

PILOT FACILITY FOR THE PRODUCTION OF SILICON CARBIDE FIBRILS

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ABSTRACT

This project was delayed for over one year due to an unfortunate accident by a freight shipper, when the 4,500 pound Fibrils synthesis reactor was dropped from a loading dock. The unit suffered significant damage, a six month insurance company dispute and a six month repair activity. The repaired Fibrils Synthesis Reactor has now been moved to a materials development company in Alfred, NY, near Alfred University. The unit will be operated under the supervision of a Ph.D. level ceramic scientist. The reactant gas control system has been installed and tested. The electrical, vacuum and the microwave systems have been activated and tested. Initial microwave Fibrils synthesis experimental runs have been conducted. The results of those first experiments will be reported. The U.S. Patent has been filed on the process. The experimental plan for the remainder of 2007 will be discussed, as well as, the future plans for 2008. The focus of the 2007 work is providing adequate Fibril quantities to Fossil Energy companies to allow initial evaluation of the product to resolve severe materials problems. A secondary benefit of this project is the interest that is coming from other advanced materials areas. The presentation will discuss these applications in aerospace, commercial aircraft engines, defense activities, and commercial steel production.

INTRODUCTION

This research was sponsored by the U.S. Department of Energy, Fossil Energy Advanced Research Materials Program. The U.S. Department of Energy projects using the Silicon Carbide Fibrils as a primary structural component for fiber reinforced silicon carbide composite heat exchanger tubes that would be fabricated by chemical vapor infiltration.

The VLS silicon carbide fibrils are grown when gaseous reactants are dissolved into a liquid catalyst and precipitated on to the growing fibril to form a perfect single crystal structure. ReMaxCo Technologies has access to a commercial ceramic fiber papermaking process. When SiC fibril development work produces adequate quantities, silicon carbide fibril paper will be produced and rolled into the required geometric shapes for the heat exchanger tube, joints and elbows. These shapes will be treated with a binding process capable of liquid and pressure impermeability at high temperatures in a corrosive environment.

The major limitations of the previous "state of the art" fibril growth were the high temperatures required (1600oC to 1700oC), the slow fibril growth rate (~0.17 mm/hr), and the large quantity of excess of expensive methyl trichlorosilane gas, which is wasted¹. The commercial process is complicated by the processing of large quantities of hydrogen gas at high temperatures and the generation of corrosive hydrochloric acid². This current work continues a proof-of-concept, microwave based, VLS process development completed in 1999 by ReMaxCo. The catalyst was heated to the experimental temperature (1200oC to 1300oC) while a mixture of MTS and hydrogen were introduced into an aluminum oxide ceramic container. The MTS is dissociated and the carbon and silicon components are dissolved into the catalyst. The catalyst saturates and precipitates silicon carbide onto the surface of the growing fibril. These experiments yielded fibril growth rates of 0.75 mm/hr. That was an improvement of approximately 4.4 times faster than the best graphite furnace runs³. Volume scale up of the process was demonstrated.

The current project moves the commercial process development to a pilot scale commercial reactor that will lead to sufficient quantities of fibrils to allow expanded work by Oak Ridge National Laboratory and combustion chamber component suppliers to develop heat exchanger tubes, robust combustion chamber tiles and hot gas filters.

A semi-continuous, microwave heated, vacuum reactor was previously designed, fabricated and tested in earlier experiments. The major obstacles that had to be overcome during this current project was the questionable performance of the reactor. The original design of the reactor focused the microwaves in such a manner that they missed the catalyst/fibrils growth zone. The microwaves did react with the insulation and the reactor was heated by coupling with the insulation. Modifications were made to the reactor to focus the microwaves on the catalyst. SiC Fibrils were produced using both MTS and Starfire SP4000 (a commercial silicon carbide organic precursor material) as feed-gas precursors. Both precursors produced fibrils at temperatures of less than 1000°C. The new Starfire SP4000 produced fibrils as low as 800°C, without the use of hydrogen and without producing the hazardous hydrochloric acid.

