac{3 P L}{4 b h^2}$$

where

- S - Flexural strength in MPa
- P - Peak load (N)
- L - Outer span (0.04 m)
- b - Specimen width (0.004 m)
- h - Specimen height (0.003 m).

It is known that the mechanical properties of a brittle material, such as SiC, show substantial data scattering even the material is tested under the same testing condition. The mean ($\bar{S}$) and the standard deviation (S.D.) of the tested CVC SiC specimens are determined with the formulas

$$\bar{S} = \frac{\sum_{i=1}^n S}{n}$$

$$S.D. = \sqrt{\frac{\sum_{i=1}^n (S - \bar{S})^2}{(n-1)}}$$

where

- n - Number of the specimens.

The flexural strength and S.D. of the CVC SiC composites, at room and elevated temperatures, are given in Table 6. The strength data show a rather substantial scattering, due to statistical

variations in critical flaw size. At room temperature, the flexural strength of the fully dense CVC SiC can be as high as 468 ± 29 MPa from the results of run #3507 material which is at the high end of flexural strength (255-465 MPa) typically found in CVD SiC materials (Engineering Materials Handbook, 1996). On the other hand, even a low level of porosity in the CVC SiC composites would reduce the flexural strength by more than 60%, as can be seen from the results of run #4001 material. At 1,200°C, the strength of the same material decreases by approximately 20%.

TABLE 6. FLEXURAL STRENGTH OF CVC SiC AT ROOM AND ELEVATED TEMPERATURES.

Test I.D.	Run Number	Tester Codes*	Samples Tested	Test Temp.	Strength (MPa)	S.D. (MPa)	Strength (ksi)	S.D. (ksi)
1	3483	A	14	RT	221.0	29.0	32.1	4.2
2	3486	A	17	RT	332.0	63.0	48.2	9.1
3	3488	A	18	RT	308.0	25.0	44.7	3.6
4	3507	B	10	RT	468.2	29.2	67.9	4.2
5	3508	B	10	RT	427.5	44.1	62.0	6.4
6	3508	C	10	RT	403.2	72.5	58.5	10.5
7	3512	B	10	RT	304.8	44.1	44.2	6.4
8	3514	B	10	RT	295.1	35.2	42.8	5.1
9	3576	B	10	RT	292.3	29.0	42.4	4.2
10	4001	C	10	RT	168.3	20.5	24.4	3.0
11	4002	C	10	RT	174.2	19.4	25.3	2.8
12	3507	B	3	1200°C	358.5	19.3	52.0	2.8
13	3508	B	3	1200°C	384.1	29.6	55.7	4.3
14	3512	B	3	1200°C	257.2	22.8	37.3	3.3
15	3514	B	3	1200°C	260.6	6.9	37.8	1.0
16	3576	B	3	1200°C	173.8	45.8	25.2	6.6

*Tester Code A: *manLabs, Cambridge, MA, by 4-point bending per ASTM C1161.*

Tester Code B: *Worcester Polytechnic Institute, Worcester, MA, by 4-point bending per ASTM C1161.*

Tester Code C: *TTC, San Diego, CA, by 4-point bending per ASTM C1161.*

Weibull modulus is the measure of variability in the strength data of brittle materials. The smaller the Weibull modulus, the greater is the scatter in strength. The Weibull modulus of the CVC SiC is found to vary from 9.2 to 21.6. The level of confidence for the Weibull parameters is not very high because of the limited number of specimens tested. The ASTM C1211 suggests the use of at least 30 specimens from the identical material to estimate the Weibull moduli.

Fracture Toughness

Fracture toughness is usually the limiting property in ceramic materials. Ceramics tend to have excellent creep properties and wear resistance, but are excluded from many engineering applications because they are relatively brittle. Therefore, the brittle fracture has been a primary area of concern in ceramic materials (Anderson 1995). Wide-spread use of today's advanced SiC ceramics still requires a significant improvement in fracture toughness and reliability. A promising way to achieve this aim might be the reduction of grain size down to nano-size range. The other way to achieve this goal is to use fiber-reinforced SiC composites. SiC fibers are of

considerable interest as reinforcements for ceramic-matrix composites. These fibers help to increase the fracture resistance of ceramic matrix composites.

The plane strain fracture toughness, K_{IC} , is one of the most important material properties for advanced ceramics. It represents the material's resistance against unstable extension of macroscopic cracks under plane strain conditions. The typical K_{IC} value for SiC coating materials is approximately $3.0 \text{ MPa}\sqrt{\text{m}}$ (Ohring 1992).

