Development of a Commercial Process for The Production of Silicon Carbide Fibrils

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ABSTRACT

Phase I of this project demonstrated 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 microwave energy approach was designed to heat only the fibril growth balls, reducing the MTS reaction gas quantities needed to feed the fibril growth process. The continuation of this process development can significantly reduce the fibril growth time and the consumption of expensive raw material gases; therefore, decreasing the future commercial price of the fibril product. The previous Carborundum work concluded with a fibril growth rate of approximately 0.17 millimeters per hour. The Phase I microwave growth process experiments resulted in 0.75 millimeters per hour growth rate. Therefore, the new technology achieved a factor of five increase in growth rate, with minimal optimization work. The near stoichiometric use of raw materials and the increase in fibril growth rate, makes it feasible to attain a volume production price for fibrils of less than $300 per pound, using the microwave process.

Phase II (FY 2002) investigates growth process parameters and optimization of those parameters. A pilot line semi-continuous microwave furnace and reaction gas control equipment are designed and fabricated to provide more accurate process operation and data acquisition functions to allow potential commercial scale-up of the process. Experimental work optimizes the fibril growth reaction in the pilot equipment. Materials analysis of the fibril product with electron microscopy is used to characterize and improve the silicon carbide fibril product, during the pilot line development. Oak Ridge National Laboratory's capabilities will be used to evaluate mechanical and thermal stability properties of the fibrils, to complete the 2002 work. Phase II will conclude with a reasonable definition of the future production process, an approximate specification of the silicon carbide fibril product, and an estimate of the volume fibril price.

Introduction

The U.S. Department of Energy Fossil Energy Program has an interest in Silicon Carbide Fibrils as a material for high temperature heat exchange and recuperation components in advanced coal combustion plants. A recent report by K.L. Reifsnider, et. al. has shown evidence that the fibrils provide significant improvements in composite ceramic materials[1]. Work conducted by the Principal Investigator at Lawrence Livermore Laboratories in 1986, demonstrated that perfect silicon carbide single crystals, such as the fibrils, did not show evidence of oxidation up to temperatures of 1,600^{o}C; standard silicon carbide whiskers exhibited rapid oxidation at 1,200^{o}C. Work conducted by Terry Tiegs at ORNL proved that fibrils were 50% more effective in reinforcing composites than standard silicon carbide whisker products.

The slow growth of the fibrils and excessive waste of raw materials have been the major impediments over the last 19 years. The microwave energy process has eliminated the cumbersome SiO gas generation and demonstrated the ability to concentrate all energy and raw material resources specifically to the reaction chamber for silicon carbide fibril growth. The Phase I program bench-scale experiments significantly reduced the fibril growth time, the use of expensive raw material gases, and process energy consumption. The previous Carborundum work concluded with a fibril growth rate of approximately 0.17 millimeters per hour. The initial microwave growth process experiments resulted in 0.75 millimeters per hour growth rates. Therefore, the new microwave technology achieved a factor of five increase in growth rate, with minimal optimization. The future commercial use of the fibril product is made feasible by the microwave fibril growth process due to a potential price reduction from $2,000/pound to $300/pound and a volume production potential of tons per year.

Technical Approach

A semi-continuous microwave reactor was constructed to scale up the bench top work. A significant number of experimental runs are necessary to debug the reactor and it operating parameters. The microwave furnace and reaction gas control equipment will be refined to provide more accurate operation and data acquisition functions. Materials analysis of the fibril product using electron microscopy and x-ray diffraction will be used to define and improve the silicon carbide fibril product. Oak Ridge National Laboratory's equipment will be used to evaluate mechanical and thermal stability properties of the fibrils. Phase II will conclude with a reasonable definition of the future production process, a definition of the expected fibril product, and an estimate of the predicted volume fibril price.

Project Objectives

1 Continuous Microwave Furnace Equipment
   - 1.1 Electronic controls
   - 1.2 Fibril growth chamber enlargement
   - 1.3 Improve growth chamber data collection instrumentation

2 Reaction Gas Control Equipment
   - 2.1 Mass control meters for gas feeds
   - 2.2 Gas feed measurement instruments
   - 2.3 Gas feed corrosion resistance improvement

3 Initial Equipment Improvements Debugging and Process Parameter Definition Experiments
   3.1 Five adjustment runs
   3.2 Modification of furnace and gas control feed equipment
   3.3 Materials analysis of fibril product

4 Process Optimization Experiments
   4.1 Define the experimental matrix base on Step #3
   4.2 15 to 20 experimental matrix trials
   4.3 Materials analysis of the matrix experiment fibril products
   4.4 Evaluation of results and selection of the optimized parameters

5 Process Definition Experiments
   5.1 5 consecutive runs using the optimized process parameters
   5.2 Materials analyses of the fibril products
   5.3 Statistical evaluation of the process and materials data
   5.4 Calculations of predictions for a volume production process

6 Fibril Characterization
   6.1 Consult with Edgar Lara-Curzio on characterization procedures
   6.2 Optical characterization
   6.3 Mechanical characterization
   6.4 Thermal stability characterization

2002 Status

A continuous microwave fibril synthesis reaction furnace concept was established as shown in Figure 1. Figure 2 shows a method to scale the furnace concept to large volume production capacities.