TECHNOLOGY APPROACH

The previous low-productivity, semi-continuous, microwave heated, vacuum reactor is shown in Figures 1.

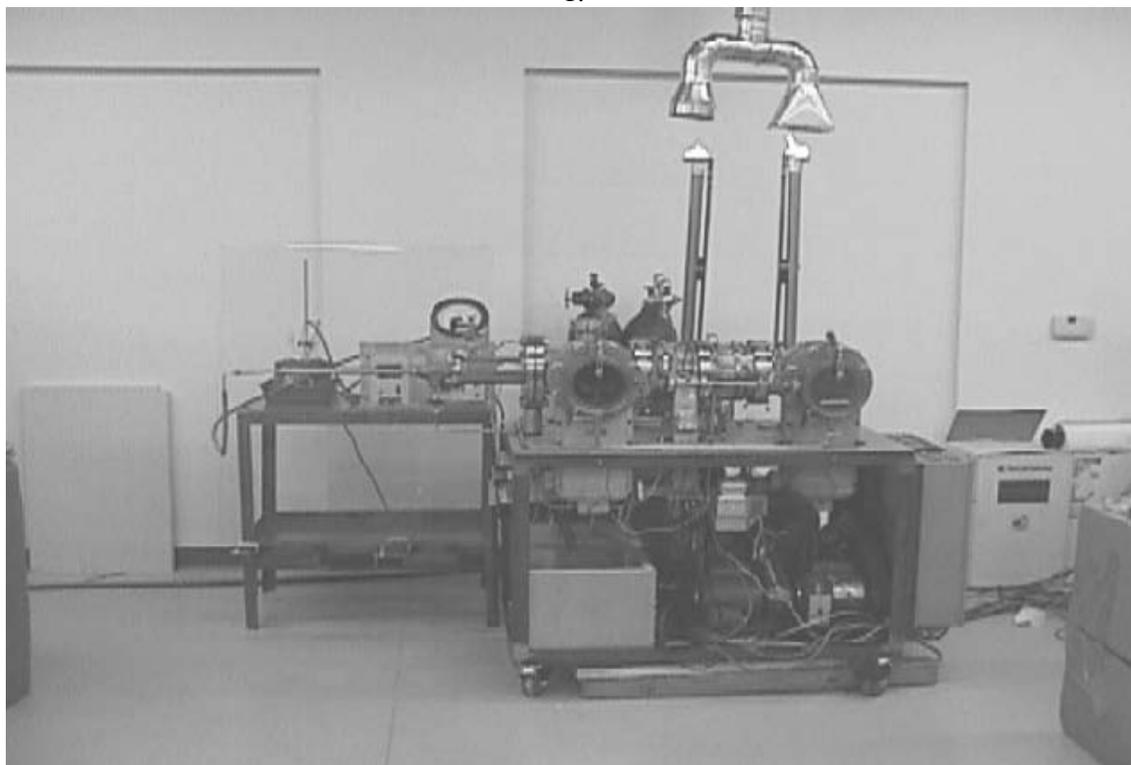


Figure 1. Fibril microwave reactor in operation

The boundary conditions for the experiments were determined by running a computer thermodynamic analysis on the raw materials system. The results are shown in Figure 2.

