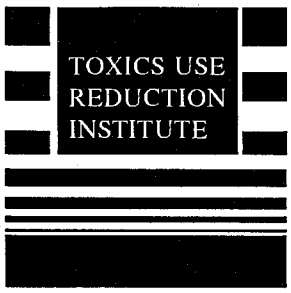

THE MASSACHUSETTS
TOXICS USE REDUCTION INSTITUTE

SYNTHESIS OF SILICON CARBIDE FIBERS

Technical Report No. 17 **1993**

University of Massachusetts Lowell

Synthesis of Silicon Carbide Fibers

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The Toxics Use Reduction Institute Research Fellows Program

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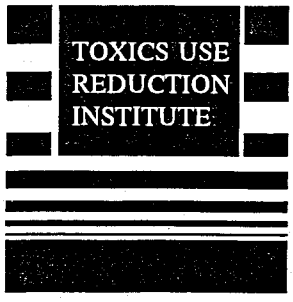


The Toxics Use Reduction Institute is a multi-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to governments to promote the reduction in the use of toxic chemicals or the generation of toxic chemical byproducts in industry and commerce. Further information can be obtained by writing the Toxics Use Reduction Institute, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854.

Abstract

The objective of this project is to synthesize single crystal silicon carbide fibers without the use of any toxic chemicals. This would be accomplished by following a two step procedure. The first step is to grow single crystal silicon fibers using the Czochralski technique. The second step is to diffuse carbon, from methane, into the fibers to form silicon carbide through a gas-solid reaction in a quartz-tube reactor. Several silicon fibers were grown and identified, through electron diffraction, as single crystals. The quartz-tube reactor was designed and built. Final testing of the silicon fibers was delayed because of several problems, however, at present all systems are ready for operation.

Background

The main objective of the project is to demonstrate that silicon carbide fibers can be synthesized as a single crystal structure. Silicon carbide fibers are primarily used in the reinforcement of metals and ceramics. Silicon carbide is an excellent candidate for reinforcing applications because it has properties which include high thermal conductivity and high corrosion and thermal shock resistance. Presently, silicon carbide fibers in a polycrystalline form are being produced by Textron Specialty Materials in Lowell, MA. These fibers are made up of many individual crystals called grains. Within each of these individual crystals all unit cells are arranged in the same crystallographic orientation. At the boundary of two grains this single orientation no longer exists. The disorder at these grain boundaries results in an increase of strain and a decrease in strength

of the material. By synthesizing the fibers as single crystals the grain boundaries will be eliminated and a stronger material will result. Both theory and experiment demonstrate that single crystal whiskers of many materials are stronger than the corresponding polycrystalline material, but whiskers are too small for many applications.

Introduction

Single crystal silicon carbide has been grown in two separate structures. These structures are large diameter rods and microscopic whiskers. Rods are generally classified as larger than five centimeters in diameter while whiskers are usually less than one micron in diameter and are generally not much greater in length. Single crystal fibers, though not previously grown in silicon carbide, are smaller than rods but larger than whiskers. They traditionally have diameters of about 100 microns or slightly thicker than a human hair. Single crystal fibers of other materials, such as high melting oxides, have been grown by a technique known as the laser heated pedestal (LHP) technique, but this method requires the ability to create a molten mass of the material to be grown. Silicon carbide does not exist in liquid form at any reasonable pressure, and so the LHP technique cannot be applied.

The polycrystalline fibers currently being produced by Textron require the use of large quantities of toxic chemicals such as methyl dichlorosilane and silicon tetrachloride for production. Chemicals such as these not only threaten the environment but also substantially increase production costs as a result of the additional

costs of waste disposal. The second chief objective of the project was to eliminate the use of such chemicals in the synthesis of the silicon carbide fibers. Incorporating our proposed production scheme should not only result in a stronger, more reliable product and eliminate the use of toxics and the potential release of toxic chemicals into the environment but also ultimately result in a more cost efficient procedure.

Process Description

Production of the fibers can be divided into two major steps. The first step is the growth of single crystal silicon fibers. To form a single crystal silicon structure, one starts with a silicon "seed" crystal which serves the purpose of providing a single crystalline material onto which the silicon atoms can grow in an orderly fashion. The generation of the silicon fiber is accomplished by mechanically pulling material from a liquid silicon melt, held at the melting point of silicon (1410 ^{o}C), using the single crystal silicon seed. As the seed is pulled upwards, silicon solidifies on the seed crystal at the point where the seed dips into the top surface of the melt, growing a structure which is the analog of an icicle. The solidifying silicon continues the single grain structure of the seed. This growing method is known as the Czochralski technique. The melt is produced by liquifying bulk pieces of pure silicon in a water-cooled copper crucible under the action of radio frequency power. This entire portion of the process was carried out inside a furnace having an argon atmosphere. See figures 1 and 2 for photographs of furnace setup. An inert gas such as argon is required to eliminate

contamination of the silicon. Heat is supplied to the furnace via a radio frequency generator.

