Commercial Process for Silicon Carbide Fibrils

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A History of the Fibrils Product

1965 - VLS Silicon Carbide Fibrils were discovered by Phillips Electronics in Sweden

1980 - Los Alamos National Laboratory spent several years on developing the technology for the US Government

1985 - Los Alamos turned the development over to MER and Arco who spent over one million DOD dollars on the development with little progress

1990 - The product development was resumed by the DOE Fossil Energy Program and awarded to Carborundum. Carborundum abandoned the program when purchase by St Gobain (Best commercial price estimate was $2,000/lb.)

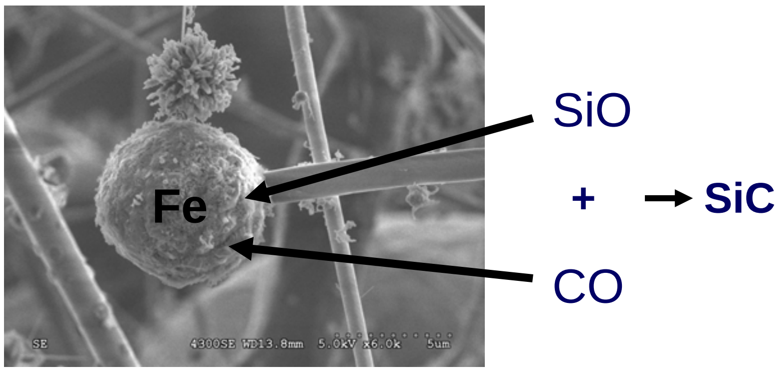
A History of the Fibrils Product

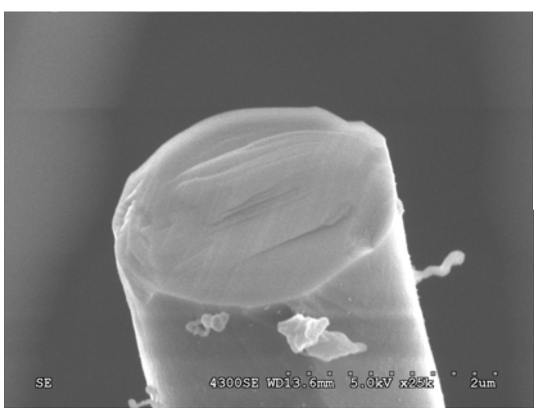
1998 - ReMaxCo was asked by DOE to continue the development effort after Carborundum (had scaled two previous SiC whisker technologies to commercial production)

1999 - ReMaxCo studied that past work and decided that a new approach was necessary to make a commercial product. Microwave synthesis was selected as this new approach

2000 - ReMaxCo conducted the first microwave synthesis bench-top proof-of-concept with significant success (Commercial price estimate = $300/lb.)

What Are Silicon Carbide Fibrils?





- 5 to 10 um diameter single crystal needles x 0.2 to 10 mm in length
- Use temperature in air to 1,600°C
- Tensile Strength to 2,300,000 PSI (16,000 MPa)
- Elastic Modulus to 84,000,000 PSI (580,000 MPa)
- Stronger and more durable than any existing ceramic fiber material

What Is Special About Properties?

- Silicon Carbide Whiskers significantly improved the properties of both metal and ceramic materials
  - Toughness of Al_2O_3 improved from K_{1C} of 4 to 10
  - Al_2O_3 high-temperature creep resistance was doubled
  - Modulus of aluminum metal was increased beyond titanium

- The SiC whisker market died because their 0.3 to 0.5 um diameter was associated with asbestos
  - OSHA classifies any ceramic fiber below 2.5 um in diameter as a respirable and hazardous fiber
  - The 5 to 10 um diameter Fibril is non-respirable and safe to handle without special precautions

What Is Special About Properties?

