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**Development of a Commercial Process for the
Production of Silicon Carbide Fibrils**

FINAL REPORT

April 1999

Prepared By:

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Under

Subcontract No. 86X-SZ337V

For

Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

Managed By

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Advanced Research and Technology Development Materials Program

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1 Abstract

A patent was issued on "VLS" silicon carbide fibrils to North American Phillips Corporation in 1975. Various laboratories and companies have been attempting to improve this process and scale it to larger quantities since that time. All of these efforts met with minimal success because they were using the original technology while attempting to improve the equipment. The principal impediments have been:

- 1 Slow crystal growth during fibril production
- 2 Sensitive stoichiometry factors in the crystal growth chamber
- 3 Precise control of a high temperature process

The principal investigator has scaled silicon carbide whisker production at American Matrix and the SiC fiber process at Advanced Composite Materials Corporation from grams in the laboratory to tons per year production. This project is a proof-of-concept effort to apply some of the recent technology to the problems listed above in the fibril growth process. Two different technology approaches were investigated. A major problem with fibril growth has been generating a consistent supply of the required SiO gas reactant, which is a product of reducing SiO₂. The first approach, in this project addresses the SiO gas production, involved mixing silica and carbon fibrous raw materials in the immediate proximity of the graphite fibril growth plates to generate SiO nearer to individual sites of fibril growth. Iron bearing catalyst was painted on the graphite plates and the SiO generator mix was placed above the plate. This system was then heated to 1600/1650°C in a graphite resistance furnace. Some fibrils were started but the growth rate and fibril quality were unacceptably low. A second approach, which uses MTS + H₂ gases to address stoichiometry control, was investigated to improve fibril growth rates while reducing the previous high temperature requirements for the process. A partial vacuum chamber was constructed inside a commercial microwave furnace. The fibril growth container was coated with an iron catalyst and brought to 1200°C by the microwave field. A mixture of hydrogen and methyl trichlorosilane gases were fed to the fibril reaction container. Excellent silicon carbide fibrils were produced at a growth rate that was over four times greater than previously reported processes. The next phase of the development will be an optimization of operating parameters to improve fibril yield in the microwave growth process. The development activities will then move to the construction and testing of a pilot unit.

2 Introduction

The U.S. Department of Energy's Fossil Energy Materials Program has an interest in Silicon Carbide Fibrils for their high temperature performance in an oxidizing atmosphere. Previous testing on Fibrils has shown that fossil energy

plant design engineers can expect tensile strengths of 2,300,000 PSI, an elastic modulus in the range of 84 million PSI, and resistance to oxidation and creep allowing operation above 1,300°C¹. A process is needed to produce the Silicon Carbide Fibrils in commercial quantities to make them available as a reinforcement for fiber-reinforced SiC matrix heat exchanger tubes fabricated by chemical vapor infiltration, as a practical material in high performance fossil fuel plant designs.

Various Government laboratories and companies have been attempting to improve this process and scale it to larger quantities. All of these efforts met with minimal success because they were using the original 1967 North American Phillips patented technology by simply attempting to improve the processing equipment. The principal impediments have been:

- Slow crystal growth during fibril production
- Sensitive stoichiometry factors in crystal growth chamber
- Precise control of a high temperature process

The principal investigator has scaled silicon carbide whisker and fiber processes from grams in the laboratory to tons per year production. This project is a proof-of-concept effort to apply some recently developed technology in silicon carbide fiber production to the problems of developing a commercial fibril manufacturing process. The current work makes no attempt to optimize either tested process or to generate any significant quantity of fibrils. It is an investigation to find an innovative, scalable technique to manufacture silicon carbide fibrils.

3 Technology Approach

Two different technology approaches were investigated. A major problem with fibril growth has been generating a consistent supply of the required SiO gas reactant, which is a product of reducing SiO₂. The first approach, in this project, involved mixing silica and carbon fibrous raw materials in the immediate proximity of the graphite fibril growth plates to generate SiO nearer to individual sites of fibril growth. Iron bearing catalyst was painted on the graphite plates and the SiO generator mix was placed above the plate. This system was then heated to approximately 1700°C in a graphite resistance furnace. A schematic of this approach is illustrated in Figure 1. The goal of this effort is to be able to use a uniformly controllable SiO generator mix that can be continuously feed to the reaction process with the fibril growth plates.

