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Final Technical Report

As a result of the Phase I research, we can reproducible clad silicon carbide films onto graphite rod substrates. During the course of our research we varied the melt composition, temperature and crucible material. The resultant silicon carbide films were confirmed independently by Charles Evans Associates using electron microscopy and elemental x-ray analysis.

The minimum temperature for silicon carbide formation was determined. The relationship between film thickness and maximum melt temperature was studied. The importance of complete oxygen exclusion was determined. The presence of the proprietary flux was found to be essential in this regard

The thickness and integrity of these films are not yet suitable for commercial applications. It is anticipated, that the use of higher temperatures will yield silicon carbide films suitable for extreme environment applications. A new high-efficiency high-temperature furnace was designed with a maximum working temperature of 2000° C.

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1. Project Overview

Silicon carbide is an important industrial material due to its unique electronic, chemical, and physical properties. Its large energy band gap allows applications as blue LED's, ultraviolet photo diodes and high temperature rectifiers. In metallurgy, SiC is added to molten iron for its intense exothermic reaction and to getter oxygen. The hardness of SiC is greater than sapphire and it is extensively used as an abrasive. At high temperatures, the oxidation of SiC in air is a self limiting process; a protective SiO_2 coating forms on the SiC surface preventing further oxidation. This resistance to oxidation at elevated temperatures, combined with its electrical conductivity, allow its use as heating elements in high-temperature furnaces. In air, its maximum usable temperature is up to 1600°C. It's very high decomposition temperature (>2800°C) allows it to be used as a refractory in oxygen-free environments. Finally, SiC has a relatively low neutron cross section and is resistant to nuclear radiation damage.

The purpose of this proposal was to develop a process whereby high-density, high-purity SiC can be cladded onto an arbitrary shape, quickly and economically. In the proposed fabrication process, the desired shape is cut from easily-machined graphite and then converted to SiC using a liquid-phase Si-diffusion process at high temperature. This process can provide complex structures that are refractory, wear-resistant, corrosion-resistant, radiation-damage resistant with relatively high compressive strength and are electrically conductive. Applications would include high-temperature heating elements, heat exchangers, hot-pressing dies, and spray nozzles. More exotic applications include extreme-environment fasteners, nuclear fuel cladding, gas turbines, turbochargers, and rocket nozzles and nose cones.

The potential for such a cladding process was happened upon accidentally when a crucible failure at high temperature allowed a copper-silicon melt to come in contact with a graphite support. A reaction occurred which resulted in a 2 mm thick layer of smooth, void-free SiC that was well-bonded to the underlying graphite. It was not clear at what temperature the failure occurred or for how long the liquid was in contact with the graphite. The furnace had been operated at temperatures as high as 2000°C and the total time at temperature was less than a day. The main thrust of the phase I proposal was to determine the process parameters required to reproduce this serendipitous event.

As a result of the phase I research, we have successfully and reproducibly clad SiC films on graphite substrates using copper-silicon melts. Comparison of cladding runs with varying melt compositions indicate that copper plays an essential role in the formation of void free SiC films. Unfortunately the thickness and integrity of these films are not yet as good as the original accidental film. As will be discussed below, the short comings of these films can be attributed to the limited temperature range used in the experiments (<1600°C). The following is a brief chronological summary of the research accomplished during phase I.

A controlled-ambient furnace, capable of reaching 1200°C, was assembled using Kanthal A-1 heating elements. The first set of experiments was conducted at 1160°C using a series of Cu-Si melts with varying amounts of Si. Graphite rods were immersed in the melts for 4 hours but no SiC was observed to form on any of the rods. Before abandoning this low temperature regime, an attempt was made to plate SiC from the Cu-Si melt via slow cooling. The melt was allowed to cool from 1160 to 1060°C at a rate of 10°/hour. Again, no SiC was formed.

A second series of experiments was conducted in the range of 1400 to 1600°C. A furnace was assembled using a small Pt-Rh hot zone; the entire furnace was placed in a fused-quartz argon-purged bell jar. A variety of melt compositions and crucible materials was explored. Graphite rods were immersed in melts from 2 to 4 hours. No significant SiC formation was observed until the temperature was increased to 1450°C. All runs above 1450°C showed some amount of SiC. These experiments demonstrated that: 1) the presence of oxygen (whether as a gas or as SiO_2) degrades the SiC-graphite interface, 2) copper bearing melts resulted in clean SiC-graphite interfaces, 3) the presence of elemental boron in the melt does not increase the growth rate of the SiC layer, and 4) higher temperatures result in thicker, smoother, more contiguous films. Based on these observations, it is concluded that thick, smooth SiC films can be made using graphite forms and copper-based melts, but a practical process speed will require temperatures greater that 1600°C.

Finally, in view of the limited film thickness found in these experiments, it was decided to reexamine the thick SiC film that was first made during the accident described above. Electron imaging and X-ray analysis revealed that: 1) the film was indeed void free, 2) that a sharp, flat interface separated the graphite and the cladded SiC, 3) there are no voids or extraneous phases at the graphite-SiC interface, 4) a small concentration (~1%) of boron was detected in the SiC layer and the remaining Cu-Si melt. A more detailed account of all of the foregoing results will be given below in section 2.

2. Phase I Objectives and Results

The original phase I proposal outlined four research tasks which were directed toward the development of the SiC cladding process. These tasks are restated below along with the results obtained.

Task I. Construct a small high temperature furnace system with an argon atmosphere using existing components. A small platinum furnace capable of a maximum temperature of 1600°C is available. A carbon element will be constructed if higher temperatures are required. A computer-controlled temperature control and data collection system manufactured by COM:ONE is available to power the furnaces.

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Task I Results: In the course of this research, two furnaces were designed and assembled and the designs for a third were completed. All the designs incorporate an argon purged hot zone and a magnetic sample manipulator. The manipulator allowed the samples to be inserted and extracted from the melt without compromising the melt ambient. The first furnace was based on Kanthal A-1 heating elements and had a maximum temperature of 1200°C. The second furnace was based on a platinum-wire heating-element and could achieve 1600°C. The final furnace, which is not yet constructed, is a proprietary design based on carbon heating elements and is capable of reaching 2000°C. The construction of this furnace will be the first task of phase II.

