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COATING OF GRAPHITE WITH SILICON CARBIDE BY
REACTION WITH VAPOR OF CONTROLLED SILICON ACTIVITY

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COATING OF GRAPHITE WITH SILICON CARBIDE BY REACTION WITH VAPOR OF CONTROLLED SILICON ACTIVITY

John M. Blocher, Jr., Don P. Leiter, Jr., and Robert P. Jones

In the reaction of silicon halides with graphite to form silicon carbide, thermodynamic conditions were determined for the formation of SiC, free of elemental silicon. The use of these conditions was designed to limit the rate of coating formation by the rate of diffusion of carbon through the coating, and render the operation independent of the vapor-flow factors which normally limit the uniformity of vapor-deposited coatings.

Although a wide range of pressure-temperature-composition conditions was explored, it was not possible to duplicate the success previously obtained in applying the method to NbC, TaC, TiC, and ZrC coatings. Fundamental differences in the characteristics of the carbides which may account for the difference in behavior are the lack of a range of homogeneity in beta SiC crystal structure, and the fact that SiC undergoes a modification from the cubic beta to a hexagonal form at 1900 to 2000 C.

There remains the prospect of forming a uniform SiC "sponge" by the present process which can be subsequently impregnated with metallic silicon to form an oxidation-resistant coating.

INTRODUCTION

The oxidation resistance of silicon carbide is well known, and it has been recognized that a truly impervious coating of SiC on graphite would protect the graphite from oxidation at elevated temperatures. The potential advantages of applying the coating by vapor-deposition techniques have also been recognized, i. e., construction of the coating on a molecular scale should enhance the surface conformity and uniformity of the coating. The vapor deposition of SiC and other coatings is discussed in a recent book.⁽¹⁾

Vapor-deposition processes, as normally carried out, have the disadvantage that the rate of coating formation depends upon a diffusion-controlled mass-transfer mechanism in the vapor phase and is, therefore, influenced strongly by the mass-flow characteristics of the vapor. To offset this disadvantage in coating the inside bore of long graphite tubes with NbC, TaC, and ZrC, a procedure was developed at Battelle^(2, 3, 4) in which the rate of deposition of the carbide coating was made dependent upon the rate of diffusion of carbon from the graphite base to the surface of the coating. In this way, the rate of coating formation was primarily a function of temperature and independent of vapor-flow conditions over a wide range.

(1) References at end.

The present research was undertaken with the thought that this procedure would have advantages in applying uniform SiC coatings to complex graphite shapes.

The principle of the choice of conditions for this process can be understood by reference to the deposition of a metal by thermal dissociation of its volatile halide. Figure 1 shows the effect of halide pressure on the efficiency of deposition of niobium from the pentahalide on a niobium surface at a given temperature. At very low pressures, where the rate of evaporation of niobium from the surface exceeds the rate of collision of halide molecules with the surface, a net loss of niobium occurs. At higher pressures, deposition of metal occurs by thermal dissociation of the halide and, if the halide NbX_5 were the only stable gaseous species containing niobium, the efficiency would go to zero asymptotically with increased pressure of halide vapor feed, as indicated by the dashed line. However, because of the stability of gaseous lower halides, such as NbX_2 and NbX_3 , a limiting pressure exists for each temperature above which the formation of lower halides predominates, and metal is lost from the surface in a "chewing" process. It was hypothesized, and later confirmed experimentally and by thermodynamic considerations, that a limiting pressure exists at a higher level for the formation of a metal carbide by reaction of the metal halide vapor with carbon:

If one carries out the coating process, for example, in the shaded area shown in Figure 2, the coating can form only as rapidly as carbon diffuses from the base through the coating to meet the halide atmosphere. As long as the halide is supplied to the surface at a sufficient rate to prevent its being depleted appreciably, the diffusion of carbon through the carbide can be made the rate-limiting mechanism.