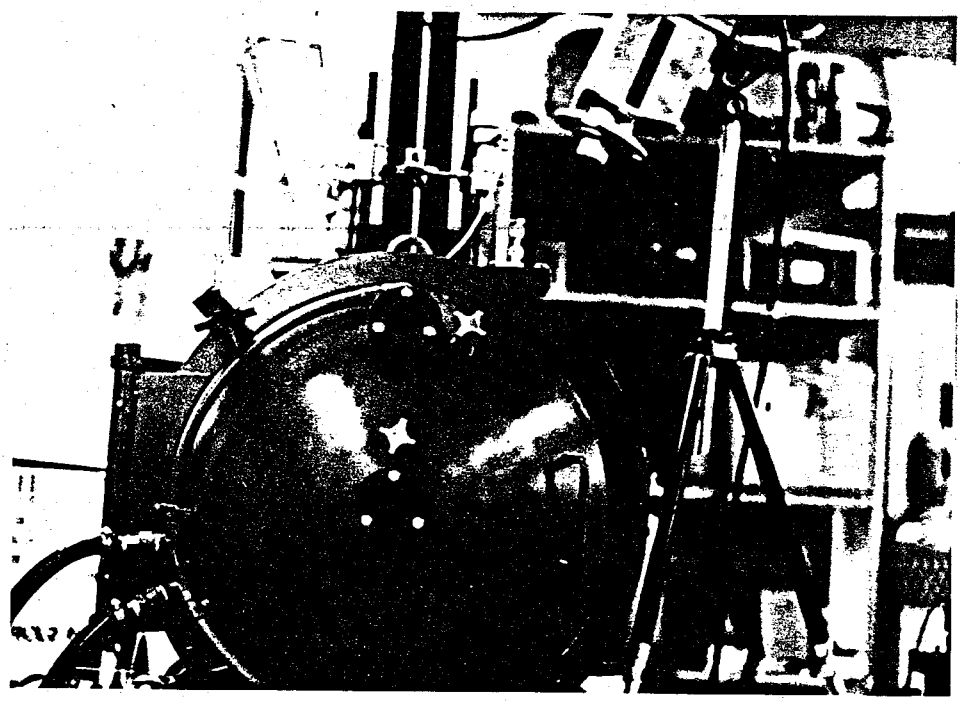


Figure 1: Furnace Setup-1

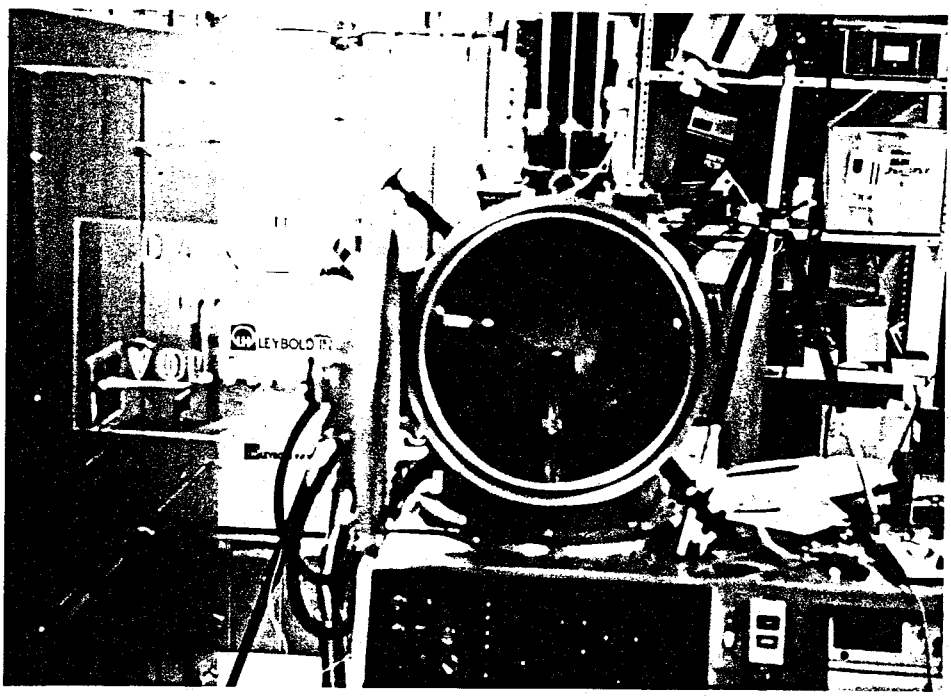


Figure 2: Furnace Setup-2

To initiate the process, the generator supplies power to heat a graphite disk suspended immediately over the solid silicon. See figure 3 for photograph of disk and crucible. The disk in turn emits enough optical radiation to heat the solid silicon to the point where it produces electron hole pairs. The