There are two techniques to determine the fracture toughness of a material: tensile testing and flexural (bend) testing. In principle, the K_{IC} value of a material can be determined by the maximum load (peak load), $F_{\max}$ specimen width (B), specimen height (W), and the pre-crack penetration depth (a), by a general formula (Anderson 1995):

$$K_{IC} = \frac{F_{\max}}{B\sqrt{W}} f(a.W)$$

where $f(a/W)$ is a specimen geometry correction factor determined by a/W ratio.

The fracture toughness of the CVC SiC composites was determined per DIN 51-109 specification, using 4-point bending of notched rectangular bar specimens (3.0 mm x 4.0 mm x 45 mm). The fracture toughness of advanced ceramics measured by 4-point bending is given by DIN 51-109 specification:

$$K_{IC} = \frac{F_{\max}}{B\sqrt{W}} Y$$

$$Y = \frac{L_o - L_i}{W} \frac{3\sqrt{\alpha}}{2(1-\alpha)^{3/2}} \left[1.9887 - 1.1326\alpha - \frac{(3.49 - 0.68\alpha + 1.35\alpha^2)\alpha(1-\alpha)}{(1+\alpha)^2} \right]$$

$$\alpha = \frac{a}{W}$$

where

$F_{\max}$ - Peak load (N)

B - Specimen width (0.003 m)

W - Specimen height (0.004 m)

L_o - Outer (bottom) span length (0.04 m)

L_i - Inner (top) span length (0.02 m)

a - Notch penetration depth (0.001 m)

Required : $0.2W \leq a \leq 0.3W$.

The results obtained are given in Table 7. The K_{IC} value of the CVC SiC composite varies from 2.8 to $3.6 \text{ MPa}\sqrt{\text{m}}$, with a weighted average of $3.2 \text{ MPa}\sqrt{\text{m}}$. This value is substantially higher than the $3.0 \text{ MPa}\sqrt{\text{m}}$ which is typically found in CVD SiC. During flexural testing, it was noted

that the specimens showed a relatively slow separation once the peak load was reached, accompanying by a gradual load drop at the end of the testing.

TABLE 7. FRACTURE TOUGHNESS OF CVC SiC AT ROOM TEMPERATURES.

Test I.D.	Run Number	Tester Code*	Samples Tested	Fract. Toughness (MPa√m)	S.D. (MPa√m)	Fract. Toughness (ksi√)	S.D. (ksi√)
1	3507	B	4	3.50	0.15	4.83	0.21
2	3508	B	5	2.75	0.12	3.79	0.17
3	3512	B	5	2.90	0.13	4.00	0.18
4	3514	B	4	2.80	0.21	3.86	0.29
5	4001	C	10	3.19	0.46	4.40	0.63
6	4002	C	10	3.59	0.44	4.95	0.61

*Tester Code B: Worcester Polytechnic Institute, Worcester, MA, by 4-point bending of notched rectangular bars.

Tester Code C: TTC, San Diego, CA, by 4-point bending of notched rectangular bars.

The improvement in the fracture toughness is believed to mainly result from the addition of fibers and particles. It is known that the fiber/matrix or particle/matrix interface acts as barrier to transversal cracks: stopping or deviating them. In a previous work (Cook 1964), it has been found out that deviating the cracks at weak interfaces would increase the global toughness with respect to the toughness of the single ceramic phase.

Fractography

The post-test specimens were examined with an SEM, at magnifications of 25 to 1,000x. The fracture surfaces of the dense or near-dense CVC SiC specimens are characterized by many cleavage steps (Figures 23A and 23B) and relatively large, flat areas of cleavage (Figures 23C and 23D). The fracture mode of the material is transgranular cleavage, which is probably a consequence of its relatively high density and freedom from intergranular porosity. The crack initiated at the micro-flaws on the specimen bottom surface, where the maximum tensile stress occurred, and propagated toward the specimen top surface until final separation took place.

Figure 24A shows crack initiating from an internal pore. It is well known that pores in polycrystalline materials would form equatorial cracks approximately one-half grain deep into the matrix and thus become sharp flaws. The strength reduction from porosity was previously viewed as resulting from stress concentration effects of pores increasing the stress on nearby flaws. The grain boundaries intersecting the pore were weak enough to fail, owing to the stress concentration of the pore, so that a crack would propagate into the matrix, along grain boundaries, until it encountered the next set of grains. For very porous CVC SiC composite, the crack propagated along the internal pores (Figure 24B). No sign of cleavage was observed.

Rupture of fibers with axis perpendicular or near-perpendicular to the fracture plane was observed on every specimen examined (Figures 23C and 23A), indicating that the load applied to the specimens was partially transferred to the fibers. When the fiber axis was parallel to the

(A) Cleavage steps on the fracture surface. Run #3703.

(B) Cleavage steps and SiC fiber fracture. Run #4001.

Figure 23. Fractographs of the dense or near-dense CVC SiC composites.

