ThermoTrex Corporation

TTC-3838-R
25 July 1997
Copy No. 2

DOE/GO/10020--T1

Development of Chemical Vapor Composite, (CVC) Ceramic Materials

Status Report
April 1995 - June 1997 for
Contract #DE-FG36-94G010020

Submitted to:

Office of Industrial Technologies
Energy Efficiency and Renewable Energy
U.S. Department of Energy
Washington, DC

Submitted by:

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

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

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

TABLE OF CONTENTS

1.0	INTRODUCTION.....	1
2.0	MAJOR ACHIEVEMENTS.....	3
3.0	SIGNIFICANT ACTIVITIES UNDER DOE PROGRAM.....	4
4.0	CRITICAL ISSUES.....	5
5.0	FUTURE PROGRAM PLAN.....	7
6.0	ORGANIZATIONAL PLAN.....	9
7.0	FINANCIAL STATUS	10

1.0 INTRODUCTION

The objective of the 94 DOE Chemical Vapor Composites (CVC) ceramics materials grant is to develop a reliable and flexible process to produce, in a single step, ceramic composites to final shape. The DOE grant has 5 tasks to perform:

Task 1 CVC Reactor Modifications. Design and implement fiber feeders which will avoid the tendency of fibers to agglomerate when incorporated in the reactant gas stream. The fiber feeder will be capable of accurately monitoring and controlling the fiber feed rate (grams/hour) to the CVC reactor. The inlet manifold must be designed to control the distribution of fibers, powder, and vapor reactants across the substrate surface. The 500 kW CVC reactor will be modified to deposit CVC SiC material.

Task 2 CVC Material Fabrication. The objective of this task is to fabricate ceramic CVC material. The CVC materials are expected to be tougher than powder-reinforced composites; however the uniform addition of fibers to the matrix will be the key issue, primarily as a result of agglomeration. (The program used various sizes of SiC powders as well as Nextel, Nicalon [SiC/SiO₂ (10%)] and C fibers.)

Task 3 Materials Characterization. Develop and understanding for the physical and mechanical properties of CVC materials and their relationship to the microstructure and deposition conditions.

Task 4 Technology Transfer. ThermoTrex Corporation (TTC) will address two industrial applications of CVC silicon carbide: ceramic fans and radiant tubes.

Task 5 Reporting. TTC shall establish a management organization and structure required to insure that all technical, schedule and cost requirements for the program are met. TTC will provide technical progress reports and attend program meetings.

This report is a brief summary of activities in the development of the Chemical Vapor Composites (CVC) ceramics materials program. A detailed presentation including a complete run history of all CVC experimental parameters (gas flow, particulate flow, vapor reactant flow, temperature, pressure and reactor geometry), photomicrographs and material properties will be in the final report.

Under the program TTC made progress on Tasks 1-3 while the facility was in Waltham. Beginning in March 1996 the Waltham facility was closed and the materials fabrication department was relocated to San Diego, CA at TTC's expense. The facility in San Diego is now on-line and we are resuming contract work.

During the past year the major activity for the CVD/CVC group was relocating from Waltham, MA to San Diego, CA. The CVD/CVC department was shut down in March 1996 when disassembling and packaging of the six reactors for relocation began. The CVD/CVC department successfully relocated, and set-up and began operating at the San Diego location in March 1997. Four CVD/CVC reactors are now fully operational at the new San Diego location. In addition, all other ThermoTrex departments which were in four separate buildings in San Diego have also relocated to the newly constructed facility.

The following list highlights the TTC-funded relocation activities which have culminated in a superior materials fabrication facility for this program:

- Construction and set-up of four new stainless steel hoods enclosing CVD/CVC reactor chambers, flow panels and particle feeders.
- Installation of new exhaust ducts and fans for each hood.
- Fabrication of four new welded mass flow panels for reactant delivery to CVD/CVC chambers.
 - New mass flow controllers (35 total) for H_2 , W_2 , WF_6 , SiH_4 and MTS.
 - New stainless steel bellows valves (85 total) and pressure gauges.
- Construction of new water recirculation system continuously monitoring and controlling temperature, pressure and resistivity up to 150 gallons per minute at 80 psi.
- Set-up four new scrubber systems and plumbing for products of all CVD/CVC reactant chambers.
- Installed new H_2 and N_2 inlet gas system to four hoods with three extra drops for expansion.
- Designed and set-up new safety system with the following features:
 - Eight H_2 detectors
 - Three emergency exhaust fans