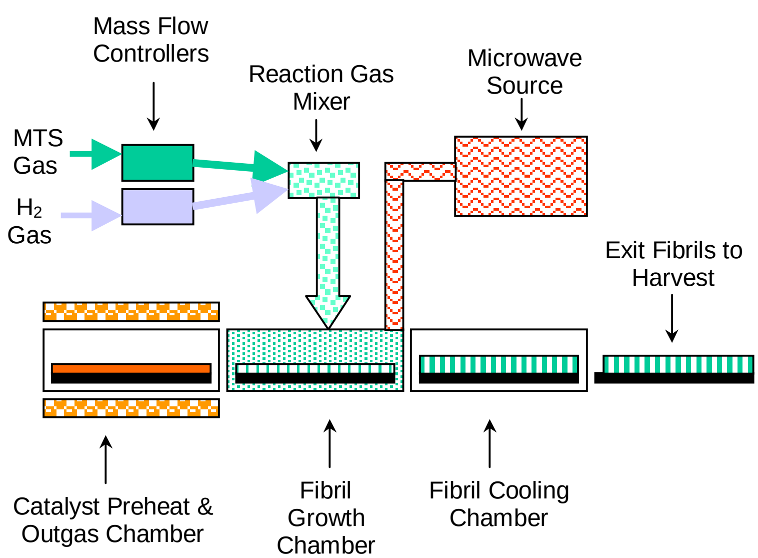

Figure 1

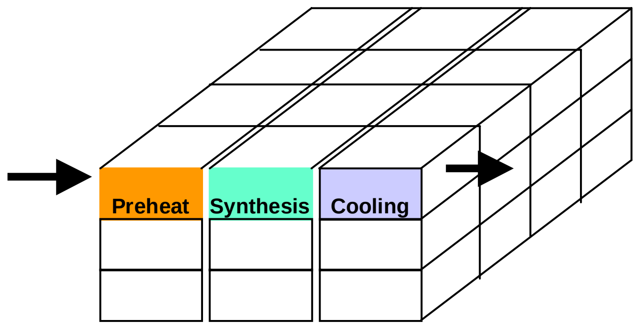

Figure 2

With the continuous pilot-scale equipment in place, work was conducted to optimize the size and shape of the microwave-heating chamber of the synthesis furnace. Uniform distribution of the microwave energy within the fibril growth region was the principal design constraint. A finite-element computer program was used to define the chamber geometry, the microwave source size and the microwave entry points. Figure 3 is a schematic diagram of this design. The continuous pilot-scale microwave synthesis furnace was fabricated according to the design criteria. The completed equipment is shown in Figure 4.

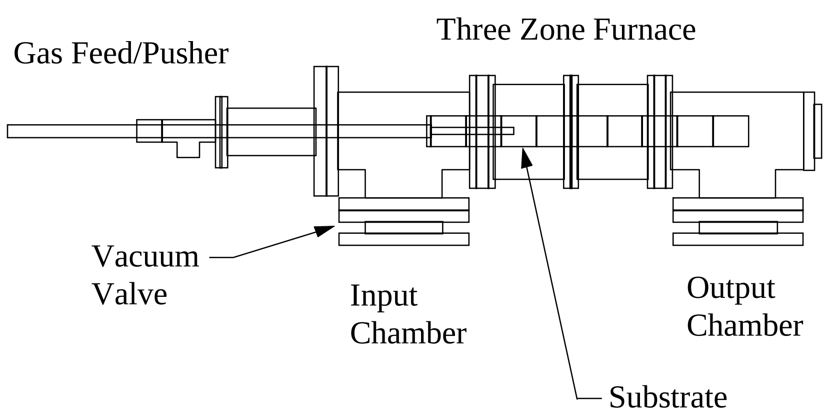

Figure 3

This furnace was operational in February 2002. The initial operation required approximately two months to begin producing fibril in the furnace through equipment debugging and experimental optimization runs.

Furnace Experiments

Prior to initiating actual fibril growth experimental runs, thermodynamic analysis was conducted to determine the optimum gas feeds and operating temperatures. An example of that analysis is displayed in Figure 5.