(C) Low-magnification view, showing features of transgranular cleavage. Run #4002.

(D) High-magnification view, showing fiber rupture. Run #4001.

Figure 23. Fractographs of the dense or near-dense CVC SiC composites.

(A) Crack initiation from internal pores (arrow). Run #3611.

(B) Fracture along the pores. No sign of cleavage is observed. Run #3622.

Figure 24. Fractographs of the porous CVC SiC specimens.

fracture plane, fiber delamination (fiber pullout) occurred (Figure 25B). For notched fracture toughness specimens, the crack initiated at the notch root and propagated towards the top surface of the specimen, following an irregular crack growth path (Figure 26A). When the crack encountered with a fiber or a particle, a by-pass propagation by a deviating mechanism took place along the fiber/matrix interface (Figure 26B).

Mechanical properties of CVC SiC composites are strongly influenced by fiber/matrix and particle/matrix interfacial characteristics (Mah 1984, Sawyer 1985, Clark 1986, Sawyer 1986) and also by inherent properties of the fibers, the particles, and the matrix. The interfacial properties, in general, are controlled by processing variables and procedures. The processing variables include fiber content, post-fabrication densification, and fiber surface condition.

In a fiber-reinforced ceramic-matrix composite, where strengths of both fiber and matrix are high or are of comparable value, both components are brittle and it is the fracture properties that need to be addressed. Of particular importance in this respect is the adhesion of the fibers to the matrix in which they are embedded. To a large extent, the fracture properties of a fiber-reinforced ceramic composite are determined by how the fibers adhere to the matrix (DiCarlo 1985, Mah 1987, Singh 1989), in general, *a relatively weak interface is desirable* in this case because it stops the propagation of a crack in the matrix from crossing into the fiber and causing catastrophic failure of the composite. For this reason, in ceramic-matrix composites, it is the fiber/matrix interface that is of prime concern.

Optimum fiber/matrix interfacial debonding and frictional sliding stresses are important to ensure sufficient matrix-to-fiber load transfer and extensive fiber pullout during fracture, thereby leading to toughening of the composite (Yamamura 1987). Moreover, it has been demonstrated that such interfacial properties as toughness and sliding frictional stress affect the matrix cracking stress of ceramic matrix composites. Dependence of interfacial debonding and frictional sliding stresses was found to decrease with increasing fiber content.

Interfacial properties are also known to be influenced by fiber surface characteristics such as roughness and coatings. Surface roughness of fibers can affect interfacial sliding stress because of the resistance offered by surface asperities to fiber slippage. Fiber surface coating, such as the carbon coating on Hi-Nicalon SiC fibers and SiC coating on Textron carbon fibers used in the present study, can be used to modify fiber surface roughness and also to prevent formation of any chemical bond at the interface during fabrication and service conditions. Although the carbon coating process causes some decrease in Nicalon fiber strength but the characteristics of the coating are favorable for a weak composite matrix interface (Fischbach 1990).

The control of mechanical properties can also be achieved by adjusting the process parameters. For CVD SiC, the toughness is maximum at the grain size of 1-5 μm , and decrease below and above this value (Niihara 1983). Similar grain size effects on the fracture energies are also reported for the sintered ceramics with non-cubic structure (Rice 1981). This is attributed to microcrack forming due to the combined effects of the applied stress and the local micro-stresses produced by thermal expansion anisotropy. Besides, the structure of the deposit also can be controlled. In general, the laminar SiC is weaker than SiC characterized by columnar grains and has lower Young's modulus (Gulden 1969).

Figure 25. Fractographs of the CVC SiC specimens, showing fiber fracture when the fiber axis is perpendicular to the fracture plane (A) and fiber pullout when the fiber axis is parallel to the fracture plane. Run #4001.

(A) Crack initiation at the notch root. Run #4002.

(B) Crack deviating along the fiber/matrix interface. Run #4001.

Figure 26. Fractographs of the notched CVC SiC specimens.

5.6 Thermal Properties

Coefficient of Thermal Expansion (CTE)

Thermal properties of CVC SiC composites are important for applications at elevated temperature. Addition of powders and fibers into the CVD SiC matrix is expected to change the thermal properties of the CVD SiC, depending upon the volume fraction of the additives and the porosity induced by the additives. The coefficient of thermal expansion (CTE) of selected CVC SiC specimens was measured over a wide range of temperatures from 100°C to 1,400°C, per ASTM E228 specification.

The CTE values from 4 specimens processed with different conditions are given in Table 8. For all the specimens, the CTE value increases with increased temperature. However, the rate of increase varies for different specimens. Run #3573 material shows the most dramatic increase over the temperature range studied, whereas Run #3580 has the minimum increase among the four specimens tested.

TABLE 8. COEFFICIENT OF THERMAL EXPANSION OF CVC SiC (ppm/°C) AT EVALUATED TEMPERATURES*.