- The Japanese Nicalon SiC fiber is the strongest commercially available at 500,000 psi tensile strength.
  - Silicon carbide whiskers exhibited 300,000 psi tensile
  - SiC Fibrils, as tested at Los Alamos National Laboratory exceed 2,300,000 psi

- Silicon carbide fibers and whiskers exhibit rapid oxidation above 1,000^{o}C
  - Oxide fibers are all polycrystalline and rapidly lose strength above 1,000^{o}C due to phase transitions
  - Oxidation testing of the single crystal SiC Fibrils at Lawrence Livermore National Laboratory showed no oxidation damage up to 1,600^{oC}

Value of Silicon Carbide Fibrils as a Fossil Energy Material

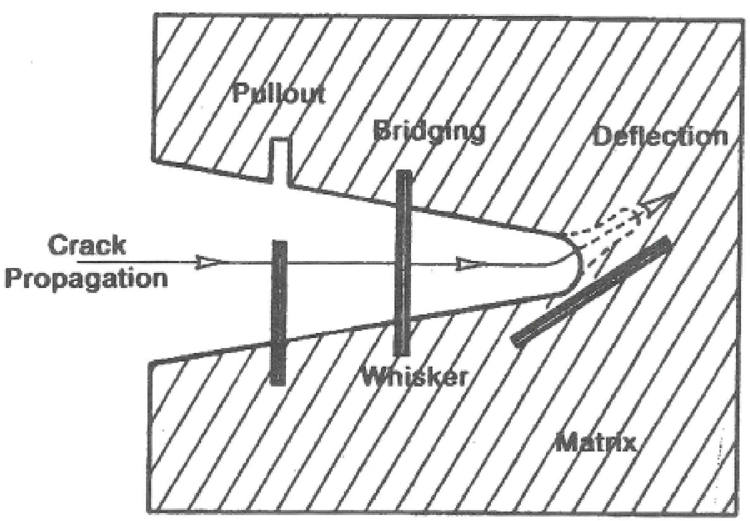
- **Demonstrated oxidation resistance to 1600º in air**
- **Composite tubes for high temperature heat exchangers in the combustion chamber**
- **Combustion chamber refractory tiles**
  - **High-temperature creep durability improvement as reinforcement for chrome oxide and aluminum oxide tiles**
  - **Slag erosion resistance**
- **2.5 PM compliant filter media for hot gas filters**

Specific Applications to Future Coal Combustion Technology

- Super-heated steam and coal gasification requires improved refractory materials. Silicon Carbide Fibrils can:
  - Improve high-temperature fatigue of aluminum oxide to replace chrome oxide
  - Improve corrosion and fatigue of chrome oxide to reduce refractory weight by 30%
- Silicon Carbide Fibrils can be formed into heat exchanger tubes that will operate to 1,400^{o}C
- ReMaxco owns filter media technology to produce Silicon Carbide Fibril filters that will operate to 1,400^{o}C and comply with 2.5 PM regulations

Commercial Applications of Silicon Carbide Fibrils for Coal-Fired Power Plants

Fibrils Can Increase of Fatigue Strength and Life of Combustion Chamber Refractory Tiles



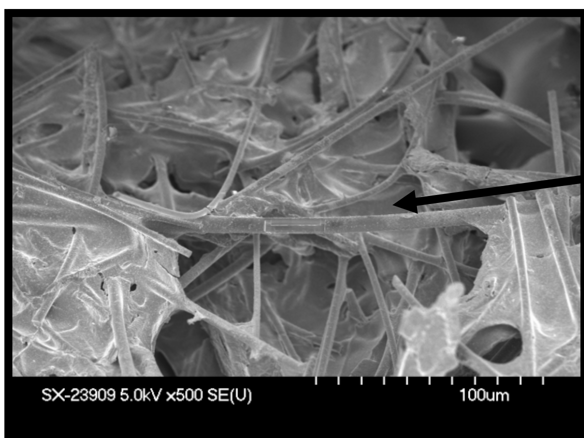
SiC Fibrils act as high-temperature rebar in ceramic tiles to add strength and stop cracks that cause fatigue failure

Aluminum oxide ceramic tiles exhibit significant fatigue failure above 1,200°C, Fibril reinforcement can move that limit to above 1,400°C

