JOURNAL OF MATERIALS SCIENCE **36** (2001) 1389–1394

Thermal cycling of siliconized-SiC at high temperatures

P. A. LESSING, A. W. ERICKSON, D. C. KUNERTH
Idaho National Engineering & Environmental Laboratory, INEEL Research Center, 2351 North Boulevard, Idaho Falls, Idaho 83415-2218, USA
E-mail: pal2@inel.gov

Thermal cycling (between 1340 °C and 1480 °C) experiments were conducted using two types of reaction-bonded (siliconized) silicon carbide. A commercial material (Crystar^{TM}) and various silicon carbide pieces that had been joined together using electrophoretic deposition (EPD) followed by reaction bonding were evaluated. During the thermal cycling, residual "free" silicon metal rapidly vaporized from the Crystar^{TM} and cracks developed within its large SiC grains. In contrast, the EPD/reaction-bonded silicon carbide joints did not lose an observable amount of their residual silicon nor develop cracks. The reduced loss was attributed to reduced silicon content with the silicon residing largely in closed pores of the EPD layer. Reduced vaporization of the silicon that resided in surface-connected pores was engineered by applying a thick SiC surface coating. The morphology of the resulting coating was microscopically evaluated and two sequential growth mechanisms were postulated. An implication of this research is that hermetic (gas-tight) joints could be formed using EPD-derived SiC as a filler material. © *2001 Kluwer Academic Publishers*

1. Introduction

Certain high-temperature applications for ceramics could utilize joined parts to fabricate large and/or complex structures (e.g. a ceramic heat exchanger). A good candidate material for these type of applications is 'silicon carbide". Choices for "silicon carbide" include materials that were fabricated using either sintering, chemical vapor deposition (CVD), or reaction bonding using molten silicon. It has been demonstrated that any of the silicon carbide-based materials can be joined using different variations of reaction bonding [1, 2, 3]. For service conditions that include exposure to temperatures near (or above) the melting point of silicon, critical concerns exist for both reaction-bonded (siliconized) bulk SiC and reaction-bonded joints. These concerns include low creep resistance and loss of hermeticity associated with the level of residual "free" Si found in the part and/or the joint. This study was instituted to examine the high temperature loss of residual Si due to vaporization and determine if any remedial steps could be taken to reduce or eliminate the Si loss.

2. Experimental procedures

The reaction-bonded (siliconized) bulk SiC material used in this study was "Crystar^{TM} Si/SiC" [4] that had (according to company literature) a large grain size, 3.05 g/cc density, with a 170 MPa bend strength at room temperature, and contained 13–15 vol % residual Si. The Electrophoretic Deposition (EPD) technique was chosen to place SiC filler and carbon powder precursors into the joint between pieces of reaction-bonded SiC. EPD allows particles to be directly deposited from a liquid/powder slurry [5]. We have demonstrated that the use of EPD with optimized slurry formulations can result in a very densely packed powder layer (coating on one piece) that minimizes "free" silicon after the reaction bonding process [6]. The optimized EPD slurry used had a SiC : C ratio of 1.28 : 1 comprised of 37.3 w % Carbon black [7], 8.0 w % graphite [8], 23.9 w % Cerac SiC [9], and 23.9 w % Starck A-1 SiC [10] with 6.8 w % organic binder. These powders were mixed with a liquid consisting of 90 vol. % acetone [11] mixed with 10 vol. % *n*-butylamine [12] to make a slurry. The *n*-butylamine increases the base character of the surface of the powders (negative charge on the powder particles) via proton-exchange reactions. This results in a negative direction of electrophoretic mobility, where both SiC and C particles are deposited on the positive electrode (piece of reaction-bonded SiC). The voltage used was 20 volts. The solids were added to 200 ml of the liquid and the organic binder was added as weight percentage of solids content in the mixture. After the EPD process the coating was dried and the coated piece held in close proximity to an uncoated piece. Powdered Si metal was placed at the perimeter of the joint and the assembly heated to a high temperature. The reaction bonding took place at 1450 °C in an inert gas (helium) atmosphere where molten silicon ($T_m \sim 1410$ °C) wicked into the packed powder layer and reacted with the carbon black and graphite. The reaction bonding process took approximately 15 minutes.