increase in electron carrier density allows the radio frequency to couple directly to the silicon, which then heats the silicon to reach its melting point of 1410 degrees Celsius. At this point the graphite preheater is moved out of the way so that the top of the silicon melt is accessible to the seed crystal. The melt is maintained while the fibers are pulled.

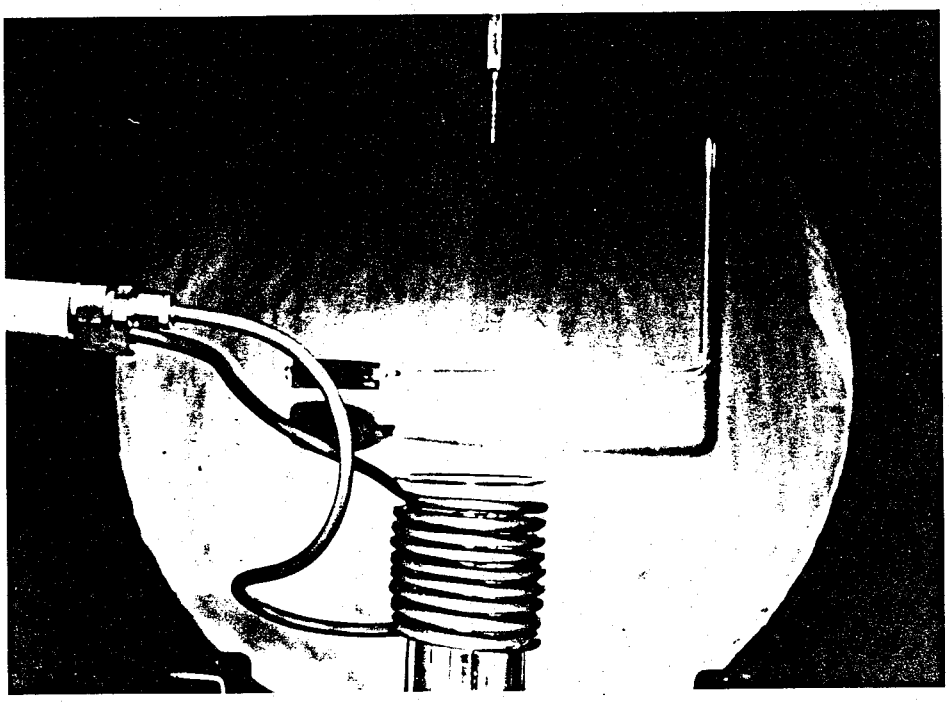
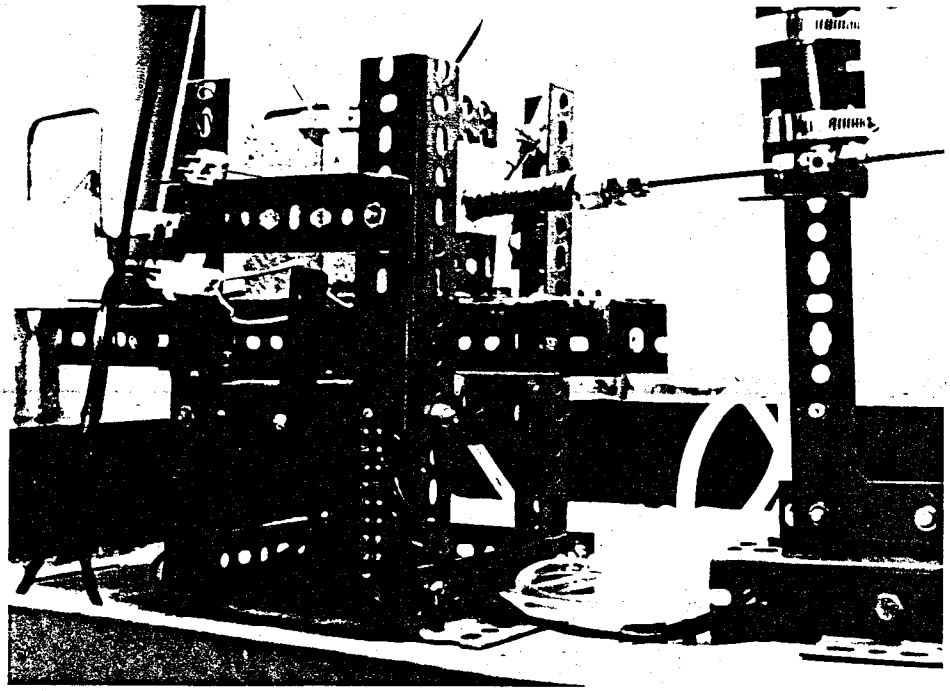