Temperature (°C)	Run #3573	Run #3580	Run #3585	Run #3593
100	-	0.82	0.45	0.41
200	0.60	0.91	0.70	0.77
300	0.94	1.01	0.96	1.18
400	1.17	1.16	1.15	1.33
500	1.36	1.24	1.30	1.56
600	1.52	1.40	1.43	1.62
700	1.61	1.52	1.54	1.74
800	1.70	1.58	1.62	1.88
900	1.82	1.55	1.60	1.86
1000	1.89	1.54	1.61	1.88
1100	1.96	1.48	1.64	1.90
1200	2.04	1.20	1.67	1.92
1300	2.13	-	1.65	1.95
1400	2.15	-	1.60	1.92

*Tests conducted at Theta Industries, Inc., Port Washington, NY, by single push rod dilatometry, per ASTM E228.

The CTE of CVC SiC composites is approximately 0.8 ppm/°C at 100°C and is approximately 2 ppm/°C at 1,400°C. The typical CTE values for SiC are 3.9 ppm/°C at 25°C (Pierson 1992) and 4.9 ppm/°C at temperatures up to 1,000°C (Galasso 1991). It appears that the CTE value of the CVC SiC composite is abnormally lower than that of pure SiC. The reduced CTE value observed in CVC SiC is most likely due to the presence of porosity in the material.

Thermal Diffusivity

Transient heat transfer problems occur when the temperature distribution changes with time. The fundamental quantity that enters into heat transfer situations not at steady-state is the thermal diffusivity. It is related to the steady-state thermal conductivity through the equation:

$$D = \frac{\lambda}{\rho C_p}$$

where D is the thermal diffusivity, λ is the thermal conductivity, ρ is the density, and C_p is the specific heat. The diffusivity is a measure of how quickly a body can change its temperature. It increases with the ability of a body to conduct heat (λ) and it decreases with the amount of heat needed to change the temperature of a body (C_p). All three quantities on the right hand side of above equation, as well as the thermal diffusivity, are functions of temperature.

Thermal diffusivity of selected CVC SiC composites was measured at room temperature by the Laser Flash method, per ASTM E146 specification. As shown in Table 9, the thermal diffusivity of CVC SiC composites varies from 0.268 to 0.675 cm²/s. Again, the significant scattering of the measured data is attributed to (1) the internal porosity of the material, and (2) the limited number of specimens measured. Additional tests are proposed in the future work.

TABLE 9. THERMAL DIFFUSIVITY OF CVC SiC AT ROOM TEMPERATURE.

Run Number	Temperature (°C)	Thermal Diffusivity (cm ² /s)
3573	26	0.675
3580	26	0.602
3585	26	0.268
3593	26	0.483

6.0 TASK – TECHNOLOGY TRANSFER

The two goals of this task are to transfer CVC technology for 1) fabricating SiC fans for high temperature heat treating furnaces at atmosphere and; 2) fabricating SiC combustion tubes for vacuum heat treating. The industrial user for the SiC fans was Holcroft Inc. in Livonia, MI. The industrial users for the combustion tubes was Surface Combustion Inc. in Ohio.

6.1 SiC Fan

TTC worked with Holcroft which is a leading supplier of thermal processing equipment and designs and builds equipment for steel mills, automotive industry and aerospace. Their product range covers various types of high temperature furnaces.

The first part of this task focused on characterizing the existing furnaces with metal recirculating fans and calculating the technical and economical benefits of a SiC recirculating fan. The next part of this task was to fabricate a prototype CVC SiC fan based on the design requirements the heat treating furnace. Figure 27 shows a cross section of a heat treating furnace with radiant heating tubes and a recirculating fan. The parts are heated by convection and radiation. The metal fan operates at 1,700 RPM up to a temperature of 1,000°F; however, the metal fan speed is reduced to 800 RPM up to a temperature of 1,700°F. The goal of this task is to fabricate a prototype (7" diameter) SiC fan. This fan would be capable of operating at 1,700°F RPM at a temperature of 1,700°F. Advantages of operating a SiC fan at higher temperatures and at higher RPM are:

1. Increase convection heat transfer resulting in faster and more efficient heating of load;
2. Dense load can be heated with improve uniformity;
3. Carburizing rates can be increased;
4. Can improve uniformity of carbonization;
5. Reduction of endothermic gas needed for carburizing as circulation is increased;
6. Radiant tube can be fired at greater heat input due to increased heat transfer;
7. Improve fan design to improve efficiency;
8. Increase fan lifetime by eliminating carbonizing of alloy fan.

Figure 27. Heat treating furnace.

Figure 28 shows the reduced heating time of part load with a SiC fan operating at 1,700 RPM.