After reaction bonding, some samples were exposed to a methane-bearing atmosphere at a high temperature

0022–2461 © *2001 Kluwer Academic Publishers*

(1390 ± 5 °C) in an effort to react with the "free" Si to form new SiC at the surfaces and thus restrict the vaporization of any underlying Si. The atmosphere used was a flowing gas mixture of 95% Ar + 4% H_2 plus 1.0% CH_4. The Si metal [13] used for reaction bonding was of 99.9995% purity.

After joining, standard petrographic techniques were used to cut and polish cross-section samples for optical microscopy. A "Bausch & Lomb Research II Metallograph" was used to take photographs at up to 400× magnification. Some photographs were then converted into digital images at 300 pixels per inch, using a "Hewlett Packard ScanJet 6100 C" image scanner. The digital images were analyzed using "Image Pro" software [14] on a personal computer (Microsoft NT operating system). The samples were analyzed (on an area percentage basis) for different phases (e.g. SiC, Si, and porosity). Some samples were etched to reveal grain boundaries using a molten mixture of KOH and 10 w % KNO_3 at 450 °C. This hot chemical etch also removed residual "free" Si metal.

After joining and/or exposure to the methane gas, joined pieces were then exposed to 42 thermal cycles (1340 °C to 1480 °C) during about 100 hours in an inert gas (helium) atmosphere. The number of cycles was the maximum allowed by the particular programmable controller that was used.

3. Results

A typical microstructure for as-received Crystar^{TM} SiC is shown in Fig. 1, where the residual "free" Si (lightest colored phase) was measured at 14.55% using image analysis. The microstructure resulting from thermal cycling tests of Crystar^{TM} is shown in Fig. 2. Fig. 2 shows cracks (possibly enlarged by the repeated freeze-thaw cycles of the test) and the complete loss of Si from the larger (likely interconnected) pores. Some Si remained in the smaller (possibly isolated) pores. The surface of the sample was coated with a deposit identified as SiO_2 (using X-ray diffraction).

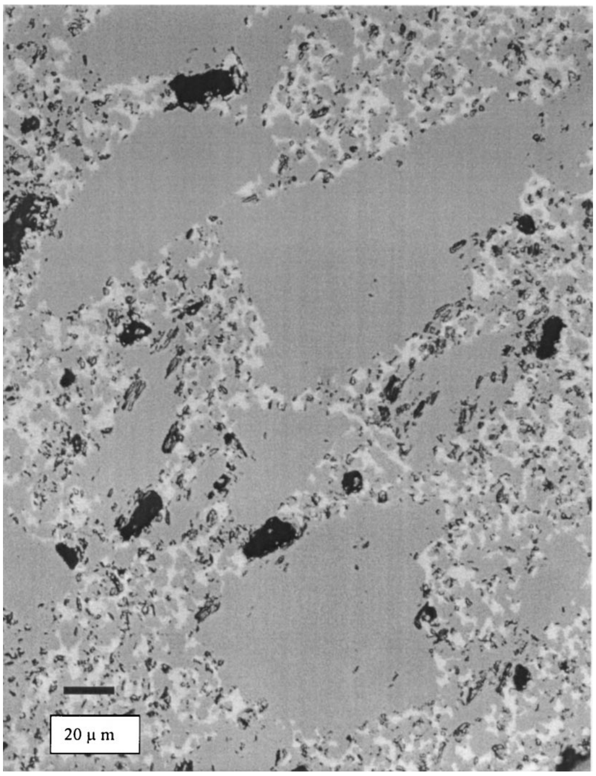

Figure 1 Microstructure of Crystar siliconized SiC (533× magnification). Image Analysis: 14.55% Si, 8.10% Porosity, 77.15% SiC.