Figure 3: Disk and Crucible

The second step of the process is the diffusion of carbon into the silicon fibers to form silicon carbide using methane in a quartz tube reactor. See figure 4 for photograph of reactor setup. The reactor consists of a quartz reaction tube which passes through a furnace, and is supplied with gases via a metering system.

Figure 4: Reactor Setup



The fiber is aligned within the central section of the 31 centimeter long tube. This central section is encased by two half pieces of molded insulating brick to prevent heat loss. When power is supplied to the four symmetrically situated silicon carbide heating elements, enough heat can be generated to bring the fiber close to its melting temperature of 1410 degrees Celsius. A variac unit is used to supply the power to the heating elements. As methane is pumped into the reactor, the supply of carbon will slowly diffuse into the silicon fiber at the elevated temperature. Diffusivity of carbon into silicon is determined by the strength of the silicon-silicon and silicon-carbon bonds and the temperature. Higher temperature provides higher diffusivity because atoms have a higher energy and therefore a greater probability of being activated over energy barriers. The temperature is monitored with chromel-alumel thermocouples on the outside surface of the quartz tube. The methane enters the reactor through 1/4 inch stainless steel tubing

connected at the opening of the quartz tube. The methane flow rate is controlled by a mass flow controller connected into the methane line. The mass flow controller is operated through the use of a computer. Code has been written to also log the temperature data collected from the system using an analog to digital input board. Any excess methane exits the reactor through a similar connector and tubing as the entrance and is burned off. Argon is used to purge the system before and after all testing. Both gases are stored in large cylinder tanks connected to the system and need to pass through a series of safety valves before reaching the reactor. Because the reactor operates at approximately 1400 degrees Celsius, water-cooled coils, made from copper tubing, are placed at either end of the quartz tube during operation to prevent the Teflon ferrules in the stainless steel connector fittings from reaching their melting temperature.

Results and Discussion

In the first production step, several silicon fibers were grown with acceptable diameters to be used in the second step of the process. See Figure 5 for fiber photograph. These fibers were grown using manual control of the pull rate of the silicon seed. While this step of the process clearly has been demonstrated to work, manual control of the pull rate is quite tedious. Slight variations in the operator's technique can lead to variations in the diameter of the single crystal fiber, or even accidental termination of growth. However, ways to control and to further decrease the diameter of the fiber have been examined.