The industry needs a cost-effective answer to hazardous chrome oxide materials

Commercial Applications of Silicon Carbide Fibrils for Coal-Fired Power Plants

Heat Exchanger Tubes



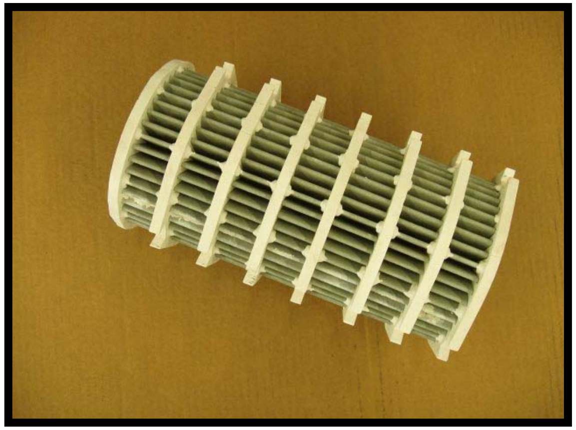
Silicon Carbide Fibrils can be formed into a paper

The paper can be rolled into tubes and u-joints prior to rigidifying – any size is possible, prior to rigidifying

The tubes can be infiltrated with CVD ceramic materials to rigidify the tube after shaping tube arrays

The result is a heat exchanger tube capable of operating to 1,400ºC

Commercial Applications of Silicon Carbide Fibrils for Coal-Fired Power Plants



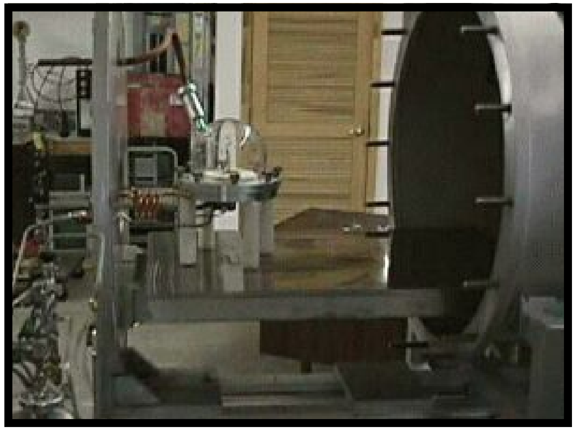
Hot Gas Filters

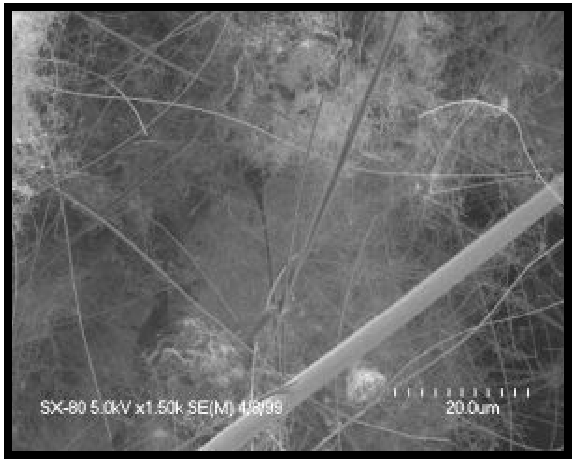
Fibrils can be formed into an inexpensive pleated filter media capable of withstanding 1,400ºC gas temperatures

Filter efficiency of 95% on 0.01 um particle size is achievable

Filter size is unlimited; moving belts could handle the total exhaust of a coal-fired steam plant