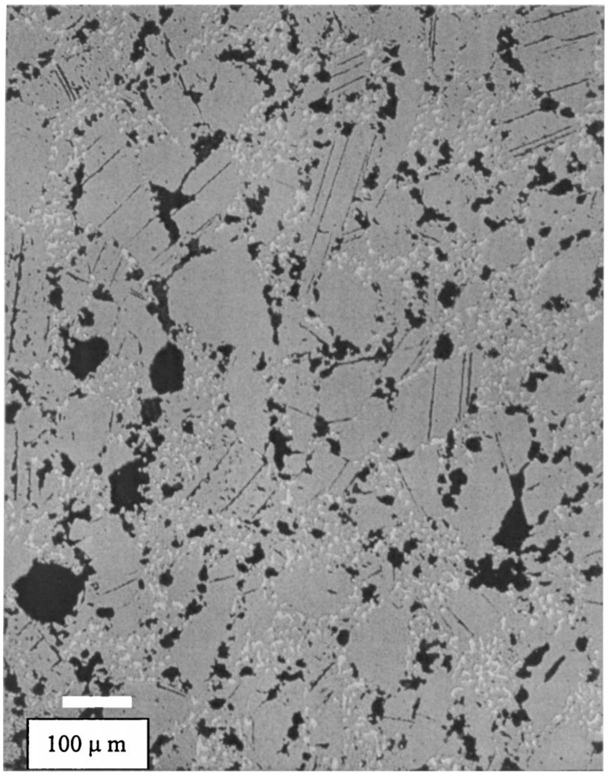

Figure 2 Crystar SiC after thermal cycle test (100× magnification).

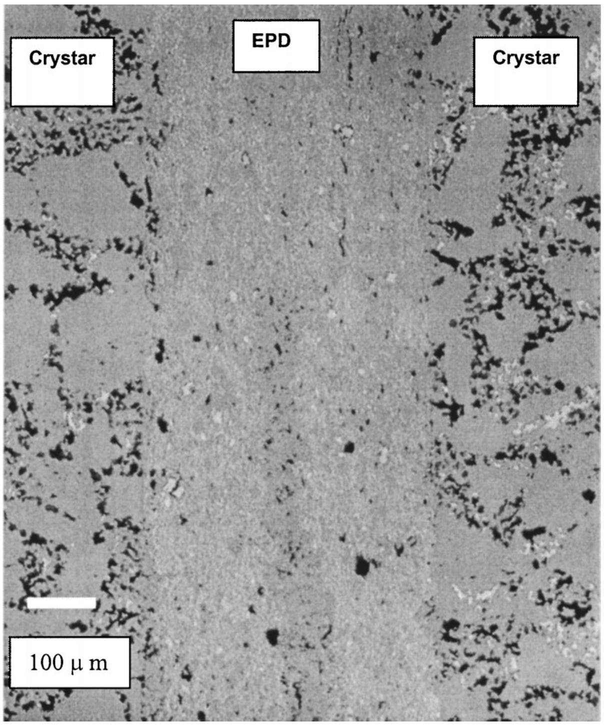

Figure 3 Crystar SiC pieces joined by EPD process (after thermal cycling test, 100× magnification).

Fig. 3 shows the microstructure of Crystar^{TM} pieces that were joined using the EPD process and then thermal

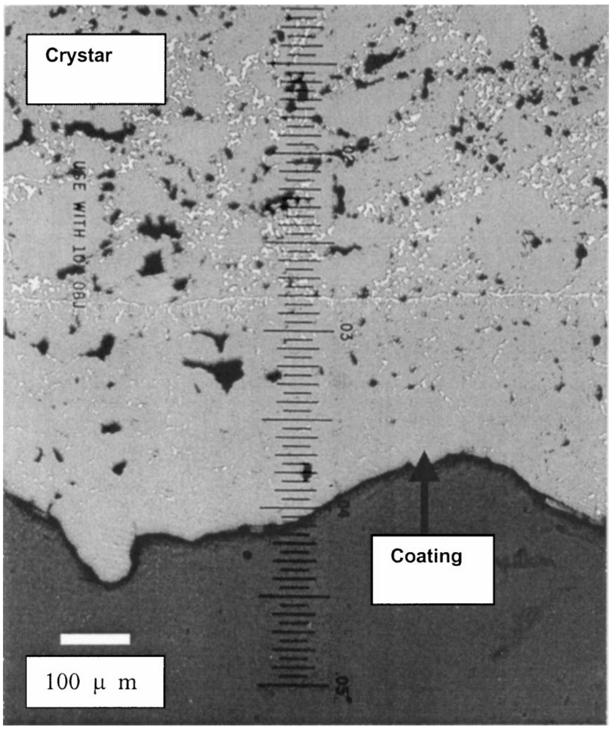

Figure 4 Edge of Crystar SiC after exposure to CH$_4$ containing gas atmosphere (100× magnification).

cycled. Fig. 3 is a representative area of the cut and polished cross-section of the joint, where the central portion (consisting of much finer grains) resulted from the reaction bonded EPD layer. The residual Si was almost entirely gone (vaporized) from the Crystar$^{\text{TM}}$, again resulting in dark colored pores. However, the residual "free" Si (light colored specks) largely remained in the EPD layer.