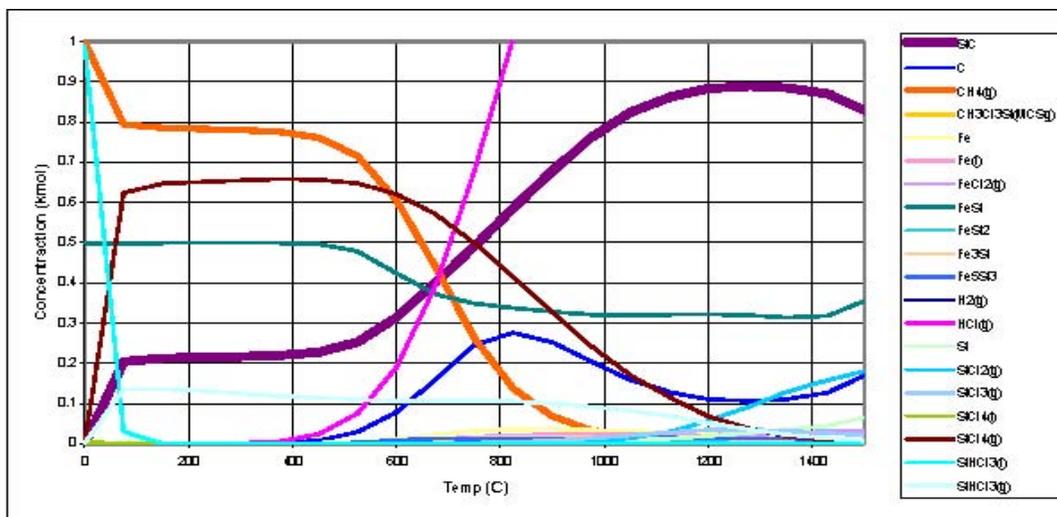


Figure 2. Thermodynamic analysis showing optimum temperature range for growing silicon carbide fibrils

Cylindrical aluminum oxide reaction boats were coated, on the inner surface, with a catalyst and placed into the reactor under a light vacuum. Several catalyst options were tested including ferrous silicon, iron powder and several mixtures thereof. A series of reaction boats traveled, one at a time, through the reactor. Each boat is first preheated with resistance heaters to 850o C to 900o C, measured by a Type K thermocouple. Each reaction boat was then moved, in turn, to the microwave heated section. The catalyst is heated to the required temperature of 1200oC to 1300oC, measured by a Mikron M90-Q Infrared Pyrometer while a mixture of MTS (methyl trichlorosilane) and hydrogen were introduced into the catalyst-coated area of the boat. The MTS forms the carbon and silicon components, which dissolve into the catalyst to grow the Fibrils.

Once the furnace was debugged and running consistently, process optimization experiments were conducted to achieve fibril growth and define operating parameters. The operating results from these experiments were used to design a second-generation microwave reactor to solve the problems that became apparent in operating the current reactor. There was also a group of experiments to identify a less hazardous raw material gas than the methyl trichlorosilane.

EXPERIMENTAL PROCEDURES

A number of runs were made to debug the microwave reactor and the reaction gas feed system. The MTS reaction gas is generated by bubbling hydrogen through liquid MTS in a steel container. The steel container was replaced with a transparent, heated glass bubbler to allow the operator to view the hydrogen flow through MTS liquid and control the vapor pressure of the MTS gas (Figures 3 and 4).



Figure 3. Metal bubbler



Figure 4. Glass bubbler

Silicon Carbide Fibrils Reaction Vessel Runs

The fibril catalyst seed paint was prepared using metallurgical grade -325 mesh ferrous silicon mixed in a dispersant paint purchased from YZP Corporation in a 1:1 ratio. The paint was applied in a 0.1-millimeter thick coating to the interior diameter of a 7.6 centimeter diameter x 7.6 centimeter long high-density aluminum oxide cylinder. When the paint dried, the boats were loaded in the vacuum chamber of the microwave reactor. A boat that exhibits some Fibril growth is shown in Figure 5



Figure 5. Ceramic boat with microwave grown Fibrils

The microwave reactor was evacuated by vacuum pumps to approximately 30 mTorr, and then flushed with nitrogen gas at a pressure of 150 Torr. After the nitrogen flush, the furnace was backfilled with hydrogen gas to a pressure of 150 Torr and maintained at less than 180 Torr throughout the microwave fibril growth run. The preheat zone resistance heaters were stabilized at 800oC and held there throughout the run. Each one of the two 2-KW microwave sources was stabilized at 1.8-KW. Hydrogen flow was run through the MTS bubbler at a rate of 0.13 liters/minute for a period of one to three hours. Figure 6 shows the reaction zone during microwave assisted silicon carbide fibril growth.