Figure 28. Furnace heating time.

A report summarizing the productivity of operating a fan at 1,200 RPM in an indirect-fired heat treating furnace is enclosed in the appendix. A cross-section of a metal heat treating fan is shown in Figure 29.

Figure 29. Cross section of heat heating fan.

The fan geometries required for efficient air recirculation were investigated in industrial brochures. Performance data was related to material properties of the fan material at 1,700°F in air. The following data were related:

9. Fan blade geometry (height x width);
10. Amount air moved (CFM);
11. Pressure (inch of water);
12. Rotation RPM.

Various fan geometries and shapes of metal fans were assembled to determine what architectures would be easiest to fabricate by CVC deposition with a minimum of machining. The minimum height to width ratio was determined to be 5. Figure 30 shows the cross section of the graphite substrate used to deposit CVC SiC.

Figure 30. Fan blade substrate.

Unfortunately TTC was unable to fabricate a CVC SiC fan with a blade height to width ratio of 5. TTC was successful in fabricating a CVC SiC fan with a blade ratio of 1 as shown in Figure 31. Dense CVC SiC deposits could not be obtained with high blade ratio. Figure 32 shows the sequence of CVC deposits on the top outside surface and forming a hollow cavity in the blade.

Figure 31. CVC SiC fan prototype.

Figure 32. CVC deposit of blade structure.

Over 30 experiments were conducted in order to deposit a dense blade geometry with a ratio of 5. The following modifications were attempted to reduce the formation of the cavity in the blade geometry during the CVC SiC deposit:

13. Injector nozzle position and outlet size and shape for both powder and gas reactants;
14. Single and multiple injectors;
15. Pre-heating powders (700°C);
16. Vacuum CVC deposition (40 torr);
17. Various powder sizes 30 μ to 90 μ ;
18. Various fibers Textron and Nicalon;
19. MTS & H₂ gas flows;
20. Varied geometries (taper and vent holes) of blade.

None of these modifications could change the relative deposition rates on the vertical and bottom surfaces of blade substrates. All deposits produced a hollow, weak CVC SiC deposit in the fan blade. Table 10 summarizes the SiC CVC experiments with powder and fibers to fabricate a prototype fan.

The basic problem was flowing the MTS gases into the grooves of the blade geometry. The CVC material on the surface was 99% dense while the CVC material at the bottom of the tapered groove was porous. This indicates that the MTS to powder ratio was not uniform. The MTS to powder ratio at the graphite surface was higher than in the bottom of the tapered groove. The result was that CVC SiC material in the groove was less dense and not as strong. The deposited strength is critical because the tip of the fan blade has the highest pressure during rotation.

TABLE 10. SUMMARY FOR CVC SiC PROTOTYPE FAN FABRICATION.

<u>DATE</u>	<u>RUN #</u>	<u>DEP</u> <u>HOURS</u>	<u>MTS</u> <u>USED</u>	<u>H2</u> <u>USED</u>	<u>TEMP</u> <u>DEG C</u>	<u>PRESS</u>	<u>SIC POWDER</u> <u>SIZE & TOTAL</u>	<u>COMMENTS</u>
4/12/95	3536	10	15.6 lbs.	9.5 slpm	1345	763 torr	159.4 g of 30 um	inside deposition mandrel coated with BN releasing agent 4 coats of BN releasing agent applied to mandrel w/20 min heat curing between coats furnace ran with 2 H2O cooled injectors set to outer graphite cover feed through MTS injector outlet ~1" from and parallel to mandrel w/outlet aimed at powder stream standard H2 flows are : MTS 5 slpm, Powder feeder 3 slpm, Optic block 1.5 slpm SiC adhered to mandrel despite releasing agent and graphite was burned off SiC did not densify base of blades nor did blades bond well to SiC shaft 30 micron SiC powder found at base of fan blades
5/16/95	3560	5.5	9.6 lbs.	9.5 slpm	1345	750 torr	38.7 g of 30 um	flat mandrel w/ a series of 10 holes of various diameters and depth drilled into it holes ranged from 1/8"x1/8" to 1/4"x1/2" and were placed 1" from center and from edge same injector configuration as run 3536 SiC did not densify the holes
5/19/95	3564	3	4.4 lbs.	9.5 slpm	1345	741 torr	16.4 g of 30 um	same mandrel configuration as in run 3560 SiC powder injector moved from outer to center inlet MTS injector remained at previous location SiC did not densify the holes
5/23/95	3566	5.3	9.0 lbs.	9.5 slpm	1345	758 torr	29.1 g of 30 um	same mandrel configuration as in run 3560 SiC powder injector located in the center inlet MTS injector outlet angled down 45 DEG to mandrel and aimed at powder stream MTS injector remained at outer inlet SiC did not densify the holes
5/25/95	3570	5.25	9.4 lbs.	9.5 slpm	1345	755 torr	27.2 g of 30 um	same hole pattern in mandrel as in run 3560 1"dia x 1" tall graphite dowel added to center of mandrel so simulate SiC shaft of fan MTS injector outlet angled down 45 deg to mandrel and aimed at powder stream SiC powder injector relocated from center feed through to previous off center inlet SiC did not densify in the holes