In prior work at Battelle, it was possible to obtain the proper conditions by suitable control of the temperature of the graphite surface and the pressure of a given halide feed. However, in the case of SiC formation, the relative stabilities of the halides were such that, to operate at a convenient pressure, it was desirable to use mixed halides of controlled composition as a means of controlling the activity of silicon in the vapor.

DETERMINATION OF COATING CONDITIONS

The technique for determining the conditions for metal-free carbide formation was similar to that used in the earlier work. However, no effort was made to determine the pressure above which neither metal nor carbide would be deposited. It was thought sufficient to determine the limiting conditions for the deposition of free metal and then, in the coating experiments, to explore the area on the carbide side. Figure 3 gives the conditions for metal-free SiC deposition from SiI_4 as calculated from the data of Schäfer and Morcher⁽⁵⁾ and the thermodynamic relationship derived in References (2) and (3). These results have been confirmed experimentally in other unpublished work at Battelle. It can be seen that, to operate at convenient pressures of 1 atm or below, one would be limited to temperatures in the range of 1400 C, where the rate of diffusion of carbon through SiC should be prohibitively slow.

Since SiI_4 is too unstable for this application, conditions were explored for the deposition of SiC from the more stable bromide. However, it was found necessary, for

FIGURE 1. EFFECT OF HALIDE PRESSURE ON DEPOSITION EFFICIENCY

FIGURE 2. CONDITIONS FOR METAL-FREE NbC FORMATION IN REACTION OF $\text{NbCl}_5(\text{g})$ WITH GRAPHITE

FIGURE 3. CONDITIONS FOR METAL-FREE FORMATION OF SiC BY REACTION OF SiI₄ WITH GRAPHITE

example, to reduce the pressure to 0.1 mm of mercury to obtain SiC at 1900 C. At temperatures above 2000 C and pressures of the order of 1 mm of mercury and above, graphite rapidly deteriorated in the SiBr₄ atmosphere. Therefore, to permit operation in a convenient range of pressure, SiBr₄-SiI₄ mixtures were used to control the silicon activity in the vapor phase. These mixtures were fed to the deposition surface by displacing solutions of iodide and bromide of known concentration from the feed reservoir (16 in Figure 4), and then flash vaporizing the solution upstream of the deposition surface against a controlled back pressure. The lower practical limit of operating pressure was fixed by the vapor pressure of the SiI₄-SiBr₄ solutions at the liquidus. Since the composition of the vapor was found to be relatively more important than the total pressure, data taken at pressures from 100 to 300 mm of mercury are combined in the temperature-composition diagram of Figure 5. These data do not determine the boundary for metal-free carbide formation with the precision obtained in similar determinations in the earlier work. This resulted from the unpredictable spontaneous nucleation of solutions of carbon in liquid silicon on the graphite deposition surface. The silicon in these solutions was present at something less than unit activity and control of the deposition condition was lost. One is limited in this regard by the fact that there are no materials available for the construction of a deposition surface which is truly inert to liquid silicon. It would have been possible to obtain more precise data below the melting point of silicon; however, the extrapolation of these data into a temperature range of interest would probably have been no more reliable.

PREPARATION AND EXAMINATION OF COATED SPECIMENS

Specimens of SiC-coated ATJ graphite were prepared for examination both as resistively heated rods in the apparatus shown in Figure 4 and as inductively heated hollow cylinders in the apparatus shown in Figure 6. The latter specimens were supported by a rotating rod through the center to provide a moving point of support.

The most significant feature of the SiC coatings prepared in the present program was their striking dissimilarity to the coatings of NbC, TaC, TiC, and ZrC prepared earlier. Figure 7 is a photomicrograph of a NbC coating on ATJ graphite prepared by reaction with NbCl₅ for 20 min at 2000 C and 50 mm of mercury pressure. NbC coatings applied at lower temperatures formed more slowly but were similar in appearance. This is to be contrasted with the appearance of the typical coating of SiC in Figure 8 which formed very slowly (0.0002 to 0.01/in. in 1 hr with poor surface coverage. An interesting and unexplained characteristic of these coatings is that the carbide apparently forms more rapidly in the pores of the graphite than on the surface even though the coating conditions are approached from the carbide (low-temperature) side.