The choice of furnaces was motivated by the following considerations. The 1200°C temperature range is relatively easy to obtain; Kanthal A-1 elements are low cost and readily available. This temperature range does not require exotic or expensive insulation nor is the thermometry particularly demanding. Finally, fused quartz is quite strong at these temperatures and can be used in the construction of the hot-zone enclosure and the sample manipulator.

To reach temperatures in the range of 1600°C, the available choices become somewhat limited. In this temperature range, fused quartz is too soft to support mechanical loads and cannot be used in the hot-zone. In many cases, alumina can be substituted, however, it cannot be welded into arbitrary shapes, like quartz, nor can it support a large thermal gradient without fracturing. Specialized insulation is also required at 1600°C, the least expensive are high-temperature alumina-silicas such as Fiberfrax Duraboard 3000. The possible heating-elements for a 1600°C furnace are platinum wire, $MoSi_2$, and SiC rods. The $MoSi_2$ and SiC elements are brittle and come preformed so that the furnace must be designed to accommodate one of the standard forms. Furthermore, the large cross sections required for mechanical strength result in very low electrical resistance. This, in turn, requires a high current power supply. For even modest-size furnaces, the cost of platinum becomes a significant consideration. Platinum's main advantage is the ease with which it can be wound onto an arbitrary furnace preform. In our case, a small Pt hot zone was available in-house and so became the basis of our 1600 furnace design.

Finally, to go well beyond 1600°C, the heating elements must be carbon or refractory metals, such as tungsten and molybdenum. Alternately, exotic setups such as RF induction, lasers or arc-heating can be employed. The desire for simplicity and reliability precluded the more exotic approaches. The refractory metals must be made custom to the furnace configuration. This implies a long lead time and prohibitively high costs. Carbon heating elements are comparatively inexpensive, however, they must be made with large cross sections to be mechanically robust. This results in a low electrical resistance ($\sim 0.1\Omega$) which requires a high current power supply.

The insulation that is commonly used at 2000°C is graphite felt. The graphite felt is inexpensive but has a fairly high thermal conductivity. A more contemporary material that can be used in this temperature range is based on zirconia fibers. These newer materials are somewhat expensive but very good thermal insulators. The improved insulation means that the furnace is less lossy and can be powered by a smaller power supply. The furnace that we have designed uses a carbon heating element, a zirconia insulated hot zone and a high-current low-power switching power supply. We have calculated that the increased cost of the zirconia is more than offset by the reduced cost of the power supply.

The above considerations led us to choose Kanthal A-1, platinum and carbon/zirconia as the basic technologies behind our three furnaces designs. We now describe some details of their designs and construction.

The 1200°C furnace is illustrated in figure 1. It was constructed using pre-wound Kanthal heating elements. Two inches of Fiberfrax 2600 insulation was placed around the OD of the heating elements and the entire assembly was placed in an aluminum housing. The temperature was monitored using a type S (platinum-rhodium) thermocouple. The furnace temperature was controlled by a COM:ONE TCS-2000 temperature controller operated in a PID closed loop configuration.

The growth chamber was a two piece quartz vessel with a ground glass fitting. The top piece was designed with a gas inlet and outlet and a closed-end tube to be used as the magnetic sample manipulator. The sample rods were attached to a ferromagnetic slug via a quartz rod. A samarium cobalt magnet placed on the outside of the closed-end tube was used to hold the slug in place and to lower the entire sample assembly into the melt. Manual insertion and extraction of the sample permitted precise control of the immersion time and temperature.

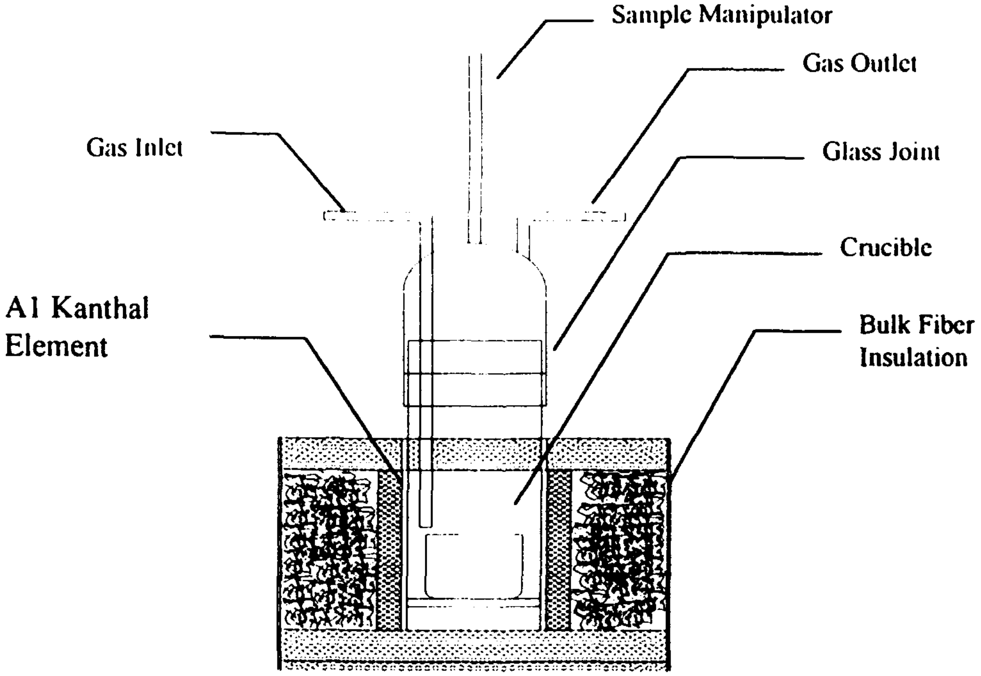

Figure 1. The Kanthal A-1 1200°C furnace design.