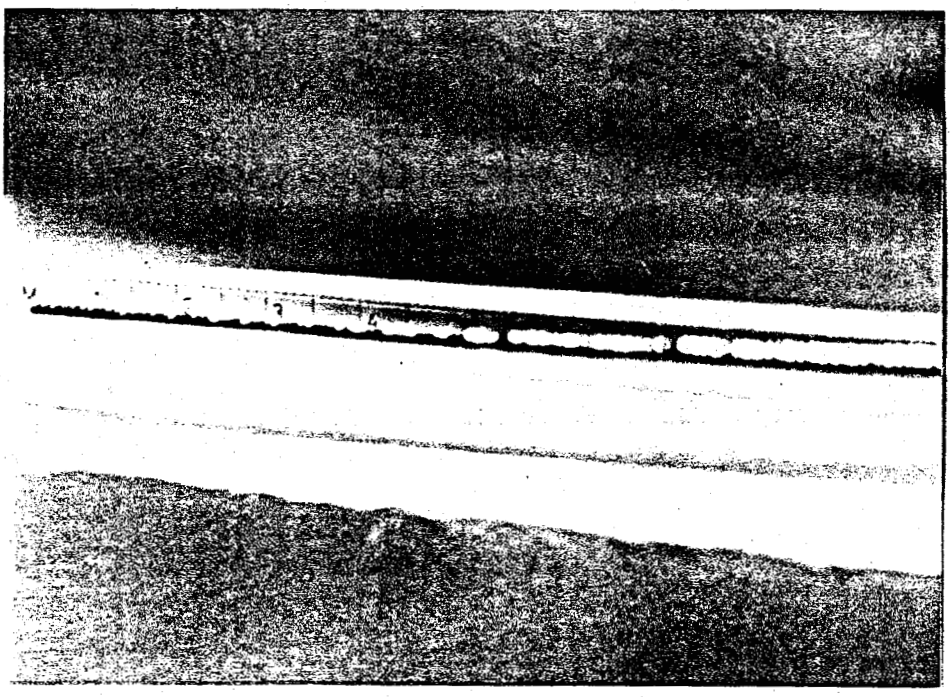


Figure 5: Silicon Fiber

An attempt to diminish fluctuations in the silicon melt caused by power oscillations during crystal growth was the first method studied. By immersing a piece of 3/4 inch diameter quartz tube into the melt, fluctuations in the melt were decreased, but no significant improvements were noticed because wetting and dewetting of the quartz tube caused a new vertical oscillation of the melt to occur inside the tube itself.

An elaborate computer program was written that will allow the seed motion to be controlled by a computer instead of the tedious manual method, and if successful, will allow predetermined pull rate profiles to be used to control the process. The program operates the seed lift system as expected, but has not yet been tested in actual fiber growth.

The fibers that were grown were examined in order to confirm their single crystalline structure. Because silicon crystallizes in the diamond cubic structure, the fibers can be assumed to be single

crystals if four facets can be detected along the length of the fiber. All fibers grown contained these four facets. Through x-ray photography, a more precise examination was performed. X-rays were reflected off cross sections of several pieces of fiber and recorded on film. The film confirms that the fibers are single crystals.

Having successfully grown single crystal silicon fibers, the conversion of silicon to silicon carbide by the gas-solid reaction remained to be demonstrated.

The construction of the quartz tube reactor was plagued with material acquisition delays and design problems. The reactor was at first built with a vertical design. It was tested to see if enough power could be generated to produce the necessary high temperature for the reaction to occur. Only about 1100 degrees Celsius could be obtained using the variac power supply wired as it was. The wiring was reconfigured in hopes that the variac could supply a greater output. This proved to be successful as over 1400 degrees was reached at only 60 percent variac capacity.

During actual operation, the temperature would be monitored outside the reactor tube. No thermocouples could be used inside because the quartz tube has to be hermatically sealed to prevent methane gas leakage. Two thermocouples, one inside and one outside the tube, were used to check for any temperature gradient between the tube wall. It was observed that the temperature outside the tube was approximately 400 degrees higher than the inside temperature. The vertical quartz tube was acting like a chimney and allowing too much heat to escape. Heat shields of

platinum and aluminum were used to try to diminish the heat loss. No improvements were noticed. It was concluded that the configuration of the tube would have to be changed from the vertical position to a horizontal position to eliminate convective heat transfer.

After the reactor was rebuilt with the quartz tube in a horizontal position, the inside and outside temperatures were again sampled. No temperature gradient occured up to temperatures of at least 1320 ^{o}C. Material acquisitions were one of the greatest problems encountered. The project was delayed a significant amount of time while waiting for necessary pieces of equipment and consumables. Because of these problems the final testing on the silicon fibers was delayed. However, all key pieces of equipment have now been received.

Means to identify the finished silicon carbide fibers have already been arranged. X-ray diffraction will determine if the fibers are truly single crystals and electron diffraction will determine the thickness of silicon carbide penetration.

Conclusions

If all factors of the project are successful, a stronger silicon carbide fiber, more reliable than what has previously been fabricated will result. Toxic chemicals, such as methyl dichlorosilane and silicon tetrachloride, will be eliminated from the production process, ultimately resulting in a more cost efficient process which does not involve toxics. With the diameter thickness of the silicon fibers that have already been grown, it is doubtful that the entire fiber will be converted into silicon carbide. The depth of carbon

penetration can only be determined through experimentation. As the fiber diameters are made smaller a greater percentage of conversion will occur. If for some chance the final silicon carbide fibers happen to be polycrystalline instead of single crystalline the project would still be considered a success because the toxic chemicals would still be eliminated from the process. If polycrystalline materials result, the product might not have improved strength properties but it will be a more environmentally safe process. Again, the crystal structure which is attained can only be determined when experimentation is complete.

Acknowledgments

I would like to thank the Toxic Use Reduction Institute for their help and generosity in funding this project. I also want to thank Professors Thomas Vasilos and Joseph Milstein for all the assistance during the experimentation of the project.

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