- Emergency shut off to power supplies, MTS and H₂
 - New MTS storage and delivery system located outside building in service yard.
- Installed new vacuum cleaner system.
- Set-up CVD/CVC plasma diamond reactor including flow panel, power supply, pumping system and control station.
- Set-up graphite machine shop including:
 - Lathe.
 - Welding shop.
 - Milling machine.
 - Diamond grinder.
- Set-up scanning electron microscope for material characterization and polish and etch lab.
- Permits for air discharge in California.
- Permits from fire department for storage and usage of hazardous materials - H₂ and MTS in San Diego.
- Permits for waste disposal in California.

2.0 MAJOR ACHIEVEMENTS TO DATE

- Increased strength of CVC SiC reinforced with 30 μ m SiC powder from 340 MPa to 470 MPa.
 - Reduced impurities in SiC matrix.
 - Reduced porosity in SiC matrix.
- Fabricated 50 inch long tube 7 inches in diameter with CVC SiC reinforced with SiC 30 micron powder. Tube has closed end spherical dome at one end.
- TTC used the knowledge gained under this program (using internal TTC funds) fabricate SiC die mold for plastic injection molding. The die is currently being tested at a manufacturing facility in Massachusetts.

3.0 SIGNIFICANT ACTIVITIES UNDER DOE PROGRAM

The following significant CVC material development activities are summarized by task from April 1995 to March 1996 and April 1997 to June 1997.

Task 1 - Equipment Modification

- Fabricated and tested fiber feeder to deliver and monitor small agglomerated fibers (5 micron diameter) with 5% control accuracy.
- Fabricated and tested fiber feeder for large diameter Textron (0.005 inch) fibers up to 1/4 inch long.
- Designed, fabricated and tested liquid to vapor MTS delivery system to reaction chambers. System allows precise control $\pm 1\%$ of MTS feed rate to each reactor chamber with central MTS storage container outside building. MTS feedrate to reaction chamber is no longer dependent on H_2 flowrate.

Task 2 - CVC Material Fabrication

- Fabricated CVC SiC composite material with 5, 15, 30, 70, 120 micron SiC powder.
- Fabricated CVC SiC composite material with carbon, Nicalon, Nextel and Textron fiber.
- Fabricated CVC SiC material with 10 ratios of powder, fiber and reactant fluxes.
- Fabricated CVC SiC tubes 4.5 inches in diameter, 10 inches long reinforced with Textron fibers and 30 micron SiC powder. Cross section shows dense deposit with 5% volume of fibers approximately 0.2 inches long. Material properties to be determined.
- Fabricated laminated CVC SiC tubes 4.5 inches in diameter by 10 inches long with 30 micron and 70 micron SiC powder. Laminated microstructure was produced by cycling feedrate of 70 micron powder feeder on and off every 30 minutes. Microstructure showed 7 concentric rings of high and low density composite material. Properties to be determined.
- Fabricated CVC SiC tubes 4.5 inches in diameter by 10 inches long 30 micron SiC powder with 1/4 inch long Textron fibers. Laminated microstructure was produced by cycling fiber

feeder on and off every 60 minutes. Microstructure showed 6 concentric rings of fibers in SiC matrix. Mechanical properties to be determined.

- Fabricated CVC SiC tubes 4.5 inch in diameter by 10 inches long with mixture of three SiC powder sizes in single powder feeder. Powder mixture consisted of 1/3 15 micron, 1/3 40 micron and 1/3 20 micron SiC powder. Microstructure showed dense deposit with mixture of three powder sizes.

Task 3 - Material Characterization

- Determined room temperature and high temperature (1200°C) strength and toughness properties of CVC SiC reinforced with SiC powder and SiC platelets.

Task 4 - Technology Transfer

- Performed 25 CVC SiC experiments to fabricate a prototype 8 inch diameter fan. Unable to deposit SiC uniformly without voids to produce fan blade geometry.
- Performed 23 CVC SiC experiments to fabricate full scale combustion tube for heat treating furnace. Combustion tube is 80 inches long by 7 inches in diameter with one end closed with spherical dome and the other end joined to SiC flange.
- Renovated 100 kW horizontal CVD/CVC SiC tube reactor 10 feet long, 4 feet in diameter. Installed new induction coil, 8 foot graphite tube substrate, insulation package, rotation jig mechanism and powder/reactant gas inlet manifold.