Fig. 4 shows the microstructure resulting from the exposure of Crystar$^{\text{TM}}$ siliconized SiC to the methane-containing gas at high temperature. This extremely interesting result shows a very thick (varied from 711 to 1029 μm) coating of new SiC that was deposited beginning at a line of residual "free" Si at the original surface boundary of the Crystar$^{\text{TM}}$. Connected to the exterior-side of the original boundary are thin perpendicular "fingers" of "free" Si (interspersed with SiC) extending toward the surface, followed by a thicker SiC layer that progressively shows a rapidly diminishing amount of "free" Si. Fig. 5 shows the outermost regions of the newly formed SiC layer where the "free" Si content was measured to be only 0.70%.

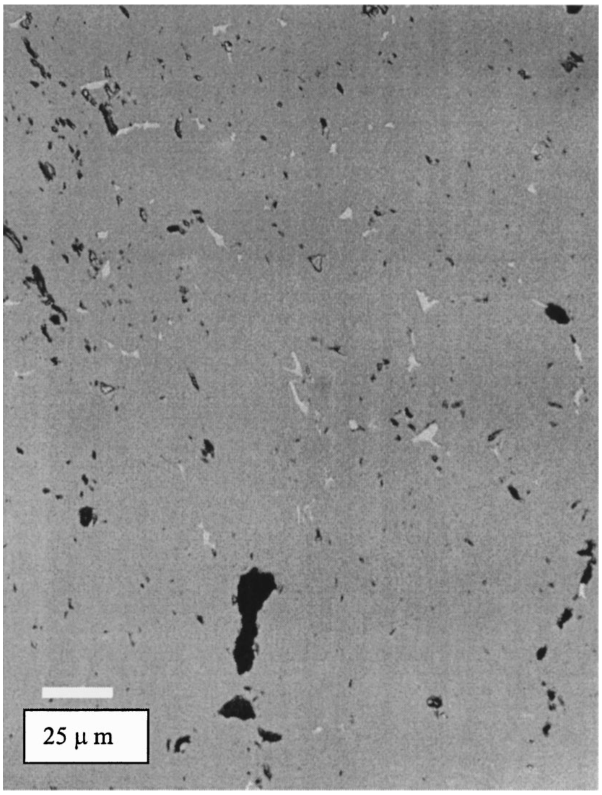

Figure 5 Outer region of deposited SiC layer (400× magnification). Image Analysis: 0.70% Si, 1.71% Porosity, 97.59% SiC.

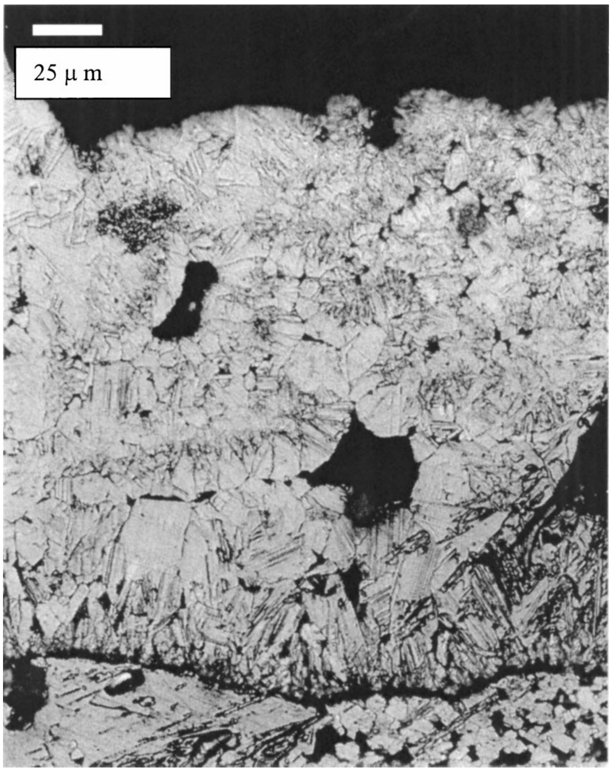

Figure 6 Etched micrograph of coating grown during exposure to methane containing atmosphere (400× magnification).