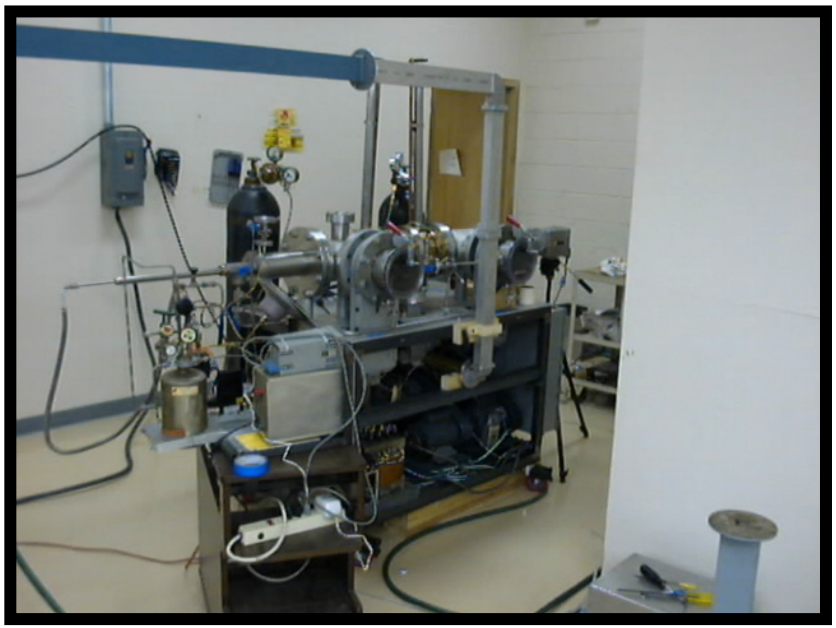
FY 2000 Proof-of-Concept Experiments

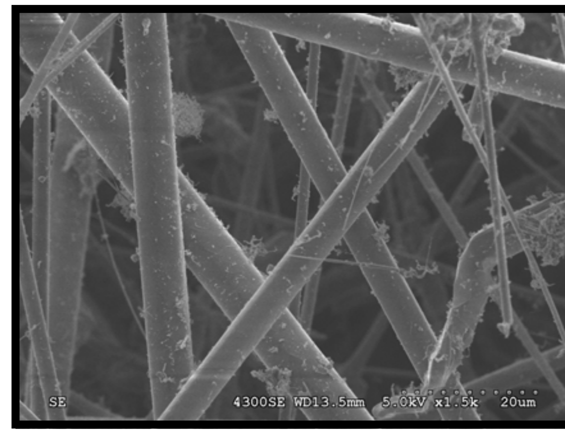


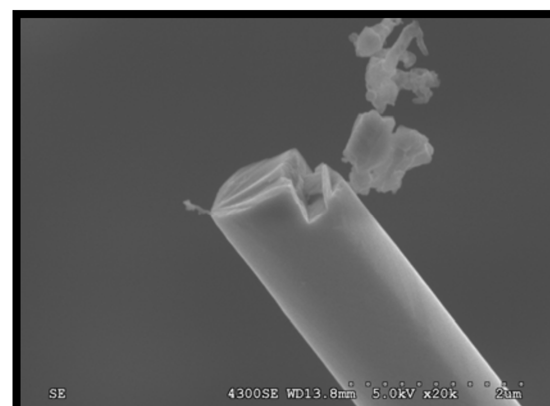


- **Increased Growth Rate from 0.17 mm/hour to 0.75 mm/hour - 4.4 X Improvement**
- **Melted Fe Seed Particles and sustained Fibril Growth with Microwave Energy**
- **No SiC Deposit on Reaction Chamber Walls - All reactant gases to Fibril Growth**
- **No HCl acid exhaust product**
- **Proved Potential for Microwave Growth Concept to reduce SiC fibril cost from $2,000/lb to a potential $300/lb**