Figure 1
Graphite Furnace SiO Generator

A second approach was investigated to improve fibril growth rates while reducing the previous high temperature requirements for the process. A partial vacuum chamber was constructed inside a commercial microwave furnace loaned to the project by Microwave Materials Technologies in Knoxville, TN. The fibril growth ceramic container was coated with an iron catalyst and brought to 1200°C by the microwave energy field. A mixture of hydrogen and methyl trichlorosilane gases were fed to the fibril reaction container, within the vacuum chamber, as raw materials to initiate and sustain fibril growth. A schematic of the microwave experiment is shown in Figure 2. The potential advantage of this approach is to be able to only heat the fibril growth balls by microwaves to conserve and concentrate energy and raw material consumption.

Figure 2
Microwave Energy Fibril Growth Equipment

The U.S. Department Of Energy desires to Silicon Carbide Fibrils as a reinforcement for fiber-reinforced SiC-matrix composite heat exchanger tubes that would be fabricated by chemical vapor infiltration . ReMaxCo began the project by manufacturing Saffil Al_2O_3 fiber paper as a substitute for the SiC Fibrils for CVD development work at ORNL. When future Silicon Carbide Fibril

development work produces adequate quantities, the Fibril paper would replace the Saffil fiber paper in the CVD tube development process. The scope of work accomplished for this project is defined as follows:

Project Statement of Work:

- 1 Formation of Shapes from CVD/Saffil Fiber Composites
 - 1.1 Fabricate Saffil papers
 - 1.2 Infiltrate papers with CVD silicon carbide
 - 1.3 Coordinate paper strengths with tube designs
- 2 High Energy Thermal Concentration at the Point of Fibril Growth
 - 2.1 Microwave energy growth chamber fabrication
 - 2.2 Fibril growth testing
 - 2.3 Process optimization
 - 2.4 Product evaluation
- 3 SiO Generation from Inexpensive Raw Materials
 - 3.1 Mixing carbon fibers and SiO₂ raw materials
 - 3.2 Graphite resistance furnace testing
 - 3.3 Process optimization
 - 3.4 Product evaluation
- 4 Final Report
- 4 Experimental Procedures and Results

Definition of the Fibril Product

Prior to beginning the experimental work, ReMaxCo needed to understand the state-of-the-technology achieved in the previous DOE funded projects. The final reports published by the previous researchers were reviewed and analyzed. Samples of the fibril product produced at both the Carborundum Company and Advanced Composite Materials Corporation were obtained from those companies. Scanning electron microscopy on these fibril samples was provided to ReMaxCo by ORNL's High Temperature Materials Laboratory. The Carborundum product is shown in the SEM photographs in Figures 3 and 4. The Advanced Composite Materials Corporation product is compared in Figures 5, 6 and 7.

Figure 3 Carborundum
VLS Fibril Growth Ball

Figure 4 Carborundum
Fibrils

Figure 5 ACMC VLS
Fibril Growth Ball

Figure 6 ACMC VLS
Fibrils

Figure 7 ACMC VLS
Fibril Surface Nodules

The fibril growth balls on the two products are significantly different in shape and size with fibril diameters of approximately 5 micrometers. The fibril morphology on the ACMC product shows a nodular structure defect that is not apparent on the Carborundum fibril. EDAX analysis of both growth balls showed approximately 25% more silicon in the ACMC fibril growth ball. This SEM work provided ReMaxCo with visual standards to use in evaluating the products of the experiments conducted for this project. The EDAX results indicated that control of SiO in the process may yield a more perfect fibril single crystal structure.

Graphite Furnace Fibril Growth

Five experiments were conducted in a cylindrical graphite boat four (4) inches in diameter x six (6) inches long. The graphite resistance furnace and the boat is shown in Figures 8 and 9.

Figure 8 Graphite Resistance Furnace

Figure 9 Graphite Furnace Fibril
Growth Container

ReMaxCo worked with ZYP Coating Service in Oak Ridge, TN to develop a slurry suspension for the iron catalyst particles. The iron slurry was painted onto

graphite substrate plates, dried and inserted in the graphite boat. The "SiO Generator Mix" (Table 1) was placed below the graphite plate (Exp. #3), above the graphite plate (Exp. #4), and on both sides of the graphite plate (Exp. #5).