Fig. 6 shows an etched microstructure of the SiC layer formed on Crystar$^{\text{TM}}$ by exposure to the methane-containing atmosphere. All of the Si was removed by the chemical etch making it somewhat difficult (in some cases) to distinguish between empty space left where Si was removed and porosity (that was present prior to etching). The etched microstructure revealed the Crystar$^{\text{TM}}$ SiC at the bottom of the figure with a line of "free" Si (definitely removed by etch) with a well-defined row of columnar SiC grains oriented perpendicular to the Crystar$^{\text{TM}}$ surface. Also visible are two or three other definable rows of columnar SiC grains that had been (prior to etching) separated by the thin "fingers" of "free" Si. Each row of columnar grains was associated with either a line or large pocket where "free" Si could have resided. These secondary lines of "free" Si are well removed from the original interface; suggesting that molten Si migrated from within

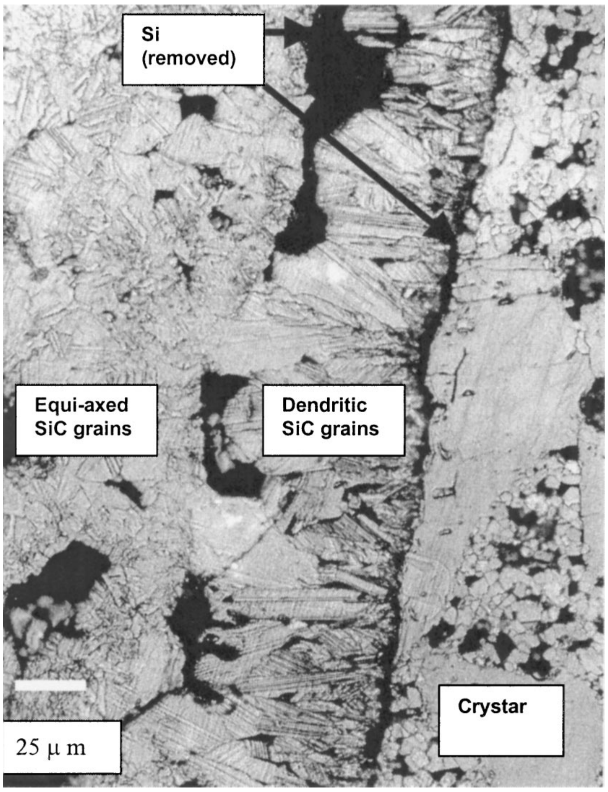

Figure 7 Etched micrograph of coating grown during exposure to methane containing atmosphere (400× magnification).

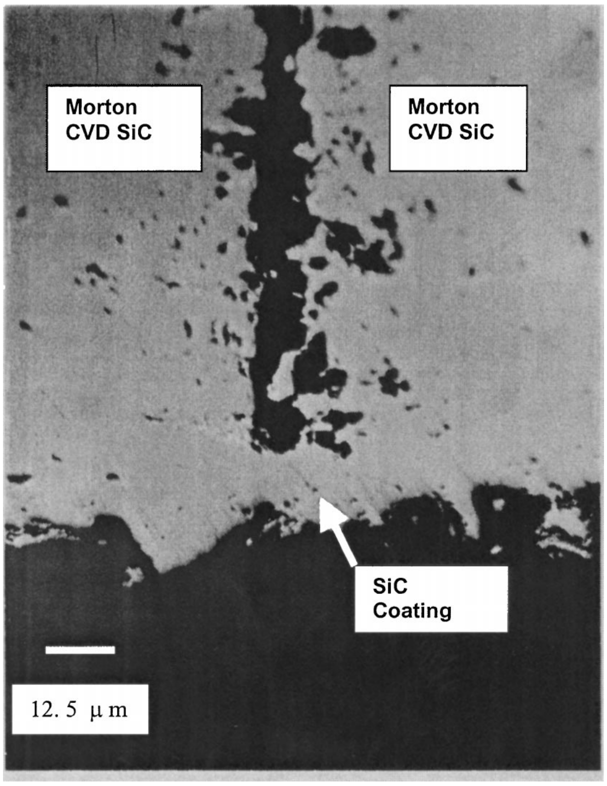

Figure 8 Micrograph of SiC coating grown over Si join of two morton CVD Silicon Carbide^{TM} plates (800× magnification).

the Crystar^{TM} body. Eventually, the columnar grains give way to more randomly orientated and equi-axed grains (with little "free" Si being present).