Figure 4. 2002 Fibril Growth Furnace

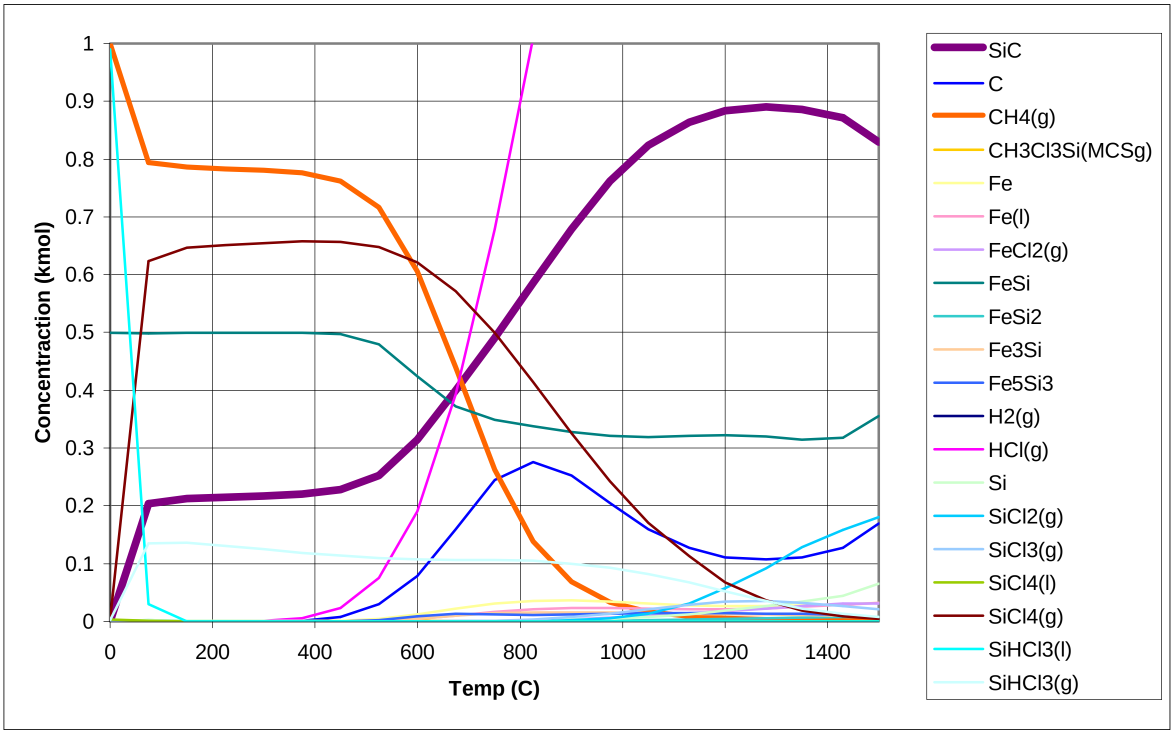

Figure 5. Thermodynamic Analysis of SiC Fibril Growth

Experimental Procedures

YZP Corporation was contracted to develop an organic paint capable of suspending the iron-bearing catalysts elements to achieve a uniform coating on the reaction boats. Although ferrous silicon ($FeSi_2$) is the preferred catalyst, pure iron was used initially because of its excellent coupling properties with microwave fields. The use of the pure iron powder provided a quick profile of the microwave energy field on the reaction surface of the aluminum oxide boats. The five iron powder experiments were used to determine reactor operating times to achieve the proper microwave heating in the reactor. The iron powder experiments showed that less than the calculated microwave energy was present on the reaction surface of the fibril boats. It was decided to continue the experiments, using longer than anticipated reaction times to test fibril growth with the preferred ferrous silicon.

A paint mixture of ferrous silicon was painted on the aluminum oxide boats and exposed to microwave heating through a series of 16 experimental runs before fibril growth was achieved. The resulting fibril product will be shown in the experimental results. Infrared photography shows the furnace interior during Run # 16 in Figure 6.

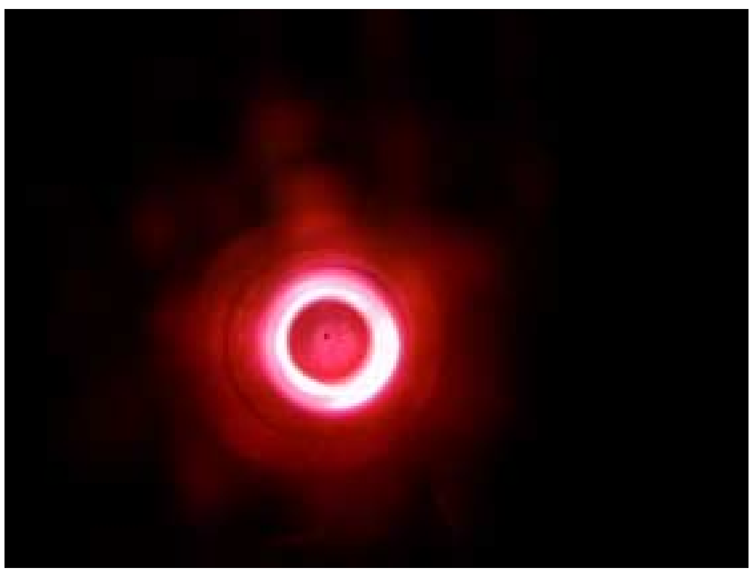

Figure 6. SiC Fibril growth during microwave heating

Experimental Results

Figures 7, 8, 9, and 10 show the fibril products obtained during the final runs in the microwave furnace.