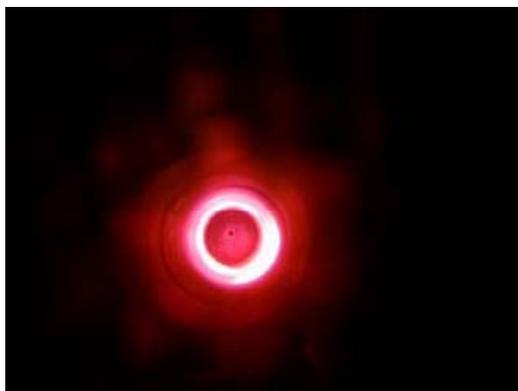


Figure 6. Fibril growth in the microwave field. Glowing annulus is the catalyst layer reacting to the microwave energy

Additional optimization testing was conducted replacing ferrous silicon with iron particles, then a mixture of 50% ferrous silicon and 50% iron by weight. In addition, the procedure described above was tested replacing the MTS liquid with a SP4000, a polysilylmethylene CVD silicon carbide precursor produced by Starfire Systems. The SP4000 can be reacted in nitrogen gas rather than the more dangerous hydrogen required by the MTS liquid and gas.

Typical Run Sheet:

5/8/02

Reactant Gas	SP4000
Atmosphere	Hydrogen
Catalyst	Fe
Fibrils Observed	Yes

A nitrogen purge was used during start up.

14:45 Hydrogen was turned on

Time	MZ1 (kW)	MZ2 (kW)	GZ1 (C)	GZ2 (C)	Press. (Torr)	Main Flow (lpm)	Bubbler Flow (lpm)	Temp. (C)
15:00	1.80	1.80	530	484	175	0.52	0.08	NR
15:04	Some glow appeared in spots							
15:07	MZ1 and MZ2 power adjusted to prevent arcing. GZ set pts to 600C							
15:18	GZ set points to 700C							
15:20	GZ set points to 800C							
15:30	1.80	1.80	NR	NR	NR	0.52	0.13	NR
16:30	1.90	1.90	801	734	165	0.52	0.13	854
16:45	2.00	2.00	801	735	160	0.52	0.13	904
17:00	2.00	2.00	802	738	185	0.51	0.13	909
17:40	2.00	2.00	802	744	175	0.51	0.13	922
17:50	2.00	2.00	800	742	180	0.51	0.13	921
18:00	2.00	2.00	800	745	160	0.51	0.13	924
18:10	2.00	2.00	800	745	170	0.51	0.13	924
18:30	2.00	2.00	800	743	175	0.51	0.13	920
19:00	2.00	2.00	800	745	165	0.51	0.12	921

RESULTS

The only fibril growth in the initial microwave field configuration happened after being in the microwave growth chamber for approximately three hours. The microwave intensity was measured in the fibril growth area and found to be zero. The furnace was rebuilt to focus more of the microwave field in the fibril growth zone. This improved the fibril growth quality and time. The fibrils grown in this sequence are shown in Figures 7, 8, 9, and 10. The fibril quality is good, but the fibril yield was very low. They are 2 to 5 micrometer diameter in size.