Table 1 SiO Generator Mix

Material	Quantity
Carbon Fiber	3 moles
Fumed Silica	1 mole
Calcium Oxalate	0.6 wt. %

It was necessary to produce a catalyst melt at the lowest possible temperature. Experiment #1 was conducted with the SiO Mix below the plate at 1400°C. There was no melting of the iron catalyst. Experiment #2 was conducted at 1600°C. There was partial melting of the catalyst paint. Experiment #3 was conducted at 1650°C for one hour then reduced to 1600°C for four (4) hours. Complete liquid state was obvious in the catalyst paint, but there was no fibril growth on the graphite substrate.

There was some fiber growth on the carbon fibers as seen in Figure 10.

Figure 10 SiC VS Whisker Growth Initiation
On Carbon Fibers

Experiment #4 and #5 were conducted using the same furnace temperature profile. There was no fibril growth apparent on the catalyst substrate. Significant fiber growth did occur on the carbon fibers, as shown in Figure 11 and 12. It is obvious in the SEM photographs that there are no fibril growth balls. Therefore, the fibers observed are simply VS type whiskers, which are available on the commercial market today.

Figure 11 VS SiC Whiskers

Figure 12 VS SiC Whiskers
No Growth Balls

High Energy Microwave Fibril Growth

Five experiments investigating the use of microwave energy for silicon carbide fibril growth were conducted in the apparatus built by Microwave Materials Technologies (Figure 2). The actual equipment used in the experiments for this work is shown in Figures 13 and 14.

Figure 13 Microwave Furnace and Gas
Feed System Figure 14 Open Microwave Furnace
Shows Vacuum Fibril Reaction Vessel

The same iron catalyst paint slurry used in the graphite furnace experiments was coated on an aluminum oxide crucible 0.75 inch in diameter x 1.0 inches deep. Hydrogen gas was fed to the mass flow control device, which divided the flow into two streams, at a rate of 250 standard cubic centimeters per minute. 1% to 10% of the hydrogen gas flow was diverted to bubble through the methyltrichlorosilane (MTS) container to carry the MTS gas into the reaction vessel. The remainder of the hydrogen gas flowed directly to the reaction vessel. The reaction vessel was operated at a vacuum of 100 torr during these experiments.

It has been demonstrated at ORNL that chemical vapor deposition of silicon carbide occurs at 1100 to 1200°C in an inert atmosphere. No previous data was available on the melt temperature of the iron catalyst, necessary for fibril growth, under these conditions. Experiment #1 was run at 1100°C. The catalyst did not

melt. Experiment #2 was run at 1200°C, which liquefied the fibril catalyst; but, produced no product because of problems with blockage in the reaction gas feed system. The 10% H₂ flow through the MTS container was transferring too much reaction gas into the system. The scope of this project did not allow the degree of precision in the mass flow control equipment required to feed reaction gasses. More accurate gas feed equipment is necessary for quality fibril growth.

Experiment #3 was run at 1200°C with reaction gas flowing to the vacuum chamber. A photograph of the reaction chamber is shown in Figure 15 and the resulting product is seen in the SEM picture in Figure 16. Two issues were obvious from the results observed in the pictures. First, microwave arcing was occurring in the reaction chamber. Secondly, fiber growth was uncontrolled due to excess reaction gas feed, even with the gas feed set at minimum.

Figure 15 Vacuum Reaction Vessel Inside Microwave During Fibril Growth

Figure 16 Experiment #3 SiC Yarn

Prior to Experiment #4, the microwave vacuum chamber was redesigned to prevent the arcing. The gas feed of hydrogen and methyltrichlorosilane was manually reduced by turning the gas feed on for five (5) seconds and off for twenty (20) seconds for a period of 20 minutes, then running with the gas on for an additional 40 minutes. The product of this experiment is seen in Figures 17 and 18. Some true silicon carbide fibril growth was observed in the SEM photographs. Unfortunately, the large quantity of non-fibril yarn indicated that the growth surface was still receiving too much reaction gas.