4.0 CRITICAL ISSUES

The following critical issues are addressed in the development of CVC materials program.

Task 1 - Equipment Modification

The 500 kW CVD reactor was not set-up for CVC powder operation in this reporting period. This was not completed for two reasons: 1) the relocation from Waltham, MA to San Diego, CA would require a needless duplication of expense. There was no logic to set-up the 500 kW reactor in Waltham for CVC operations and then disassemble and relocate to San Diego; and 2) the design set-up goal of the 500 kW reactor was to fabricate a full scale SiC CVC fan 24 inches in diameter in Phase II of program. Technical problems encountered in the fabrication of an 8-inch prototype fan have made it imprudent to follow through setting up the 500 kW reactor at present. The 500 kW reactor was relocated to San Diego but has not been set-up for operation.

Task 2 - Material Fabrication

TTC has successfully CVC deposited a high fibers volume percent of 0.005 inch diameter fibers without porosity in a SiC matrix. However, CVC SiC deposits with a high percentage of (5 micron diameter) fibers (carbon or SiC) in matrix has porosity. Cross sections of deposits with a high volume percentage of fibers reveal fibers agglomerated in the SiC matrix. The agglomerated fibers are not fully densified causing porosity and a reduction in the strength of the composite. Cross sections of deposits with a low percentage of fibers reveal only few fibers in a dense matrix. At this time TTC has been unable to fabricate a CVC SiC composite with a high fiber volume percent with 5 micron diameter fibers without porosity. Three theories explaining these CVC deposits with small fibers are currently being investigated:

- Re-agglomeration of fibers in plumbing to reactor
- Low deposition rate on fiber surfaces
- Fiber transport properties.

Task 4 - Technology Transfer

TTC has been unable to fabricate an 8 inch prototype SiC CVC fan reinforced with 30 μm SiC powder. No CVC parameters were found to fill complex substrate geometries without voids to produce a prototype fan. The following experiments and modifications to fabricate a prototype fan are briefly summarized.

- Injector Manifolds
 - Varied injector positions parallel and perpendicular to substrate surface.
 - Mixed all reactants MTS, H_2 , powder, fiber in common injector prior to entering deposition hot zone.
 - Set-up dual injectors - one for vapor reactants and other for carrier gas (H_2) and particulates prior to entering deposition hot zone.
- Vacuum Deposition
 - Added corrosion resistant vacuum pump and filter to CVC system.
 - Fabricated CVC SiC with 30 μm SiC powder at ≈ 45 torr pressure. Normal CVC deposition pressure is 760 torr.
- Mandrels
 - Varied geometry of grooves in mandrel to produce SiC fan blade geometry. Varied angle of grooves from 10° to 45° . Varied the base and shape of the groove geometry.
 - Added vent holes at base of grooves to improve reactant gas flow.

- Set-up reactor mandrel with single and dual injectors with different positions.
- Set-up CVC SiC with two types of fan reactor mandrels to fabricate SiC fan blade shape:
 - positive (ridges) substrates, and
 - negative (grooves) substrate.
- Parameters
 - Varied deposition temperature (1400°C to 1300°C).
 - Increased flow of reactant and carrier gases to fan mandrel surface.
 - Pulsed feedrate of CVC particulates to mandrel surface.

Most of the deposits on the fan mandrel geometry produced CVC SiC material with uneven deposition thickness profiles across the substrate. The SiC deposit at the bottom of the groove or at the corner of the ridge was usually porous and powdery. Only preheating the injector for particulates before entering deposition chamber improved the CVC deposit by reducing the porosity in the composite.

5.0 FUTURE PROGRAM PLAN

Task 1 - Equipment Modifications

Work completed.

Task 2 - CVC Material Fabrication

Material will be fabricated under varying process parameters. Parameters to be varied include those listed in Table 1.

Table 1. Controllable process parameters.

Hydrogen Flow Rate
Methyl-trichloro-silane Flow Rate
Substrate Temperature
Powder Type and Size
Powder Feed Rate
Fiber Type and Size
Fiber Feed Rate

The process performance will be monitored as a function of the dependant variables listed in Table 2.

Table 2. Process performance parameters.