It can be said of the data in general, that, below 1900 C the rate of coating formation was very low unless a carbide-liquid silicon solution was permitted to form, in which case the rate of coating formation was no longer controlled by solid-solid diffusion but by convection in the liquid-silicon solution or at the vapor-specimen interface. However, this condition was to be avoided since it defeated the purpose of the research.

A number of the coatings were examined by X-ray diffraction with the results shown in Table 1. Coatings formed at 1900 C and below were cubic beta SiC with a

FIGURE 4. RESISTANCE-HEATED SPECIMEN COATER

FIGURE 5. SILICON CARBIDE FORMATION FROM MIXED VAPORS OF $\text{SiBr}_4\text{-SiI}_4$ AT 100 TO 300 MM OF MERCURY

To condenser and
pressure control

Detail of support rod with specimen in
place

Scale: 2X

- 1 - Motor-drive connector
- 2 - Rotating O-ring seal
- 3 - Argon purge line
- 4 - Glass-to-metal O-ring seal
- 5 - Stainless steel connecting rod
- 6 - Standard taper joint
- 7 - Controlled-pressure line
- 8 - Dry ice-acetone condenser

- 9 - Vycor support guide,
vapor barrier
- 10 - Graphite connector
- 11 - Graphite sample-support rod
- 12 - Induction-heating coils
- 13 - Graphite support guide
- 14 - Flash vaporizer furnace
- 15 - Liquid feed line

FIGURE 6. INDUCTION-HEATED SPECIMEN COATER

lattice constant $a = 4.359 \pm 0.002$ Å, with no variation of lattice parameter with conditions of preparation to indicate the possibility of a carbon-deficient structure.

TABLE 1. X-RAY DIFFRACTION EXAMINATION OF COATED SPECIMENS

Sample	Feed-Mixture Mole Ratio	Temperature, C	Pressure, mm of mercury	Intensities of Phase Patterns ^(a)				
				Graphite	Cubic -SiC	Hexagonal -SiC (Type V) ^(b)	Metallic Silicon	Unknown
16-7	SiBr ₄	1500	0.06	VS	O	O	O	O
33-19	1.5 SiI ₄ /1 SiBr ₄	1930	100	O	VS	M	F	O
48-28	2 SiI ₄ /1 SiBr ₄	1600	150	O	VS	O	O	VVF
53-31	2.5 SiI ₄ /1 SiBr ₄	1700	200	MF	VS	O	O	VVF
66-40	2.5 SiI ₄ /0.5 TiI ₄ /1 SiBr ₄	1430	150	O	S	O	VF	O
87-47	1 SiI ₄ /2 SiBr ₄	2100	300	M	VS	M	O	O

(a) Abbreviations: S = strong, M = medium, F = faint, V = very.

(b) From Reference (7).

The main features of the crystallography of SiC have been summarized by Harmon and Mixer⁽⁶⁾. However, several other modifications of SiC have been identified since this compilation. No evidence has been reported for the existence of a range of homogeneity around SiC_{1.0}, and the fact that SiC is semiconducting would indicate that carbon deficiencies, if present, are limited to the parts-per-million range.

Coatings applied above 1950 C consisted of mixtures of hexagonal alpha and cubic beta SiC. Figure 9 shows a photomicrograph typical of such a coating. Its formation was much more rapid, such as would indicate an abrupt change in the mechanism of carbon diffusion. The porosity of the coating, evident in the photomicrograph, was confirmed in oxidation tests in which the graphite core of the sample was consumed within 30 min at 1000 C in air.