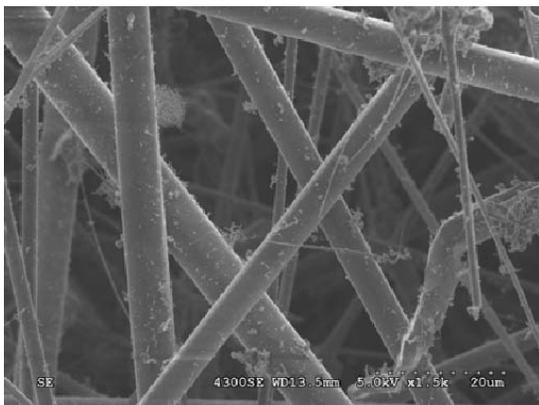


Figure 7. Fibril growth on the boat by digital camera



Figure 8. Electron microscopy of same Fibril product

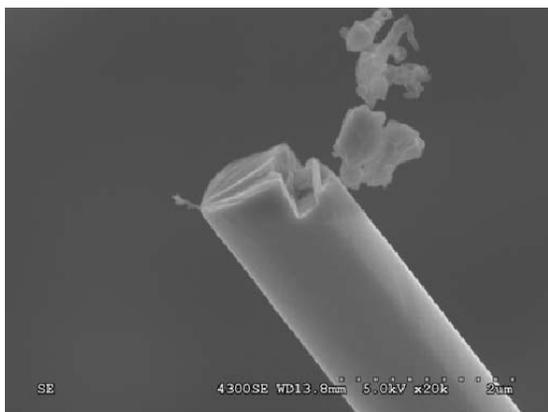


Figure 9. Electron microscopy shows perfect single crystal growth



Figure 10. Fibril growth balls indicate true VLS growth process

There are a number of issues with the fibril reactor that need to be improved and will be implemented in the next phase of this work. The microwave field uniformity was poor and can be significantly improved. The catalyst paint tended to flake off the tops and sides of the round ceramic boats. Flat ceramic plates will be more efficient. Finally, the MTS gas feed mechanism had very little mass flow control and an irregular feed pattern to the fibril growth zone. A more accurate mass flow controller and a manifold-mixer are needed for the reaction gas distribution.

One of the problems with scaling the fibril development to a large-scale commercial process is the generation of significant quantities of hydrochloric acid in the off-gas stream. This acid destroys the vacuum system and the exhaust ducts. Silicon carbide fibrils were produced using the SP4000 in nitrogen. An unexpected advantage, beyond the elimination of acid in the off-gas, was the fact that fibrils grew at 850oC. The MTS reaction required a temperature of 1200oC to 1300oC. Fibrils grown in the SP4000 experiments are shown in Figures 11, 12, 13 and 14. They are 5 to 15 micrometers in diameter. Melt growth balls in Figure 13 were observed with the fibrils indicating that they were VLS growth products.

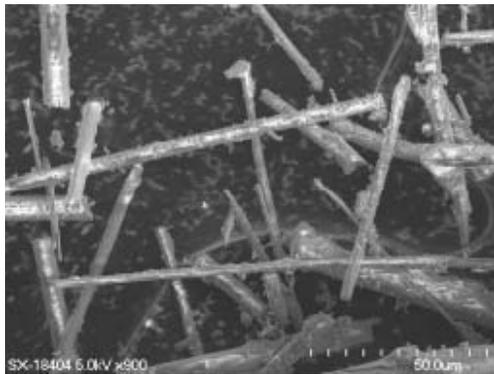


Figure 11. Scanning electron microscopy of SP4000 Fibrils

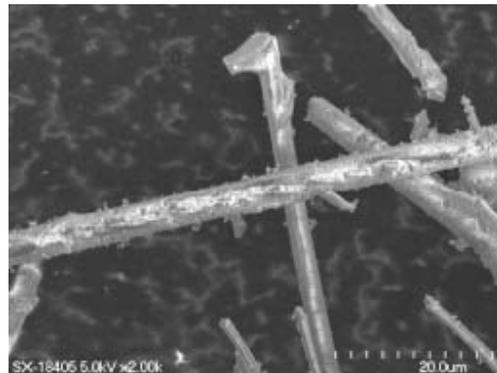


Figure 12. 2,000X magnification showing Fibril size



Figure 13. Melt growth balls indicating vapor-liquid-solid



Figure 14. Fibril from growth ball

CONCLUSIONS ON THE FIRST GENERATION PILOT REACTOR

These experiments demonstrated that silicon carbide fibrils could be produced at temperatures as low as 850oC, as compared to the 1700oC in the previous graphite furnaces. The fibril growth rate has been increased by a factor of four over previous technologies. The microwaves exhibited a significant effect on lowering the fibril reaction temperature and accelerating the fibril growth process. The SP4000 silicon carbide precursor provides a reaction without hazardous off-gas products, with a projected future volume cost of \$600/liter (kilogram).