Figure 17 Experiment #4 SiC Fibrils + SiC Yarn

Figure 18 Experiment #4 with More Mature Fibril Growth

Experiment #5 was conducted by further manually reducing the gas feed to the vacuum chamber by moving the gas feed away from the growth surface in the crucible to the outer wall of the reaction vessel. The quantity of gas feed was again manually controlled by five (5) seconds on and twenty (20) seconds off. A significant quantity of recognizable fibrils was apparent in the SEM photographs. These results are shown in Figures 19 and 20. The fibrils are more mature, with less non-fibril yarn.

Figure 19 Experiment #5 Shows VLS Fibrils with Growth Balls

Figure 20 Experiment #5 Shows Improved Fibril Structure

5 Conclusions

Graphite Furnace Fibril Growth

No fibril growth was observed on the catalyst coated graphite substrates. It was apparent also that liquefaction of the catalyst was achieved on the graphite plates. It was obvious that adequate SiO reaction gas was generated by the presence of VS SiC whisker growth on the carbon fibers. Single crystal growth of silicon carbide requires very precise conditions. Single crystal growth of Silicon Carbide Fibrils is even more demanding in reaction gas and temperature control. The graphite furnace experiments show that the conditions required for fibril growth are not feasible by the technique demonstrated in this project.

High Energy Microwave Fibril Growth

The objective of this project was to demonstrate a new technology for silicon carbide fibril growth that would remove some of the previous impediments to the scale-up to a commercial fibril process. The particular focus was:

1 Increasing the fibril growth rate

The microwave energy growth technique, with the coarse improvements that occurred in Experiment #5 achieved a fibril growth rate of 0.75 millimeters per hour (measuring the more mature fibrils under the scanning electron microscope). The fibril growth rate measured at the conclusion of the Carborundum work was 0.17 millimeter per hour². Therefore, the microwave

energy process produced a fibril growth rate that is 4.4 times that of previously reported work.

2 Removing the continuously changing conditions of the reactant gases in the fibril growth fields

Recent scale-up attempts moved away from using uniform reaction gas feed to grow fibrils because of the inefficient use of the relatively expensive MTS gas. Most of the feed gas flowed through the furnace to the exhaust as waste. MTS recovery was difficult and expensive. Processes were converted to consumable SiO generator materials which deteriorated with use and caused variation in the fibril growth process. Experiment #5 showed negligible deposits of silicon carbide on the reaction vessel or the fibril growth crucible. Since the microwave energy technology can be designed to heat only the fibril growth balls, the MTS reaction gas feed can be significantly reduced to the point required to feed the fibril growth process. Uniform reactant gas stoichiometry can be cost-effectively maintained by using MTS gas feed.

3 Achieving precise control of temperature in the growth field

This project made no attempt to control and refine the microwave energy field. It is possible, with experimental work and calculated design to focus the microwave energy on the fibril growth balls. This would allow a continuous process to keep a small entry area of the growth cavity at 1200°C to liquefy the catalyst material. Once the fibril growth started, the remainder of the fibril boat travel could be at a significantly reduced temperature, as the microwave energy would keep the fibril growth balls, only, at 1200°C.

The results of the microwave energy fibril growth work shows potential for the use this new technology to solve some of the key issues that have impeded the commercialization of the silicon carbide fibril production. The lack of precision in the experimental equipment and the limited number of trials in this proof-of-concept project opens many areas for improving the process.

6 Future Work

The next phase of the microwave energy fibril growth process will concentrate on parametric studies to optimize the fibril quality:

- 1 Improve the precision of the reaction gas feed equipment
- 2 Design and fabricate a reaction chamber to control and concentrate the microwave field
- 3 Conduct a matrix experiment to optimize reactant gas feeds, catalyst and growth plate components, and microwave energy input

The results of this future study would prepare the way for the design and fabrication of a dedicated microwave pilot scale line to begin the definition of fibril quality, process yields and costs.

7 References

1. P.D. Shalek, et all, "Scale-Up and Optimization of the VLS Growth Process for Beta-SiC Whiskers for the period of April 1982-September 1989", DARPA Final Report, DOE/OAR&TD Topical Report, LA-12119, November 1991
2. R.W. Ohnsorg, W.E. Hollar, Jr., and S.K Lau, "Engineering Scale Development of the Vapor-Liquid-Solid (VLS) Process for the Production of Silicon Carbide Fibrils" Phase II Report, ORNL/Sub/90-SD861/02, April 1995