Another etched microstructure is shown in Fig. 7 (where some of the structures are labeled). This micrograph clearly shows the dendritic-morphology SiC grains originating from a line of "free" Si at the interface. It also shows thin channels of "free" Si along the length of the dendritic grains that lead to large pockets. These large pockets could have contained "free" Si and/or were large pores. At the outer (to the left) boundaries of these pockets there tends to be another layer of shorter dendritic grains that indicates that at least a surface layer of Si existed within the pore. At the far left, the Si largely disappears and the grains are more equi-axed and randomly orientated.

When an EPD layer was used to join two Crystar^{TM} substrates and then subjected to the methane-containing atmosphere a new layer of SiC not only coated the surfaces of the Crystar^{TM} substrates but also bridged over the outer edge of the EPD joining material. Even when there was an excess of high-purity residual "free" Si between the EPD layer and the Crystar^{TM} substrates; the new SiC also bridged over the high-purity Si layer. This is evidence that the high-purity Si probably did not significantly sublime or melt and vaporize at the 1390 °C temperature of the methane experiment. Fig. 8 further substantiates this observation by showing two substrates of Morton CVD Silicon Carbide^{TM} that were joined using only a very thin layer of high purity silicon (no EPD) that was subsequently exposed to the methane-containing atmosphere at 1390 °C. Fig. 8 clearly illustrates that the SiC coating will bridge over high purity silicon. The SiC coating is much thinner than with the Crystar samples; this can be attributed to the source of the Si vapor being from remote Crystar^{TM} samples rather than from the high purity Si contained in the local region of the examined joint. The silicon layer appears to be missing from Fig. 8; however, further examination determined that the Si at the surface was removed during the polishing process and actually was present in the join prior to the chemical etch procedure.

4. Discussion of results

The thermal-cycle test, using Crystar^{TM} (siliconized SiC), clearly showed that "free" Si was quickly lost from the large interconnected porosity of the sample at temperatures near (above and below) the melting point of high-purity Si. It was assumed that the loss was due to vaporization because the upper temperature (1480 °C) of the cycle was 70 degrees over the accepted melting point for Si (1410 °C). The repeated freezing and thawing during the thermal cycle also led to fracturing of the large SiC grains within the Crystar^{TM}.

When Crystar^{TM} was exposed to the methane-containing atmosphere at 1390 °C, the microstructural evidence suggests that two sequential mechanisms of SiC growth occurred at the surface. The first mechanism appears to be a vapor-liquid-solid mechanism illustrated by Equation 1. The carbon from the methane gas dissolved in the liquid Si, saturated and then solid SiC precipitated and grew as dendritic type SiC crystals (with a preferred crystal orientation). The secondary lines and pockets of "free" Si appear to be evidence that molten Si moved (due to capillary action) through the first line of dendritic SiC grains and another layer of dendritic grains began to form at the outer surface of the pockets. The microstructure evidence suggests that the Si found in the Crystar^{TM} is a lower purity material that probably melts or sublimes rapidly below 1390 °C. The growth process might be similar to the Lanxide DIMOX^{TM} process for oxidation of aluminum [15]. In the Lanxide process, molten aluminum wicks through the pores in a "crust" layer of aluminum oxide to form a secondary layer of aluminum and the oxidation process again occurs. The oxidation takes place in a series "waves" that sweep across the surface of the sample.

$$\text{Si (l)} + \text{CH}_4\text{ (g)} \rightarrow \text{SiC (s)} + 2\text{H}_2\text{ (g)} \qquad (1)$$

In an effort to better understand the first growth mechanism, Differential Thermal Analysis (DTA) was conducted on a small Crystar^{TM} sample and on the high purity Si used for the reaction bonding. The DTA showed a melting point of 1410.54 °C for the high purity Si and 1404.03 °C for the Si in the Crystar^{TM}. The 1410 °C value exactly matches the accepted melting point for high purity Si, however, the 1404 °C value for the lower purity Si (in the Crystar^{TM}) is still above the 1390 °C measured for the furnace temperature. This leads to two possibilities: (1) the furnace temperature measurements were slightly in error and the actual process temperature really was above 1404 °C, or (2) the "free" Si that appeared within the new SiC coatings was deposited via a mechanism different from the postulated liquid phase mechanism. A possible mechanism is that Si moves via a rapid surface diffusion.