Growth Rate in gm/hour and mm/hr
Reaction Efficiency in % Methyl-Trichloro-Silane (MTS) utilized
Particulate Incorporation Efficiency in % Particulate Incorporated in the CVC Matrix

Because the process parameter space is so large, the test plan will follow the Taguchi method of experimental design. The Taguchi method utilizes a test plan designed to make the minimum number of measurements required to estimate the influence of a process variable on a process result. The design of a Taguchi test plan begins by listing controllable process parameters and then assigning 2 or more reasonable values or levels to each. Table 3 shows the 7 variable, 2 level layout currently being performed on the horizontal SiC reactor.

Table 3. Process parameters and values.

Parameter	Level 1	Level 2
1.0 MTS Flow rate	635 gm/hr	900 gm/hr
2.0 H2 carrier flow rate	6 lpm	8 lpm
3.0 H2 Shroud flow rate	5 lpm	4 lpm
4.0 H2 Bypass flow rate	6 lpm	8 lpm
5.0 Substrate Temperature	1345	1370
6.0 Powder Size	30 um	72 um
7.0 Powder Feed Rate	4 gm/hr	7 gm/hr

To construct a Taguchi test plan from Table 3, the process parameters and respective levels are arranged in a orthogonal matrix (one where each measurement is independent). Table 4 shows the 8 experiment test plan resulting from Table 3. This test plan is currently in process for the Horizontal SiC CVC reactor.

Table 4. Horizontal reactor test matrix.

Test #	MTS FeedRate	H2 Carrier Flow Rate	Shroud Gas Flow Rate	Bypass Flow Rate	Temp	Powder Size	Powder Feed Rate
1	635 gm/hr	6 lpm	5 lpm	6 lpm	1370	30 um	4 gm/hr
2	635 gm/hr	6 lpm	5 lpm	8 lpm	1345	72 um	7 gm/hr
3	635 gm/hr	8 lpm	4 lpm	6 lpm	1370	72 um	7 gm/hr
4	635 gm/hr	8 lpm	4 lpm	8 lpm	1345	30 um	4 gm/hr
5	900 gm/hr	6 lpm	4 lpm	6 lpm	1345	30 um	7 gm/hr
6	900 gm/hr	6 lpm	4 lpm	8 lpm	1370	70 um	4 gm/hr
7	900 gm/hr	8 lpm	5 lpm	6 lpm	1345	70 um	4 gm/hr
8	900 gm/hr	8 lpm	5 lpm	8 lpm	1370	30 um	7 gm/hr

The results of the test plan will be used to characterize the process with regard to the dependent variable in Table 2. Additionally, the results will guide the design of a second test matrix. Parameters shown to have little effect on the process will be discarded in future experiments. Those most important will be characterized over a wider range of values. After the completion of two test matrices, it is expected that the CVC process with powder will be fairly well characterized

for the current reactor geometry. A similar set of experiments will be performed for the CVC process with fibers in place of powder.

Task 3 - Material Characterization.

The samples prepared in the proceeding task will be characterized. Tests to be performed include those listed in Table 5.

Table 5. Characterization tests.

Parameter	Test Methodology
Micro-structure	
Void Percentage	Quantitative Microscopy
Powder Percentage	Quantitative Microscopy
Fiber Percentage	Quantitative Microscopy
Mechanical Properties	
Yield Strength	ASTM Std. 1161
Toughness	DIN 51
Density	Weight of Liquid

Using the same Taguchi analysis, the micro-structure and mechanical properties will be related to the process parameters to develop an overall model of the CVC process and the material produced. To assist in material characterization, a data base has been constructed. The data base catalogs material by process parameters as listed in Table 1 and process results as indicated in Tables 2 and 5. The data base is currently being updated to include earlier work. As the results of the Taguchi test plans are available, they will also be added to the data base.

Task 4 - Technology Transfer

Time permitting, a prototype fan will be fabricated based on the results of Tasks 2 and 3.

6.0 ORGANIZATIONAL PLAN

The following organizational chart lists key personnel at ThermoTrex Corporation.

7.0 FINANCIAL STATUS

Table 6 below summarizes the financial status through June 1997.

Table 6. Financial status through June 1997.

Net Outlays Previously Reported	\$689,429
Total Net Outlays This Report Period	\$777,052
Open Commitments	\$1,547
Total Obligation	\$778,599
Funds Remaining	\$172,039

A complete financial status report and federal cash transaction report will be provided at the next schedule reporting period. The new project administrator will need to request Standard Form 269 - Financial Status Report and Standard Form 272 - Federal Cash Transaction Report with completion instructions.