A commercial process is feasible by overcoming the equipment engineering problems encountered on this project. Those include a uniform microwave field, good control and uniform distribution of reactant gases, and the use of flat ceramic reaction boats. These improvements will get the commercial process

closer to the \$300 per pound project goal.

With these improvements in place, one can improve on previous technology to accomplish:

- 1 Lower energy consumption
- 2 Higher growth rates
- 3 Reduced reactant gas waste
- 4 Lower cost raw materials
- 5 Consistent quality fibrils product

SECOND GENERATION FIBRIL REACTOR

Introduction

The First Generation Fibril Reactor exhibited inflexible problems with microwave field distribution and control, as well as, non-uniform reactant gas feed control and distribution. A Second Generation Fibril Reactor has been designed and fabricated to overcome these principal issues. Solutions were insured by employing the design services of experienced experts in the fields of chemical vapor deposition gas distribution (MS&E Resources) and microwave field control (RF Technologies). The total system design was coordinated by an experienced furnace designer and fabricator.

Reactor Configuration

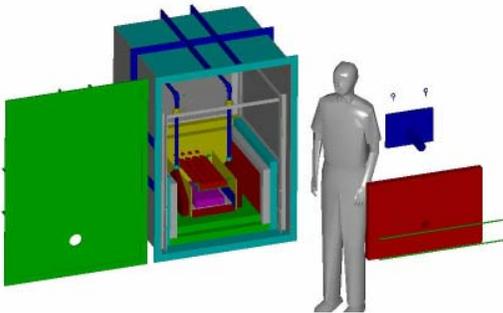


Figure 15. Reactor assembly

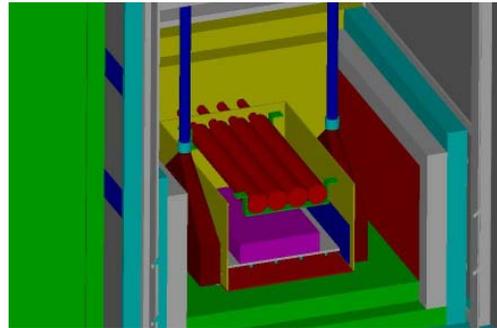


Figure 16. Fibril Growth Area

Figure 15 shows the entire reactor assembly inside the vacuum chamber. Figure 16 shows the fibril growth zone. The round tubes above the flat plat are the microwave applicators (red), designed to produce a uniform and controllable microwave field on the aluminum oxide flat plate (purple) containing the fibril seed crystals. The reactant gases are feed through the triangular gas plenums (burgundy) across the seeded growth plates. Electrical heating elements are located in the wall or the reaction chamber to maintain the chamber at a uniform 800oC. The microwave energy boosts this temperature at the seed crystal surface to 1,000oC to assure that the reactant gases only react with the seed crystals to prevent reactant gas waste and silicon carbide growth on the reaction chamber walls.

Reactor Fabrication



Figure 17. Fabricated Second Generation Fibrils Reactor

Figure 17 shows the Second Generation Fibrils reactor, as fabricated. The left view is the full unit. The middle view is the microwave units and the microwave coaxial feed system. And the right view is the fibrils growth chamber, with fibril boats coated with seed crystals.

FUTURE WORK

The Second Generation Fibrils Pilot Reactor, incorporating all of the improvements described above, should be capable of producing 200 grams of fibrils per day. This reactor started in May 2007, tested, process optimized, then operated to supply sample quantities to various researchers in the Fossil Energy Materials Program and in commercial applications. Samples should be ready for shipment to customers by August 2007. Success in testing and demand for volume product will lead to the design of a continuous reactor capable of commercial volumes of silicon carbide fibrils.

ACKNOWLEDGEMENTS

The author acknowledges the support of the U.S. Department of Energy's (DOE) Fossil Energy through the Advanced Research Materials Program under the project direction of Dr. Roddie R. Judkins for the funding of this work. Gratitude is expressed to Oak Ridge National Laboratory's High Temperature Materials Laboratory for the electron microscopy work of Larry Allard and Larry Walker and to Microwave Materials Technology for microwave equipment engineering and fabrication.

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