The second sequential SiC growth mechanism appears to be a heterogeneous nucleation and growth process at the surface without the benefit of a condensed Si phase. This would be a standard vapor-solid type of chemical vapor deposition (CVD) process as illustrated by Equation 2 coupled with Equation 3.

$$\text{Si (s or l)} + 2\text{H}_2\text{(g)} \rightarrow \text{SiH}_4\text{ (g)} \qquad (2)$$

$$\text{SiH}_4\text{ (g)} + \text{CH}_4\text{ (g)} \rightarrow \text{SiC (s)} + 4\text{H}_2\text{ (g)} \qquad (3)$$

Other CVD reactions might have occurred and Equations 2 and 3 are merely illustrative. However, the presence of 4% hydrogen in the feed gas strongly suggests the generation of SiH_4 (silane) gas according to Equation 2. Since the CVD portion of the SiC layer was extremely thick (on some samples), there obviously was a continual gaseous source (containing Si) available. This gas originating from large Crystar^{TM} pieces, probably from regions that were not sealed by the coating (e.g., from the bottom of the sample, where it sat on a sample holder). Since SiO_2 was identified on one of the Crystar^{TM} sample surfaces, the question arises if the SiO_2 would be expected to play a role in SiC formation in the methane treated samples. The amount of surface SiO_2 was quite small when compared to the amount of "free" Si that was transported from the volume of the Crystar reaction-bonded SiC. Therefore, we think that the primary vapor specie was SiH_4 with a lesser amount of Si (g). However, other vapor species, including SiO (g) probably were present since the equilibrium concentration of SiO (g) depends upon the temperature and the amount of water vapor that is present.

In addition to Equation 2, Si transporting species of SiH_4, Si (g), and SiO (g) can also be generated by the following reactions:

$$\text{SiO}_2\text{ (s)} + \text{H}_2 \rightarrow \text{SiO (g)} + \text{H}_2\text{O} \qquad (4)$$

$$\text{SiC} + 2\text{H}_2 \rightarrow \text{Si (g)} + \text{CH}_4 \qquad (5)$$

$$\text{SiC} + 4\text{H}_2 \rightarrow \text{SiH}_4 + \text{CH}_4 \qquad (6)$$

$$\text{SiC} + 2\text{H}_2\text{O} \rightarrow \text{SiO (g)} + \text{CO} + 2\text{H}_2 \qquad (7)$$

$$\text{Si (s)} \rightarrow \text{Si (g)} \qquad (8)$$

$$\text{Si (l)} \rightarrow \text{Si (g)} \qquad (9)$$

The reduction of silica by hydrogen can produce SiO (g) per reaction 4. SiC can also be reduced, with reaction (7) being favored over the reduction reactions 5 and 6, if there is water vapor available.

Relevant information can be obtained from Hallum and Herbell [16] who give equilibrium concentrations of various gas species as a function of temperature in both a "dry" system and a system containing 10 moles of SiC, 100 moles of hydrogen, and an initial amount of 25 ppm water.

For the "dry" system, Hallum and Herbell show that SiH_4 (g) predominates up to about 1400 °C where Si (g) production catches up and at about 1400 °C both species have about equivalent concentrations. Even for pure SiC, Si (g) begins to predominate above 1500 °C. Even higher concentrations of Si(g) would be expected for siliconized SiC because of the presence of "free" Si that can sublime [per Equation 8] and after it melts at 1410 °C according to Equation 9 since molten Si has a very significant vapor pressure.

For the pure SiC system with some moisture, Hallum and Herbell calculations show that at low temperatures (700–900 °C) SiH_4 has the highest concentration, however, from 900–1400 °C SiO (g) has a higher concentration than SiH_4. Si (g) increases in concentration until it becomes very significant over about 1400 °C.

Our CVD process took place at a maximum temperature of 1390 °C. Therefore, if there was some moisture present, we would expect transport of Si (to the CVD surface) via both SiH_4(g) and SiO (g) during the heat-up stage, with SiO (g) becoming exhausted when the SiO_2 surface coating was consumed. After the SiO (g) disappears, we would primarily expect SiH_4 transport with a lesser amount of Si (g) transport (at the 1390 °C "CVD" temperature).