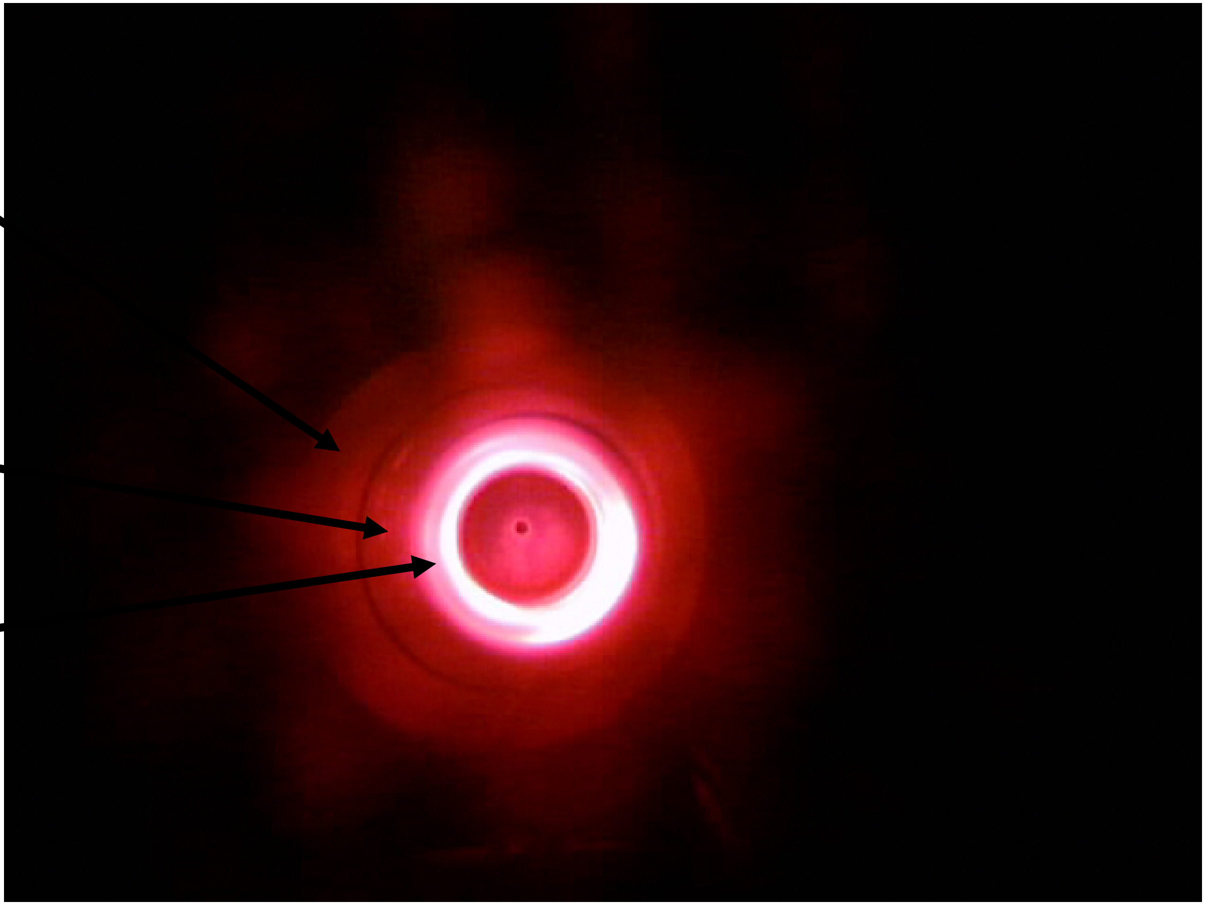
FY 2002 Scale-Up Experiments



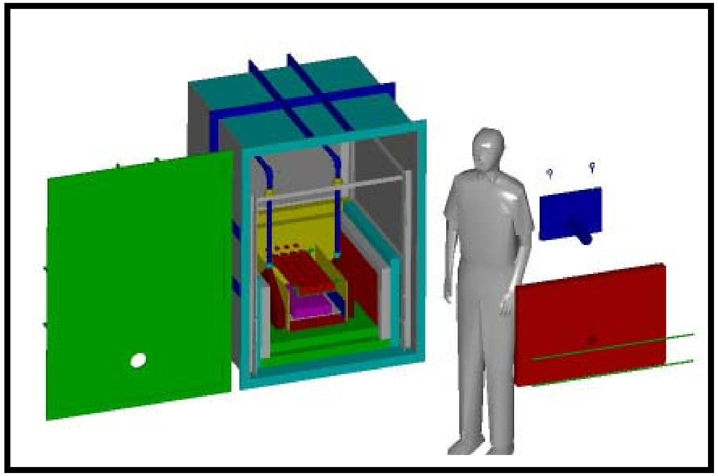


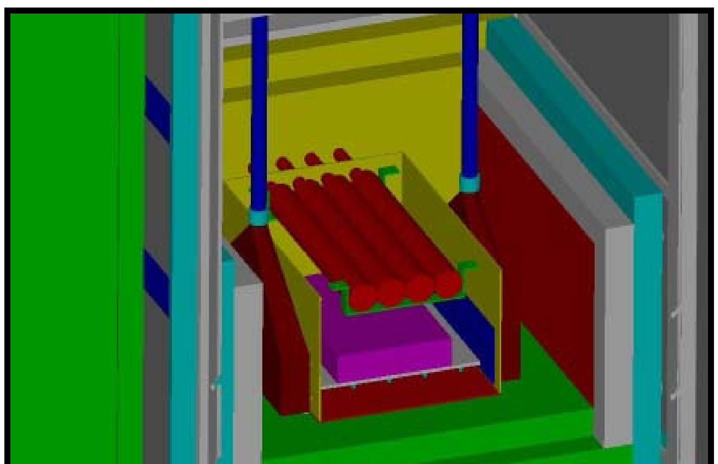


Microwave Reactor Operation Using Only Microwave Energy to Heat Fibril Growth Balls