<u>DATE</u>	<u>RUN #</u>	<u>DEP</u> <u>HOURS</u>	<u>MTS</u> <u>USED</u>	<u>H2</u> <u>USED</u>	<u>TEMP</u> <u>DEG C</u>	<u>PRESS</u>	<u>SiC POWDER</u> <u>SIZE & TOTAL</u>	<u>COMMENTS</u>
5/30/95	3574	2.75	5.6 lbs.	11.5 slpm	1345	745 torr	14.0 g of 30 um	flat mandrel w/series of 8 3/8" tapered holes of various depths and tapers drilled into it depths were of 0.375" and 0.420 w/ tapers of 60 deg and 82 deg 1" dia x 1" tall graphite dowel added to center of mandrel to simulate SiC shaft of fan MTS and SiC powder injector configuration same as in run 3570 MTS H2 increased from 5 slpm to 7 slpm SiC did not densify in the base of the tapered holes
6/1/95	3577	2.2	4.6 lbs.	13 slpm	1345	752 torr	N/A	same hole pattern in mandrel as in run 3574 except no graphite dowel in center carbon fibers used instead of SiC powder and entered the reactor via powder injector MTS injector outlet angled down 45 DEG to mandrel MTS H2 set to 7 slpm clumping of fibers noted in generated material some fibers noted in material but SiC did not densify in the base of the tapered holes
6/3/95	3579	4	unknown	9.5 slpm	1345	750 torr	N/A	same hole pattern in mandrel as in run 3574 1" dia x 1" tall graphite dowel in center of mandrel to simulate SiC shaft of fan 0.6 g of carbon fibers used and entered the reactor via powder injector MTS injector outlet angled down 45 DEG to mandrel MTS H2 set at 3.5 slpm MTS scale failed during the run, tracking prior to failure would put MTS usage at 3.8 lbs. some fibers noted in material but SiC did not densify in the base of the tapered holes
6/6/95	3583	6	6.0 lbs.	9.5 slpm	1345	747 torr	N/A	mandrel w/2 1/4" deep 90 DEG grooves 180 DEG apart w/1" dia x 1" graphite center post carbon fibers used instead of SiC powder and entered the reactor via powder injector MTS injector outlet angled down 45 DEG to mandrel MTS H2 set at 3.5 slpm material porous w/ clumps of fibers & few fibers fed into grooves
6/7/95	3587	6	9.4 lbs.	9 slpm	1345	744 torr	37.1 g of 30 um	inside deposition mandrel w/ SiC post in center extending from base of blades to 1" above edges of fan blades were turned down to give a more tapered edge MTS injector outlet angled down 45 deg to mandrel MTS H ₂ set at 5 slpm SiC very thin on sides of blades and did not form in outer corners CVC SiC fan blades did not adhere well to center SiC shaft

<u>DATE</u>	<u>RUN #</u>	<u>DEP</u> <u>HOURS</u>	<u>MTS</u> <u>USED</u>	<u>H2</u> <u>USED</u>	<u>TEMP</u> <u>DEG C</u>	<u>PRESS</u>	<u>SIC POWDER</u> <u>SIZE & TOTAL</u>	<u>COMMENTS</u>
8/17/95	3653	5.5	3.4 lbs.	6.5 slpm	1350	39 torr	19.6 g of 30 um	flat mandrel w/ 5 grooves alternating 1/2" x 1/4" with 1/4" x 1/4" MTS injector outlet angled straight down at substrate 3.9 g of HI Nicalon fibers used and mixed w/SiC powder in the injector fiber feeder mounted on powder injector above a tee for powder supply line vacuum pump installed on reactor exhaust line MTS H2 set at 2.0 slpm material was nodular with fibers in the grooves and the center of the mandrel thin layer of SiC formed in grooves
8/22/95	3657	1.5	0.8 lbs.	8 slpm	1343	47 torr	4.3 g of 30 um	flat mandrel w/same groove pattern as in run 3653 Hi Nicalon fibers and SiC powder plumbed into the MTS injector MTS injector outlet angled straight down at substrate vacuum pump installed on reactor exhaust line MTS H2 set at 2.0 slpm run aborted after 90 minutes of deposition due to equipment failure material thin w/fibers only noted on the outer edge surface of the mandrel
9/1/95	3665	6	8.8 lbs.	8 slpm	1345	743 torr	27.7 g of 30 um	outside deposition mandrel w/ 2 1/8" SiC shaft in the center MTS and SiC powder utilized separate injectors, both slightly off center MTS H2 set at 5 slpm deposited material good in general but pinched off at base of blades and at center shaft center shaft and base of 3 blades separated after burning off graphite
9/25/95	3677	6.75	9.6 lbs.	8.5 slpm	1345	756 torr	38.6 g of 30 um	outside deposition mandrel w/ 2 1/8" SiC shaft in the center fan blades were tapered at top and flared at the center SiC shaft to increase the radius of the bases of the fan blades and remove sharp edges all joints filled w/ graphite cement and sanded to a smooth radius deposited material good in general but pinched off at base of blades and at center shaft one blade and the flat area on either side broke free after burning off graphite
10/18/95	3698	2	2.4 lbs.	8 slpm	1345	756 torr	16.6 g of 30 um	flat mandrel w/ series of grooves ~ 0.010" wide SiC powder and MTS share common MTS injector no rotation of substrate due to mechanical failure SiC deposited in grooves w/ thickest under injector