5. Conclusions

"Free" Si metal rapidly vaporizes from siliconized SiC (Crystar^{TM}) during thermal cycling at temperatures below and above the melting point of the Si (1340 °C to 1480 °C). The thermal freeze/thaw cycling also opened up cracks within the large SiC grains in Crystar^{TM}. Vaporization of the Si from Crystar^{TM} potentially could be inhibited by a thick SiC surface coating that results from exposing the Crystar^{TM} to a methane plus hydrogen bearing atmosphere at 1390 °C. This coating is postulated to result from two sequential processes. The first process could involve a vapor-liquid-solid mechanism and the second a vapor-solid type of reaction. The presence of a Si liquid phase during the coating process is uncertain because the melting point of the Si in Crystar^{TM} was measured to be 1404 °C (14 degrees higher than the measured furnace temperature). However, there may have been an error in the measured furnace temperature. The deposition processes should be the subject of a more detailed investigation.

For reaction-bonded (siliconized) SiC that was fabricated using electrophoretic deposition (EPD), Si metal was not rapidly vaporized during thermal cycling (at temperatures below and above the melting point of the Si). This was attributed to a reduced "free" Si content (as low as 7 vol %) in the EPD-derived samples and microscopic observations indicating that the Si in the EPD samples resided largely in closed pores.

Relatively thick SiC coatings can be formed directly on the top of thin, high-purity Si metal joints or layers. An implication of this research is that hermetic (gas-tight) joints can be formed using EPD-derived SiC as a filler material. These joints should retain their hermeticity at temperatures above the melting point of Si because the Si in the EPD material resides primarily in closed pores. The hermeticity can also be enhanced by the use of a "seal" coat deposited over the outer joint region (by using a methane plus hydrogen treatment atmosphere in conjunction with a suitable vapor source containing Si). This coating can seal the outer surfaces of any thin, continuous layers of residual "free" Si that may be present at interfaces between EPD-derived SiC joints and SiC parts.

Acknowledgements

This work was supported by the U.S. Department of Energy, under DOE Idaho Operations Office Contract DE-AC07-99ID13727.

References

1. B. H. RABIN, *Mater. Sci. Eng.* **A230** (1990) L1.
2. M. SINGH, *J. of Mater. Sci. Lett.* **17** (1998) 459.
3. B. H. RABIN and G. A. MOORE, *J. Mater. Synthesis and Proc.* **1** (1993) 195.
4. Norton/St. Gobain Electronics, 1 New Bond Street, Worcester, MA 01615-0136.
5. P. SARKAR and P. S. NICHOLSON, *J. Am. Ceram. Soc.* **79** (1996) 1987.
6. P. A. LESSING, A. W. ERICKSON and D. C. KUNERTH, *J. of Mater Sci*., accepted.
7. Carbon Lampblack # C-198, Fisher Scientific Co., 711 Forbes Ave., Pittsburg, PA, 15219.
8. Grade 7 × 99 from Cummings-Moore Graphite Co., 1646 North Green Ave., Detroit, MI, 48209.
9. Cerac Grade # S-1169 (10 micron measured mean particle size), Cerac Inc., Box 1178, 407 N. 13th St., Milwaukee, WI, 53233.
10. C. HERMANN, Starck Inc., 280 Park Avenue, New York, N.Y., 10017.
11. Dimethyl ketone product # A18-4, Fisher Scientific Co., 711 Forbes Ave., Pittsburg, PA, 15219.
12. Butylamine, 99% Product # B8,898-5, Aldrich Chemical Co., 1001 West St. Paul Ave., Milwaukee, WI, 53201.
13. Silicon Lump <5 cm, 99.9995% (incl. 20–20000 ppm Sb), Lot # L03D08-ECMS# 02310, Alfa Aesar Chemical Company, 30 Bond Street, Ward Hill, MA 01835-8099.
14. Media Cybernetics L.P., 8484 Georgia Avenue, Silver Spring, MD, 20410 (phone 301-495-3305).
15. M. S. NEWKIRK and J. WEINSTEIN, U.S. Patent No. 4,826,643 (1989).
16. G. W. HALLUM and T. P. HERBELL, *Advanced Ceramic-Materials* **3**(2) (1988) p. 171.

Received 22 November 1999
and accepted 24 May 2000