The 1600°C furnace design required some dimensional changes from the 1200°C design. The Platinum hot-zone that was available was considerably smaller than the Kanthal heater used in the low temperature furnace. The dimensions of the heating element were 3 inches long with an ID of 1 inch. To accommodate the smaller hot-zone, a completely new support and quartz housing was fabricated. This time the entire heater and insulation pack was placed in a quartz bell jar. This prevented any softening of the quartz enclosure used to contain the argon ambient. The bell jar was equipped with a magnetic sample manipulator similar to that used in the 1200°C furnace. The design is illustrated in figure 2.

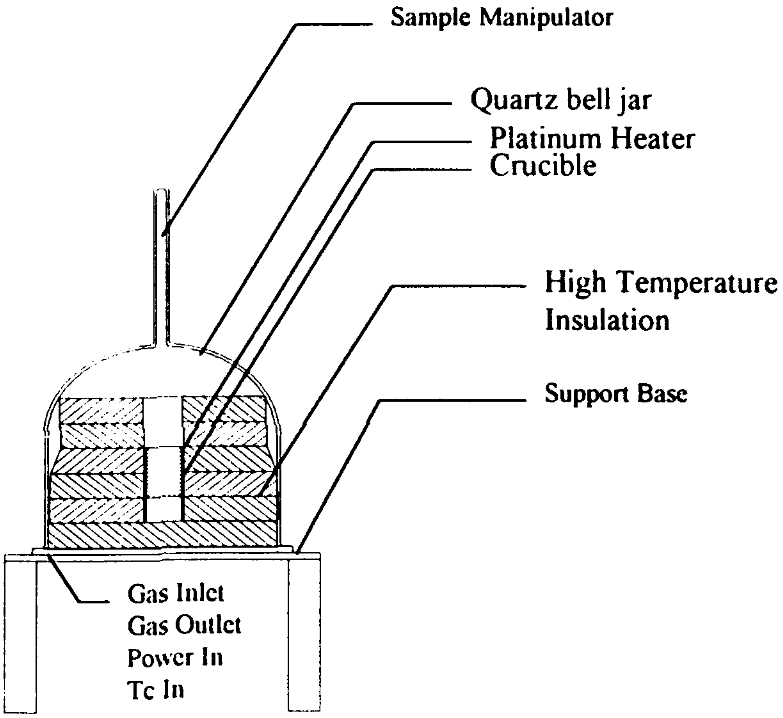

Figure 2. The platinum 1600°C furnace design.

The thickness of the Duraboard 3000 insulation that was used to insulate the 1600° C furnace was 3.5 inches. This allowed the furnace to reach 1600° C with a power consumption of 700 watts. Again, the temperature was controlled by a COM:ONE TCS-2000 temperature controller using a type S (platinum-rhodium) thermocouple.

A revolutionary approach to high-temperature furnace design was taken for our carbon furnace. Typical 2000°C furnace design is based on carbon heating elements, graphite felt insulation, and high-amperage (~200A) high-wattage (~20KVA) power supplies [1]. The carbon heating elements must be made with large cross sections to be mechanically robust. This results in a low electrical resistance (~0.1Ω) which requires a high-current power supply. The graphite felt insulation is a fairly poor insulator and as a result the furnace is lossy. The power-loss through the insulation must be compensated for by increasing the size of the power supply. The high currents involved dictate the use of water cooled transformers, power leads and terminals. Finally, the lossy nature of the insulation mandates the use of a water cooled jacket on the outside surface of the furnace. The cost of a typical system is on the order of $30K, half for the furnace and half for the power supply. The installation further requires utilities for both water-cooling and electrical power.

Our proprietary design of a 2000°C furnace incorporates state-of-the-art zirconia-based insulation as opposed to graphite felt. This insulation is more expensive than graphite but has a much lower thermal conductivity. In order to reduce the cost of the insulation, a combination of zirconia followed by alumina-silica has been studied. This "compound-insulation" approach is quit economical so long as the interface between the zirconia and the alumina-silica never exceeds the maximum temperature of the alumina-silica.

We have modeled the temperature gradients and power consumption of various furnace configurations using compound-insulation. A typical result for a 3 inch diameter hot zone is shown in figure 3 [2]. We found that a 1 inch sheath of zirconia, surrounded by 2 inches of alumina-silica (i.e. a 9" furnace diameter), gives a safe interface temperature and a very low power consumption. As shown in the figure, when the hot-zone of the furnace is at 2000°C, the interface is only at 1125°C (the alumina-silica modeled can go as high as 1500°C) while consuming less than 800 watts. As a result, less current is needed to sustain the working temperature and a much smaller power supply can be used. Furthermore, it is no longer necessary to water cool the power leads or the furnace jacket.

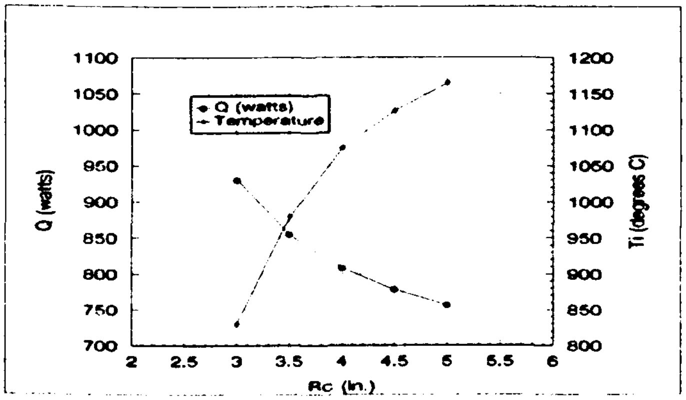

Figure 3. Modeling of a "compound-insulation" 2000°C furnace with a 3 inch diameter by 8 inch long hot-zone. The power consumption and interface temperature are shown as a function of alumina-silica thickness. The hot-zone is at 2000°C and the zirconia thickness is 1 inch.