Specimens containing the single-phase SiC were, in general, less oxidation resistant than those containing the metal phase in addition, although the behavior in this respect was not entirely consistent. Failure in air oxidation at 1000 C was clearly indicated by the appearance of dark spots on the coating. Subsequent examination showed that the carbon base had burned away to varying extents beneath the spots.

Table 2 gives oxidation-test data obtained from specimens in which appearance and method of preparation warranted the test.

FIGURE 7. NbC-COATED ATJ GRAPHITE
FORMED BY REACTION WITH
 NbCl_5 AT 2000 C AND 50 MM
OF MERCURY PRESSURE

500X

N41101

FIGURE 8. SiC COATING ON ATJ GRAPHITE
FORMED BY THERMAL DECOM-
POSITION OF A 0.67 $\text{SiBr}_4/1.0$
 SiI_4 MIXTURE AT 1900 C AND
100 MM OF MERCURY PRESSURE

The SiC coating formed at the
rate of 0.0002 to 0.001 in. per hr.

200X

N58700

FIGURE 9. SiC COATING ON ATJ GRAPHITE
FORMED BY THERMAL DECOM-
POSITION OF A 2.0 $\text{SiBr}_4/1.0$
 SiI_4 MIXTURE AT 2100 C AND
300 MM OF MERCURY PRESSURE

About 0.020 in. of this SiC coating
formed in 2 hr. The porous structure
is typical of the two-phase coatings
obtained at temperatures above
1950 C.

100X

N58702

TABLE 2. OXIDATION TESTS OF SiC-COATED ATJ GRAPHITE IN AIR AT 1000 C

Specimen	Coating Composition	Time to Failure ^(a) , min
48-28-A	SiC	30
48-28-B	SiC	20
48-28-D	SiC	90
50-29-A	SiC	60
50-29-B	SiC	90
50-29-D	SiC	60
53-31-C	SiC + silicon	240
53-31-D	SiC + silicon	240
55-32-A	SiC	180
55-32-C	SiC	360
56-33-B	SiC	60
56-33-C	SiC	60
57-34-B	SiC	120
57-34-D	SiC	90
59-35-A	SiC	180
66-40-C	SiC + silicon	240
	SiC	30 ^(b)

(a) Failure indicated by formation of dark spots on specimen surface (see text).

(b) Coated section of rod specimen resistively heated.

The coating data given in Table 3 can be summarized by these conclusions:

- (1) At coating temperatures of 1900 C and below, the rate of formation of metal-free SiC coatings by the present process would be prohibitively low, even if it were possible to obtain good surface coverage, a condition which was not evident in the current work.
- (2) At 2000 C and above, the coatings are very porous, a condition apparently related to the onset of the nucleation of the hexagonal phase.

In addition to undergoing crystal modification at 1900 to 2000 C, SiC is distinguished from the carbides considered earlier in that it apparently has no range of homogeneity around the composition $\text{SiC}_{1.0}$ which would permit diffusion of carbon through lattice vacancies. Thus, preferential diffusion of carbon along grain boundaries of the coating could explain the difference in the coatings obtained in this and the earlier work.

Two methods of overcoming this deficiency were explored briefly. The first was an attempt to modify the structure by the codeposition of TiC by admixture of TiI_4 vapor. No apparent modification of the structure was obtained, nor was the lattice constant