FY 2006 2nd SiC Fibril Batch Reactor





Microwave feed is designed to distribute uniform field over growth plates

Reaction gas feed is designed for directed laminar flow over growth plate

Small growth chamber in a vacuum box simplifies process control and data collection for future scale-up; electric molydisilicide elements preheat growth chamber, then microwave energy completes the seed melting and Fibril growth process

FY 2006 Volume SiC Fibril Reactor

Unit Assembled for Firing

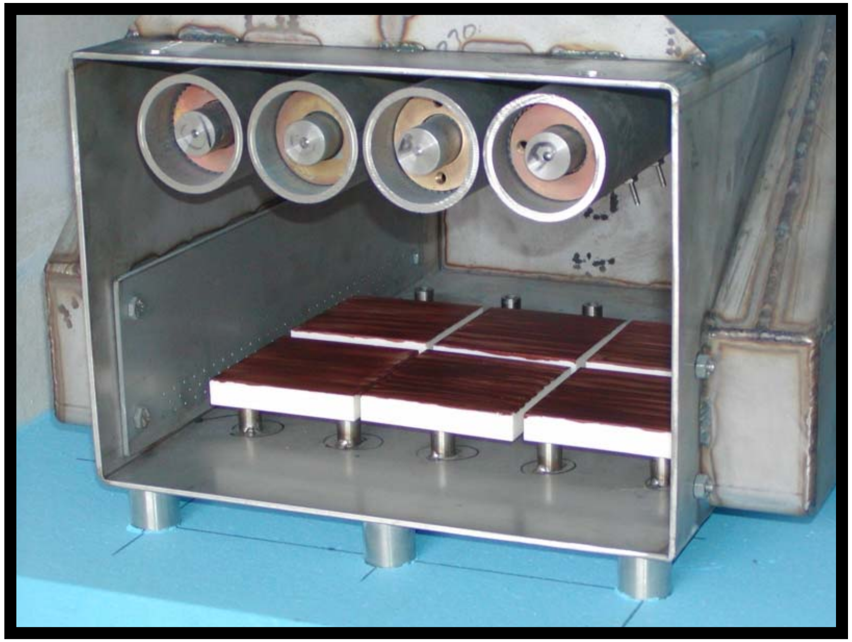
Precise Reactant Gas Feed System

FY 2006 Volume SiC Fibril Reactor

Microwave Feed System

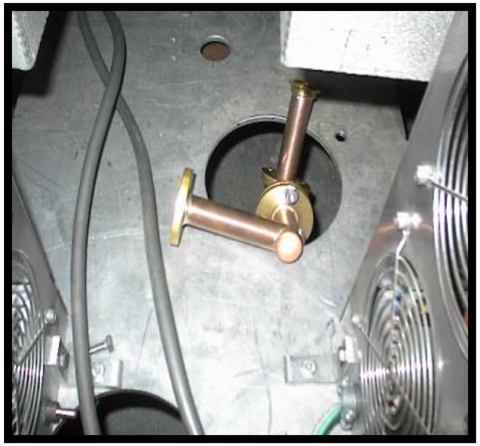
FY 2006 Volume SiC Fibril Reactor

Fibrils Growth Chamber



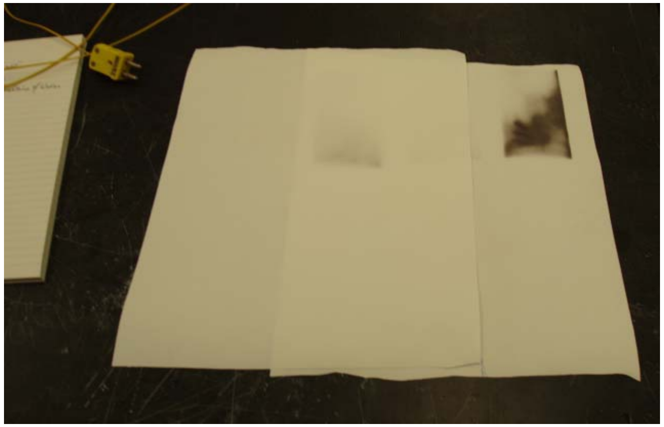
The 2006 Tech Wreck!