Our final design was based on these models and is shown in figure 4. The furnace will be able to operate with a flowing internal inert or reducing atmosphere or in a vacuum. It was designed to be compatible with our current product line and will be offered as an option to our crystal growth systems. In order to control the hot-zone temperature, exotic thermocouples such as tungsten-rhenium or boron-carbon must be used. A somewhat more expensive alternative to these is optical pyrometry. The power-supply controller, a modified version of our TCS-2000, will accommodate these various signals.

The construction of the 2000°C furnace was delayed by an 8 week back-order on the zirconia-based insulation. This material is essential to our furnace design and can only be obtained through one supplier [3]. Because the delivery time for the insulation was longer than the remaining time in the Phase I program, it was decided to postpone the construction of the furnace until phase II.

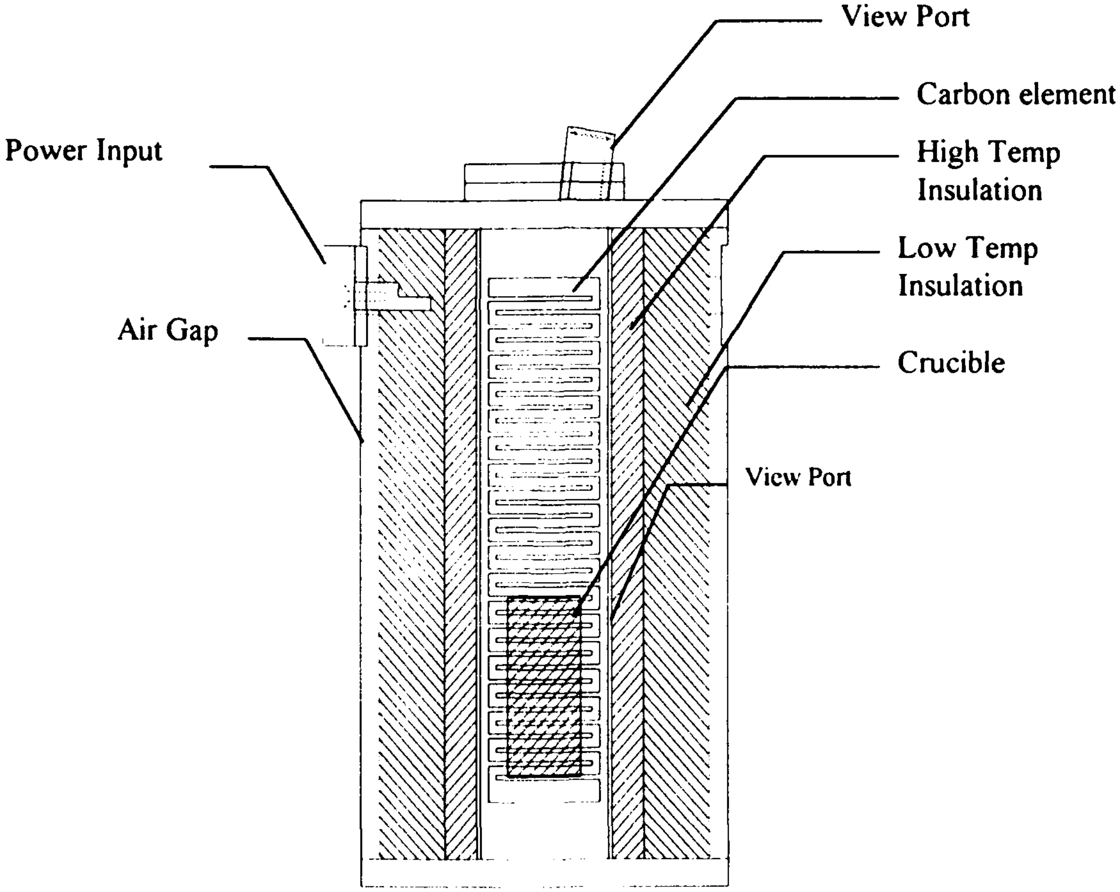

Figure 4. The 2000°C carbon-heated compound-insulated furnace

Task II. Using the furnace system constructed in Task I, produce 1/8-scale SiC-cladded-carbon rods. By using scale models the costs of producing these tests will be significantly reduced without affecting the test data.

Task II Results: The first set of experiments was performed using a melt temperature of 1160°C and a boron nitride crucible. The choice of melt composition was limited to the silicon-rich side of the phase diagram due to high liquidus temperatures (pure silicon melts at 1414°C). All of the runs at 1160°C were therefore copper-rich with varying concentrations of silicon. In each run, the graphite rod was held submerged for 4 hours. No silicon carbide was observed on any of the rods that were immersed at this temperature. It is speculated that a very thin silicon carbide layer formed on the carbon rod when it was introduced into the melt. The temperature dependent diffusion rates of Si and C in SiC are so low at this temperature that the SiC layer formed a diffusion barrier that prevented the further growth of the SiC film [4]. In one run, the temperature was ramped down by 100 C at 10 /hr in order to deposit silicon carbide, from solution, onto the carbon rods. As before, no carbide deposition was observed. The lack of SiC deposition is attributed to the low solubility of carbon in Cu at this temperature. The solubility of carbon in copper is ~0.003 atomic% at 1160°C; this is shown in the phase diagram of figure 5.