TABLE 3. SUMMARY OF CARBIDE AND CARBIDE-METAL DEPOSITION EXPERIMENTS

Feed-Material Mole Ratio	Specimen	Coating Parameters Used			Time, hr	Approximate Coating Thickness, in.	Remarks
		Pressure, mm of mercury	Apparatus(a)	Temperature, C			
SiBr ₄	4-1	50	R	1650	3	--	No coating
	9-3	5	R	1650	1.5	--	No coating
	80-42	3	R	2200	1	--	Specimen chewed
	11-4	1	R	1650	1	--	No coating
	82-44	1	R	2100	1	--	Specimen chewed
	21-10	0.1	R	1700	1.25	0.0005	Spotty SiC
	14-6	0.05	R	1900	6	0.0005	SiC
	16-7	0.05	R	1500	1	0.0005	Spotty SiC
	18-8	0.04	R	1500	2.5	0.0005	Spotty SiC
	20-9	0.04	R	1900	1.5	0.0005	Spotty SiC
0.2 SiH ₄ /1 SiBr ₄	27-14	500	R	1900	1	--	Specimen chewed
0.33 SiH ₄ /1 SiBr ₄	28-15	480	R	2000	1	--	Specimen chewed
	29-16	100	R	2000	1	--	Specimen chewed
0.5 SiH ₄ /1 SiBr ₄	87-47	300	R	2000	2	0.015	Crystalline SiC
	88-48	300	R	2100	2	0.020	Crystalline SiC
1 SiH ₄ /1 SiBr ₄	84-45	250	R	1750	2.5	0.001	Spotty SiC
	31-17	150	R	1950	1.5	0.001	Spotty SiC
1.55 SiH ₄ /1 SiBr ₄	34-20	100	R	1950	1	0.001	SiC + silicon
2 SiH ₄ /1 SiBr ₄	59-35	450	I	1700	1	0.0005	SiC
	64-38	450	I	1700	1	0.001	SiC + silicon
	85-46	200	R	1700	1.75	0.003	SiC + silicon
	63-37	150	I	1650	1.5	0.005	SiC + silicon
	46-27	100	I	1750	1	0.0005	SiC
	50-29	100	I	1750	1	0.0005	SiC
2.5 SiH ₄ /1 SiBr ₄	53-31	150	I	1650	1	0.001	SiC + silicon
3.5 SiH ₄ /1 SiBr ₄	52-30	150	I	1650	1.5	--	SiC + silicon
	55-32	150	I	1550	1	0.001	SiC
	56-33	150	I	1400	1	0.001	SiC
	65-39	150	I	1450	1	0.0002	SiC + silicon
4.5 SiH ₄ /1 SiBr ₄	57-34	155	I	1380	1	0.0005	SiC
2 SiH ₄ /1 SiBr ₄	33-19	150	R	1870	--	--	Rapid metal deposition
3 SiH ₄ /1 SiBr ₄	37-21	150	R	1710	--	--	Rapid metal deposition
4 SiH ₄ /1 SiBr	32-18	150	R	1460	--	--	Rapid metal deposition

(a) R = resistance heated; I = induction heated.

changed. However, no analysis of the coating was made to determine its titanium content. The second approach was to apply the SiC coating to a substrate of another carbide through which the diffusion rate of carbon could be limited. Accordingly, a coating of SiC was applied to an ATJ graphite specimen already coated with 0.002 in. of NbC. However, in this instance, a liquid-silicon solution was inadvertently formed, and the NbC coating was lifted from the graphite surface and curled on the edges.

RECOMMENDATIONS

Since no conditions have been found for the application of uniform, nonporous SiC coatings by the solid-solid diffusion-controlled vapor-deposition process in its elementary form, any future work must be justified on the basis of the prospect of modifying the basic process to obtain such coatings. Three possibilities are suggested:

- (1) Codeposition of other carbides with the silicon carbide with the purpose of modifying the diffusion mechanism to the extent that the coating will be continuous
- (2) Controlling the formation of the SiC coating by deposition on a substrate of one of the other carbides
- (3) The use of the present process to obtain a uniform, porous structure of SiC at 2000 C which could then be saturated with liquid silicon, either by alteration of the coating atmosphere to favor the deposition of silicon or by a subsequent dip in liquid silicon.

It is in the area of the third suggestion that others have obtained greatest success in the silicon carbide coating of graphite. The work of Dr. James Kane of UCRL, Livermore, and of the staff of the Minnesota Mining and Manufacturing Company has indicated the desirability of a two-phase coating consisting of a self-heating film of silicon metal supported in a "sponge" of SiC. It is thought that the advantages of the present process in the formation of the sponge should be explored.

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