- $110,000 unit completed in June 2005
- 4,500 lb. unit dropped from loading dock by shipper
- Significant expensive damage to microwave and electrical components; some structural damage
- Battle with shipper and insurance company was finally settled with payment in February 2006
- Damage repair was completed February 2007
- Damage and repairs cost one year in the project schedule



2007/2008 Accomplishments

Achieve a Uniform Microwave Field



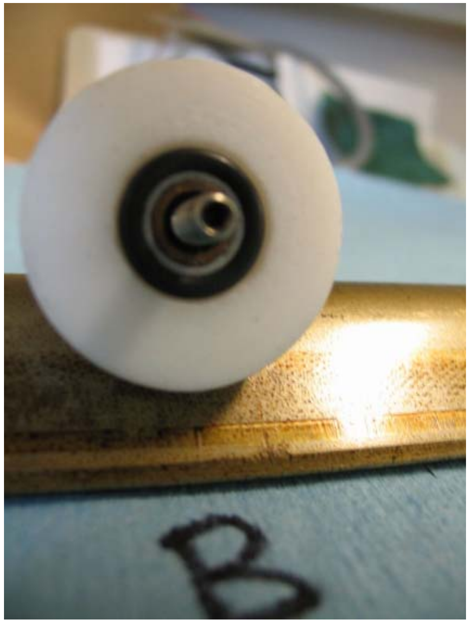
1st 2007 Microwave Uniformity Test

Microwave Uniformity Test
After Applicator Rework

The uniformity of a microwave field's energy distribution can be tested using "old-fashioned" thermal-sensitive FAX paper. The first test indicated the need for significant applicator rework.

2007/2008 Accomplishments

Eliminate High-Temperature Plasma Damage



Good Microwave Delivery Tube Seal

Plasma Burned Microwave Delivery Tube Seal

All perturbations creating plasma arcs were ground smooth on the microwave applicator (work completed June 2008)

2009 Fossil Energy Applications Work

EPRI Materials Properties Verification Program

2009 – Select ceramic matrices for SiC Fibrils reinforcement, fabricate flat tensile bars, and test room temperature mechanical properties

2010 – Good results in ambient temperature properties will lead to high-temperature mechanical properties testing

2011 – Success with high-temperature mechanical properties will lead to fabricating combustion chamber sample components for plant testing

2010 SiC Fibrils Commercialization

2009 – Fibrils testing in SiC/SiC high temperature turbine blades by Physical Sciences. Inc. and Wilson TurboPower.

2009 - A number of components in classified military applications are awaiting SiC fibrils for composite testing.

2009 - There are many ceramic wear and toughness applications available.

2009 – Several investors have conditionally committed to financing a production facility. Two large vacuum equipment companies have expressed an interest in designing and building the commercial equipment.

Microwave Process Advantages for Silicon Carbide Fibril Production

- An order of magnitude less energy consumption with microwave growth
- 4X higher Fibril growth rates to reduce production costs
- 97% use of reactant gas feed to grow Fibrils (3% in previous work)
- $300/lb projected price as opposed to $2,000/lb prior to microwave growth

Microwave – VLS Single Crystal Growth for the Future in Materials

- Growing directional single crystals for 40 years, since graduate school.
- Single crystal properties are significantly better than polycrystalline materials.
- An ORNL scientist who works with titanium aluminides complained about brittleness. TiN whiskers survived the titanium aluminide processing temperatures to add fracture toughness to the finished product.
- Some very high temperature materials, such as TiC and HfC single crystal reinforcements, might provide improvements in high-temperature energy production