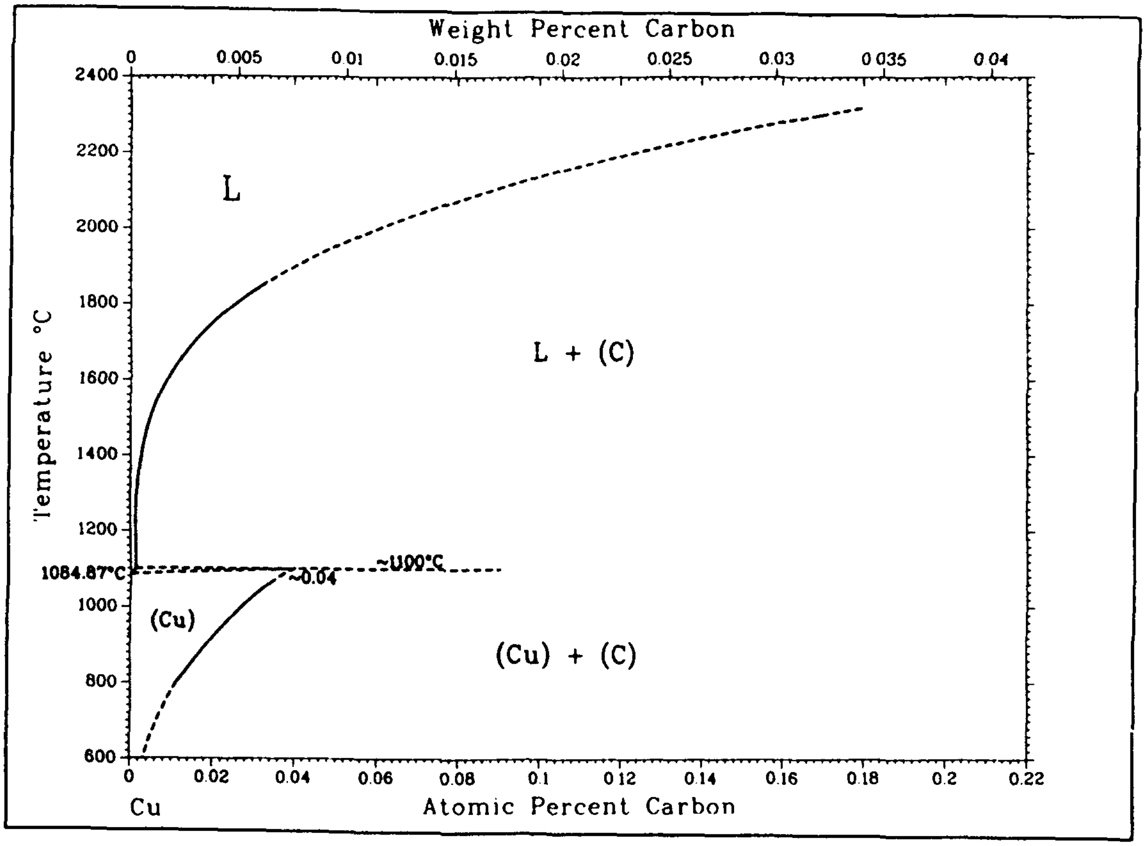

Figure 5. The copper-carbon phase diagram. Taken from ref. 5.

Upon completion of the platinum furnace, a second series of experiments was carried out in the range of 1400 to 1600°C. A new boron nitride crucible was fabricated and charged with a melt composition close to the Cu-Si eutectic (melting point ~800°C). The first run was attempted at 1400°C and a clear glass-like substance was deposited on the carbon rod. The sample was analyzed with EDS, using a light-element window, and the clear material was found to be a borosilicate glass. The only source of boron in the system was the boron nitride crucible and the oxygen is believed to have come from a leak in the bell jar seal. To avoid the future formation of glass, several steps were taken: A new crucible was fabricated out of carbon. The furnace was reassembled to allow the argon to enter just under the melt. Finally the bell jar gasket was cleaned and then held in place with tighter clamps. No borosilicate was observed in any of the subsequent runs.

Using the carbon crucible a Cu-Si eutectic melt, a set of 4hr runs with varying temperature was completed. The temperature was sequentially increased from 1400 to 1600°C in 50°C steps. The first run to show unambiguous evidence of SiC was at 1450°C. The series of runs was interrupted by a furnace winding failure during the run at 1500°C. The furnace was disassembled and the platinum element patched. More insulation was placed around the opening above the crucible in order to reduce the watt-loading of the elements. The heat-up rate of the furnace was also reduced to extend the element life. All the subsequent runs, at temperatures from 1500 to 1600°C, produced SiC cladding.

Upon completion of the above series, three more runs were designed to answer three specific questions. 1) Traces of boron were present when the serendipitous event occurred that produced the first thick SiC cladding. Is the role of boron in the cladding process significant? To answer this, a run was completed at 1600°C in a new carbon crucible using the Cu-Si eutectic but with a small amount of boron added. 2) Since the SiC formation temperature is greater than the melting point of pure Si, can the cladding be done without Cu in the melt? A run was set up at 1600°C using a new carbon crucible and a pure silicon melt. 3) Can the process be carried out in a quartz crucible, similar to the Czochrawlski setup currently used to grow Si ingots? A run at 1550°C was completed using a sealed quartz ampoule and a pure Si melt. The magnetic manipulator was not used in this run.

Task III. Evaluate the material properties of the SiC clad rods. Observe the relationship between the process variables and the resultant SiC films. Both optical and SEM microscopes will be used.

Task III Results: The formation of silicon carbide was confirmed independently by Charles Evans Inc. using a JEOL JSM-5300 EDS (Energy Dispersive X-ray Analysis). The SEM was fitted with a Moxtex super ATW window which allowed elements as low as boron to be detected. Accelerating voltages from 5 kv to 20 kv were used to excite the x rays and produce the images. Both SEI (secondary electron imaging) and BEI (back scattering electron imaging) were used to analyze the produced materials. The EDS analysis confirmed that the crystal formations that were formed on the carbon rods were silicon carbide crystals.

The SEM images of the various 4 hour runs showed that the size and continuity of the SiC film increased with temperature. At 1450°C, the crystallites were ~10μm and had minimal contact area. By 1550°C, a continuous film was formed with a thickness of ~50μm. This is shown in figures 6 and 7. This trend continued to 1600°C where the film thickness is ~100μm and the surface roughness is about half the film depth.