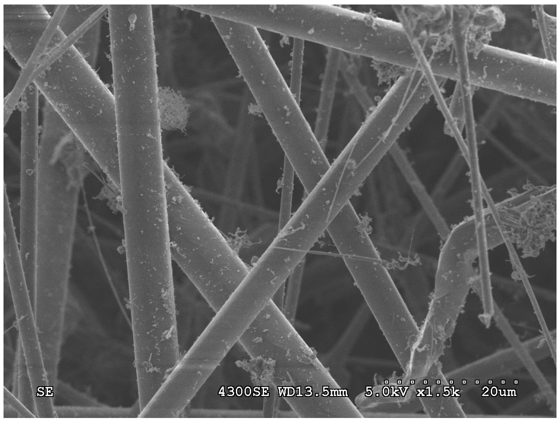

Figure 7 . 5 micon diameter SiC fibrils

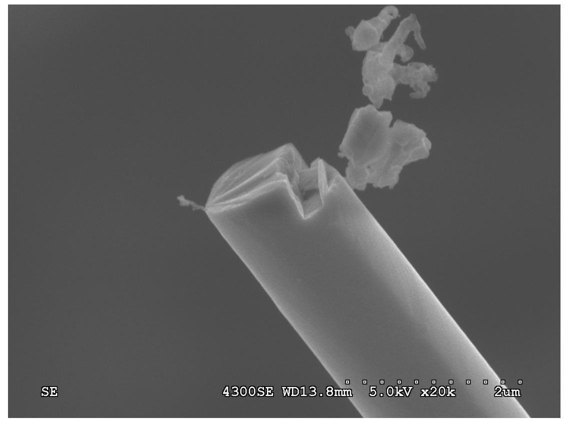

Figure 8. Perfect fibril cystal structure

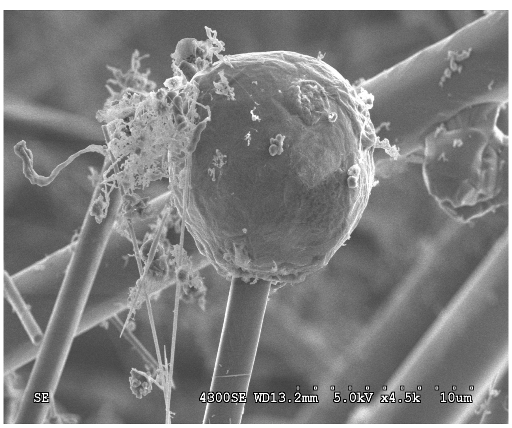

Figure 9. Ferrous fibril growth ball

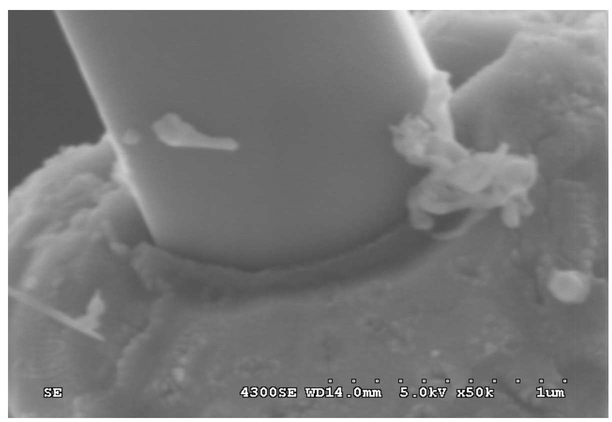

Figure 10. Interface of growth ball and fibril

Conclusions

The continuous microwave reactor has demonstrated the ability to grow the desired size and single crystal structure, high temperature silicon carbide fibrils. The lack of the proper microwave field in the fibril growth area requires the redesign of the reaction chamber to achieve the desired volume production of fibrils. This design effort has been contracted to several companies skilled in that art. A new microwave chamber will be constructed to provide the proper microwave field in the fibril growth region of the reactor. Sufficient operating parameter data, such as reaction gas feed rate and reaction vessel growth temperature have been established in these experiments to eliminate future optimization experiments. Upon installation of the new microwave chamber, the project will be able to begin producing volume quantities of silicon carbide fibrils.

Acknowledgements

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References

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