<u>DATE</u>	<u>RUN #</u>	<u>DEP</u> <u>HOURS</u>	<u>MTS</u> <u>USED</u>	<u>H2</u> <u>USED</u>	<u>TEMP</u> <u>DEG C</u>	<u>PRESS</u>	<u>SiC POWDER</u> <u>SIZE & TOTAL</u>	<u>COMMENTS</u>
11/8/95	3718	4.75	7.0 lbs.	8 slpm	1345	735 torr	17.5 g of 30 um	inside deposition mandrel w/ 2 tapered grooves: 2" wide & 2.25" wide, both 1.3" deep all edges sanded to give smooth radius MTS and SiC powder in separate injectors overall material good except at base of grooves which was porous some cracks noted at base of blades after burning off graphite
11/13/95	3723	5.5	10.0 lbs.	9.5 slpm	1345	757 torr	13.7 g of 9 um	inside deposition mandrel w/ 2 tapered grooves: 2" wide & 2.25" wide, both 1.3" deep all edges sanded to give smooth radius 1.99 g of Hi Nicalon fibers used and manifolded onto common powder injector SiC powder, fibers and carrier H2 run through a graphite tube preheater Hi Nicalon fibers pulsed on for 1 minute of every 5 minutes fiber feeder off after 2 hours then continued CVC w/ 9 um powder for 3.5 hours upon unloading, found graphite preheater had clogged due to fibers during the run material thin and porous at base of blades
11/15/95	3727	5	6.8 lbs.	8 slpm	1297	736 torr	15.5 g of 30 um	inside deposition mandrel w/ 2 tapered grooves: 2" wide & 2.25" wide, both 1.3" deep all edges sanded to give smooth radius SiC powder and carrier H2 run through a graphite tube preheater material looked good with SiC forming along side and base of the blades
12/12/95	3745	7	10.4 lbs.	8 slpm	1300	755 torr	21.0 g of 30 um	inside deposition mandrel w/ 2 tapered intersecting grooves 2" wide x 1.3" deep all edges sanded to give smooth radius SiC shaft located in center of intersection graphite SiC powder preheater used along w/ non H2O cooled powder injector little SiC deposited at the base of the blades and SiC shaft not bonded to fan
12/14/95	3746	10	14.6 lbs.	8 slpm	1300	763 torr	N/A	second deposition of mandrel from previous run (3745) MTS injector angled down at 45 DEG toward the mandrel and aimed at the center shaft no SiC powder was used SiC did not deposit well at the base of the blades nor did the SiC shaft bond well cracks in the SiC discovered upon burning off the graphite