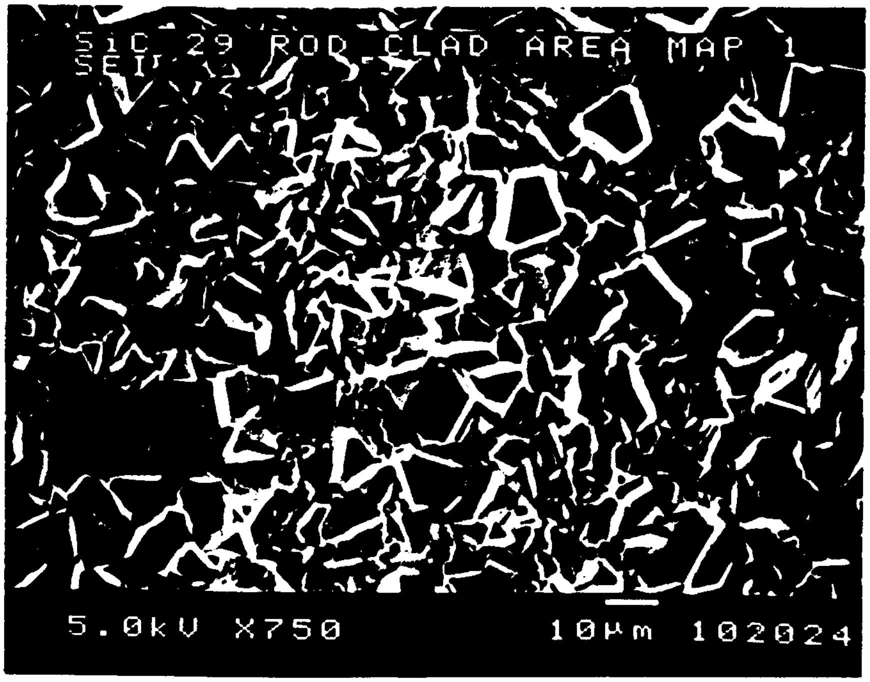

Figure 6. SEM micrographs of the carbide coating formed at 1450°C

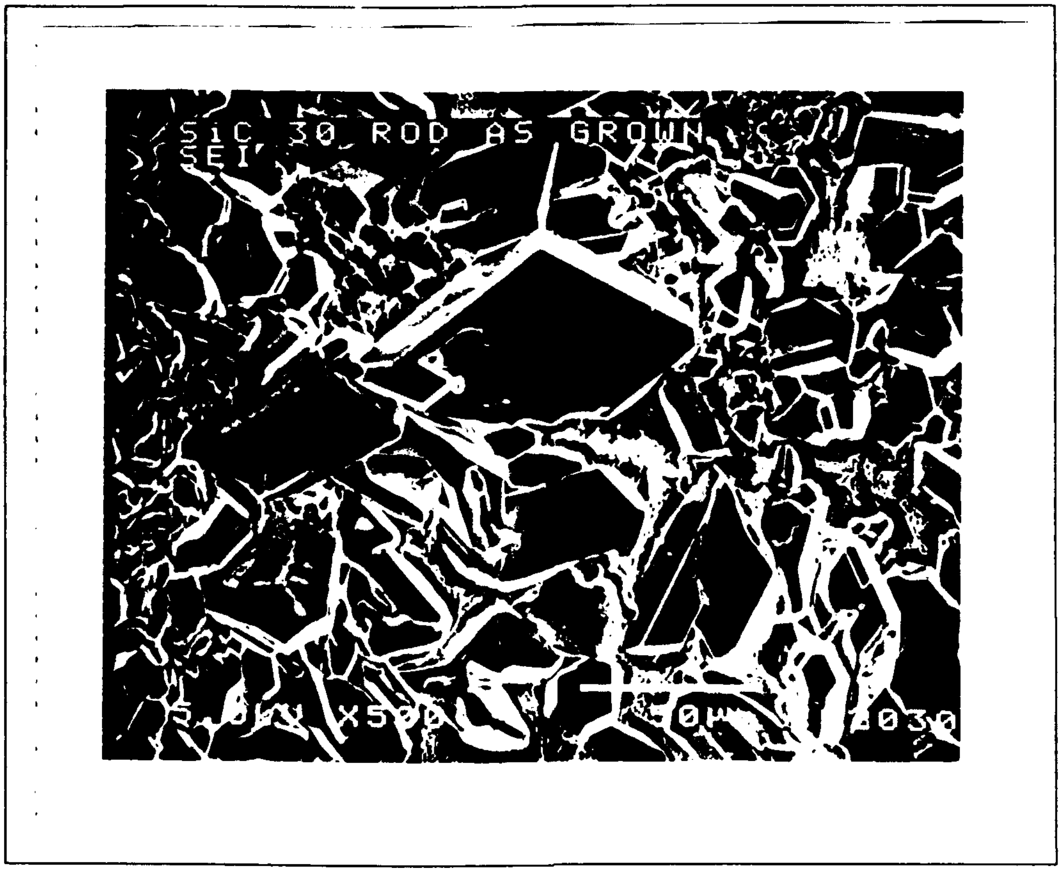

Figure 7. SEM micrographs of the carbide coating formed at 1550°C

Analysis of the run which contained the boron showed no increase in the size or continuity of the SiC film as compared to a boron free control. The only difference was the formation of an occasional grain of BC. The run using a pure silicon melt in a carbon crucible showed the formation of silicon carboxide (probably $Si_2C_2O_2$) at the carbon-SiC interface. The source of the oxygen may have been a small O2 partial pressure in the ambient -- perhaps due to a leak in the bell jar gasket. In any event, a similar run in a copper bearing melt showed no sign of carboxide. This was taken as evidence that the copper is playing an active role by removing oxygen from the SiC reaction zone. This conclusion was further supported by the experiment which enclosed the melt and carbon rod in an evacuated quartz ampoule. This resulted in exaggerated carboxide formation. The fibrous carboxide is shown in the micrograph of figure 8. Although the exact mechanism is not yet understood, the copper in the melt appears to play an essential role in the maintenance of a carboxide-free reaction interface.

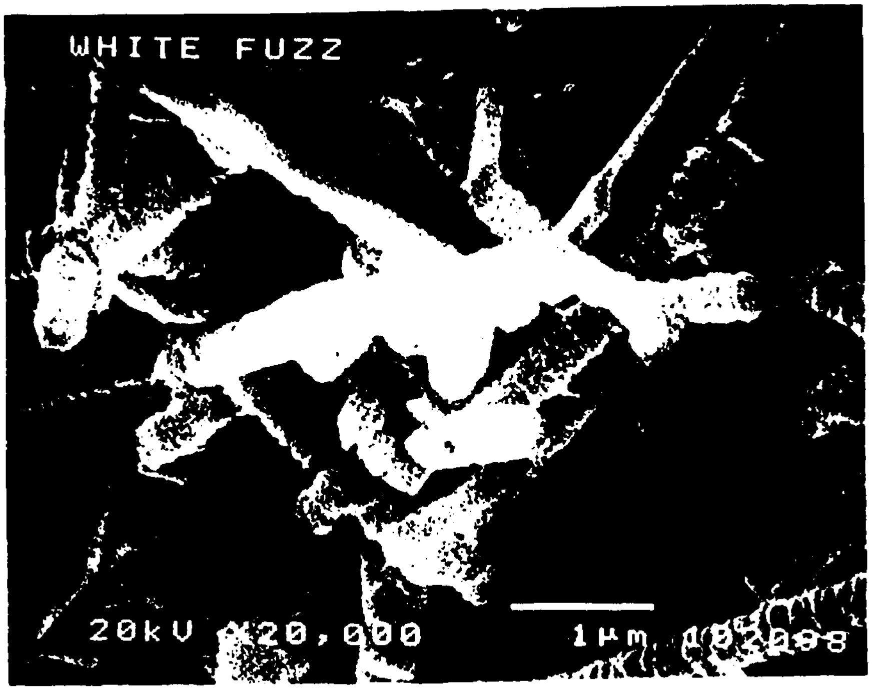

Figure 8 SEM micrographs of the silicon carboxide.

To summarize our observations, the SiC films of the highest quality were formed using the Cu-Si eutectic in a carbon crucible at the highest possible temperature (1600°C) using graphite crucibles. The presence of boron appears unimportant but the exclusion of oxygen is essential. Copper appears to play an active role in removing oxygen from the SiC-graphite interface.

Task IV. Pass a current through the SiC-cladded carbon rods and evaluate their response to high temperatures. Determine maximum surface temperature. Measure rod lifetime for specific surface temperature. Measure rod resistivity as a function of time.

Task IV Results: In order to precisely control the insertion time of the rods, the furnace system was constructed in such a manor as to allow one end of the sample rods to be attached to a lifting mechanism. The use of this procedure prevented the complete insertion of the sample rods. As a result of this sample configuration no sample was completely subjected to the melt. Resistivity measurements, using the three point method, were difficult to interpret because of the film qualities and the presence of the second phases. The presence of copper-silicon compounds made the measurements sensitive to contact placement. The measured resistivity values, however, did indicate that the resistivity of the silicon carbide films was between 2 and 4 times greater than the carbon substrate.

One sample was subjected to elevated temperature in the same way as the ring that was pictured in the phase I proposal. After the sample was heated in air to a maximum temperature of 1500°C for 2 hours, there was no carbon rod left. The silicon carbide layer was not thick enough to be self supporting and collapsed in the crucible used for the test. The silicon carbide layer was not contiguous but did survive the treatment.

In view of the limited thickness and surface roughness of our cladded SiC films, it was decided to reexamine the SiC film that was first made during the accident described in section 1. Electron imaging and EDS analysis revealed that the 2 mm film was indeed void free SiC. A sharp, flat interface separated the underlying graphite and the cladded SiC. There were no voids or extraneous phases at the graphite-SiC interface. Finally, a small concentration (~1%) of boron was detected in the SiC layer and the remaining Cu-Si melt. These results are discussed in the context of the task III results below.

3. Parameters affecting Carbide formation.

The first and most notable system parameter affecting the formations of silicon carbide on carbon rods is that of temperature. In the initial experiments at 1160°C, there was no observable silicon carbide formation on the carbon substrate. As the temperature increased to ~1450°C a discontinuous carbide layer was formed. With further increases in temperature, there is a rapid increase in the film thickness and integrity. It is speculated that the rapid increase in silicon carbide formation at temperatures above 1450° C is attributable to the onset of significant surface diffusion of species on the SiC surface. At even higher temperatures, bulk diffusion of carbon (and to a lesser extent silicon) through the SiC film results in a thicker, more uniform SiC layer.

This is illustrated in figure 9 below. The formation of SiC at 1450°C is dominated by surface diffusion. The resulting film is polycrystalline, highly faceted, and discontinuous. With increasing temperature, bulk diffusion (of both Si and C) becomes dominant and the resulting film is thicker and continuous. At temperatures higher than 1600, it is expected that the film will grow completely flat.

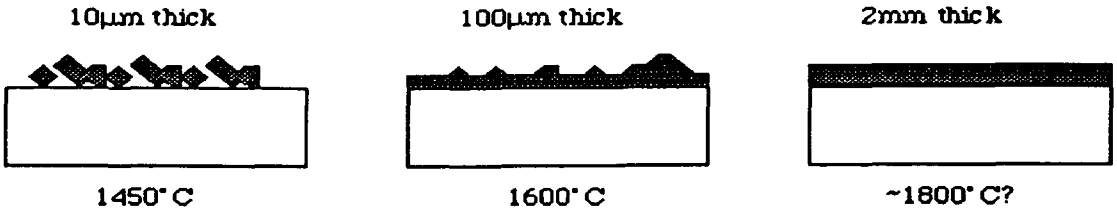

Figure 9. Change in Silicon Carbide film character with temperature

The data collected in phase I clearly indicates that the formation of quality silicon carbide on carbon parts can only be accomplished at temperatures greater than 1600°C. The highest quality films, with the deepest penetration into the carbon were formed at 1600°C. However, even at these temperatures, the film thickness is only 100μm after 4 hrs of growth and the surface roughness is about half the film depth.