<u>DATE</u>	<u>RUN #</u>	<u>DEP</u> <u>HOUR: USED</u>	<u>MTS</u> <u>USED</u>	<u>H2</u> <u>USED</u>	<u>TEMP</u> <u>DEG C</u>	<u>PRESS</u>	<u>SIC POWDER</u> <u>SIZE & TOTAL</u>	<u>COMMENTS</u>
12/29/95	3757	10	14.6 lbs.	8 slpm	1300	755 torr	30.2 g of 30 um	inside deposition mandrel w/ 2 tapered intersecting grooves 2" wide x 1.3" deep all edges sanded to give smooth radius 2 of the blades had two 3/16" vent holes drilled through the base of the blade graphite SiC powder preheater used along w/ non H2O cooled powder injector the vent holes filled in and porous SiC deposited in the base of the bladed
1/10/96	3761	8	12.0 lbs.	9.5 slpm	1295	741 torr	33.1 g of 30 um	inside deposition mandrel w/ 2 tapered intersecting grooves 2" wide x 1.3" deep all edges sanded to give smooth radius vent holes in base of the blades increased to 1/4" graphite SiC powder preheater used along w/ non H2O cooled powder injector larger 7" graphite bucket used to allow more preheating of the SiC powder upon burning off graphite material looked good except the as dep side looks slightly porous vent holes in the base of the bladed did not fill in
4/16/97	3870	6	7.4 lbs.	10.5 slpm	1330	753 torr	19.2 g of 30 um	inside deposition mandrel w/ 4 parallel grooves of different depths and taper 2 grooves 1/2 x 1/4, one tapered and 2 grooves 1/2 x 1/2, one tapered 30 g of Textron fibers fed into reactor via a vibrating fiber feeder attached to powder injector powder/fiber mix fed to reactor via a non H2O cooled injector grooves filled in w/ fibers but material is extremely porous
4/22/97	3874	8	15.4 lbs.	10.5 slpm	1335	752 torr	9.4 g of 30 um	inside deposition mandrel w/ 4 parallel grooves of different depths and taper 2 grooves 1/2 x 1/4, one tapered and 2 grooves 1/2 x 1/2, one tapered 28.5g of Textron fibers fed into reactor via a vibrating fiber feeder fiber mix fed to reactor via a non H2O cooled injector MTS and SiC powder manifolded to common MTS injector grooves filled w/ fibers but did not densify dense SiC started to "pinch off" the openings of the grooves leaving voids

6.2 SiC Combustion Tubes

TTC worked with Surface Combustion Inc. a leading supplier of thermal processing equipment for vacuum and controlled environment heat treating furnaces. Presently, the only method of heating a vacuum heat treating furnace is to use electric heating elements. Metal combustion tubes are unable to maintain the required strength at operating temperature of 2,000°F in vacuum. A SiC combustion tube however can maintain its strength up to 2,500°F. The goal of this task is to develop, fabricate and test a CVC SiC radiate heating tube for Surface Combustion. The SiC radiate tube is 7 feet long 6" in diameter with one end domed. TTC successfully fabricated 4 foot long SiC tube with and without a domed end. TTC was not successful fabricating a 7 foot long SiC tube due to the lack of induction power required to deposit the tube in one step. A graphite tube substrate was machined and set-up in the rotational gig of the 100 KW reactor. A water cooled injector was fabricated with 8 outlets for MTS, H₂ and SiC powder. The 100 KW reactor had 6 pyrometers sight ports for temperature monitoring. A cross section of the 100 KW reactor is shown in Figure 33. The SiC powder feeder was set-up and plumbed into inlet injector. The 100 KW induction power supply would only heat up a 5 foot long section. This limited the length of the SiC deposit to only 4 feet long. The program required a complete 7 foot tube for testing. This requires two overlapping CVC SiC deposits to produce a complete tube

The following key CVC parameters were adjusted to fabricate a 4' long SiC tube:

- SiC powder feed rate (20 g/min);
- Inlet manifold hole size and locations;
- H₂ and MTS flow rate.

The domed and cylindrical end of the tube had a uniform thickness profile of 0.20" ± 0.020" thick over a length of 3 1/2'. The open end of the tube thickness was tapered from 0.20" to zero over the remaining 1 1/2 ft.

Figure 33. Cross-section of CVC tube reactor.

Cross sections of the CVC SiC tubes showed uniform SiC powder distributed from the domed end and along the open cylindrical section. The CVC deposit was 99% dense and appeared

vacuum light. The CVC SiC microstructures of the large 4 foot long sections were very similar to the CVC SiC material deposited in small 4" diameter horizontal reactor. The overlapping 4 foot CVC SiC deposits required to produce a 7' tube were a serious problem because of cracking. During the second CVC overlapping deposit, all the tubes cracked at the overlapping joint area.

In order to eliminate the tube cracks TTC tried varying the tapered CVC SiC thickness profile, the CVC shut down procedure and the powder volume present in the deposit. Analysis of the overlapping joints showed a Si rich SiC deposit in the first tapered section. The second CVC SiC on top of the first Si rich SiC had a mismatch in thermal coefficient expansion (TCE). The cross section of the two CVC SiC deposits is shown in Figure 34. The different deposition temperature caused the different TCE of the two CVC SiC materials. During thermal cycling the mismatch caused the tubes to crack and delaminate at the overlapping joint. The only solution was to purchase and install a large 250 Kw induction power supply and longer copper induction coil. This would allow the CVC SiC process to scale-up to a single 7 foot long deposit. The Surface Combustion program couldn't support this change. Fifteen tubes were fabricated in this program however none could be combustion tested because of the 4 foot length. Figure 35 shows examples of large SiC CVC tubes with and without domed ends.

Figure 34. Cross section of overlapping CVC SiC.

Figure 35. CVC SiC tubes.

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