A second parameter affecting the quality of the silicon carbide film is the presence of oxygen. We found that any oxygen, whether it be in the form of gaseous oxygen in the furnace ambient, or silicon oxide used for containment, will adversely affect the formation of silicon carbide. It is believed that an adhesion problems encountered on the first few clad rods at 1450°C was due to the formation of a silicon carboxide layer between the carbon and the silicon carbide layer. The presence of this compound was determined using the EDS technique discussed above. This fibrous formation inhibits the adhesion of the silicon carbide to the underlying carbon.

Ironically, the same self-passivating effect that allows the silicon carbide to be usable at high temperatures in an oxidizing atmosphere, here prevents the adhesion of the silicon carbide to the carbon substrate. The role that copper plays in maintaining a carboxide-free growth interface is not understood. Nonetheless, the empirical fact remains: carboxide-free interfaces were only observed when using copper-bearing melts.

4. Estimates of Technical Feasibility

In our phase I work we have clearly shown that we can form a silicon carbide layer on a carbon rod substrate. Silicon carbide has long been used as a resistive heating element. The current manufacturing technology however limits the type and shape the elements can assume. The majority of shapes available are rods or other similarly simple shapes. The rods are made by extruding a slurry of silicon carbide with a binder into the rod shape. Two different formulations are extruded. One will form the low resistance contact ends and the other will form the higher resistance hot zone. Two low resistance portions are joined wet with a higher resistance portion and the whole rod is fired to fuse the segments and the slurry together.

When our process is applied to the heating element production, the higher resistance zone will be made by changing the cross-sectional area of the current path. In the section defined to be the hot zone, several radial grooves are cut into the carbon rod. These grooves are equally spaced and have the effect of reducing the cross sectional area of the current carrying path and increasing the surface area of the heating element. The increased surface area of the heating element will enable greater watt loading without sacrificing service life.

This procedure is particularly suitable to the CAM (computer aided Machining) process. The current industrial rod shaped heating element requirements range in length from 12 inches to 96 inches and greater. Each in turn has a variation in the hot zone length. Every manufacturer has a large number of different sizes that they must produce and maintain in stock. This situation frequently results in customer delivery delay.

Our design will allow the use of computer aided manufacturing. Many different hot zone lengths can be machined from the graphite blanks and be stocked in the unclad condition. Additionally, many end portions of the heating element assembly can similarly be machined and stocked without applying the cladding process. When stock levels dictate, the appropriate sets of hot zones and end pieces will be mated together and clad. Once clad, the assembled unit will look and act as a single rod. Inventory, production time and delivery time will all be reduced. It is estimated that the machining time using this technology will be less than 5 minutes per assembly. These manufacturing improvements should be economically significant when compared to the existing technology.

Another application for the silicon carbide cladding process is the formation of complex parts. Since the starting material is made of graphite, complex such as threaded fasteners (bolts and nuts) can be manufactured. Fabrication of this type of silicon carbide device is not possible using the conventional processing techniques, however by using the cladding technique, we can coat virtually any shape with silicon carbide. By fabricating the required part out of graphite first then cladding the part with silicon carbide, any shape that can be machined can be clad with silicon carbide.

The tasks that are required to be completed, in order to bring this technology into the market place, are related to the understanding of the parameters governing the quality of the SiC layers. They include, but are not limited to, the optimum reaction temperature, the best melt composition and the possibility of pre and post processing the improve the silicon carbide surface and the adhesion to the substrate. A detailed description of these tasks will be included in our phase II proposal.

5. Conclusion

As a result of the phase I research, we have successfully and reproducibly clad SiC films on graphite substrates using copper-silicon melts. During the course of our research we varied the melt composition, temperature and crucible materials. The minimum temperature for silicon carbide formation was determined. The relationship between film thickness and melt temperature was studied. Comparison of cladding runs with varying melt compositions indicate that copper plays an essential role in the formation of void free SiC films.. The importance of complete oxygen exclusion was also found. Unfortunately the thickness and integrity of these films are not yet suitable for commercial use. . It is anticipated, that the use of higher temperatures will yield silicon carbide films suitable for extreme environment applications. To that end, a new high-efficiency high-temperature furnace was designed with a maximum working temperature of 2000° C.

This research has demonstrated that: 1) the presence of oxygen (whether as a gas or as SiO_2) degrades the SiC-graphite interface, 2) copper bearing melts resulted in clean SiC-graphite interfaces, 3) elemental boron does not increase the growth rate of the SiC layer, and 4) higher temperatures result in thicker, smoother, more contiguous films. Based on these observations, it is concluded that thick, smooth SiC films can be made using graphite forms and copper-based melts, but a practical process speed will require temperatures greater that 1600°C.

6. References

1. See for example: Group 1000 - General Specifications, available from Thermal Technology, Inc., Astro furnace division, 1911 Airport Blvd., Santa Rosa CA 95403

2. The model accounts for the temperature dependence of the insulations' thermal conductivity. It assumes an 8 inch long hot-zone (3" diameter) and that the furnace has cylindrical symmetry with end caps of the same composition and thickness as the cylinder. The model assumes that the outside surface of the furnace is a blackbody radiator in still 25°C air.

3. Zirconia insulating board (ZYBF-3) is available from Zircar Products Inc. 110 North Main Street, Florida, NY 10921

4. P. Eveno, J. Li, A. M. Huntz and J. Chaumont, " Diffusion of ^{13}C and ^{29}Si implanted ions in SiC," Materials Science and Engineering **B11,** 331 (1992).

5. *Binary Alloy Phase Diagrams, 2nd ed.,* edited by H. Okamoto, P. Subramanian and L. Kacprzak, (ASM international, Materials Park, OH, 1990), p. 840.