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Deposition of Silicon Carbide Coatings on Particles in a Fluidized Bed Using Silane and Tetramethylsilane— A Feasibility Study

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DEPOSITION OF SILICON CARBIDE COATINGS ON PARTICLES IN A FLUIDIZED BED USING SILANE AND TETRAMETHYLSILANE — A FEASIBILITY STUDY

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ABSTRACT

Deposition of silicon carbide (SiC) coatings from compounds such as methyltrichlorosilane (CH_3SiCl_3) results in corrosive chlorine-containing by-products. The feasibility of depositing coatings from silane (SiH_4) and tetramethylsilane [$Si(CH_3)_4$], which contain no chlorine, was briefly studied. Coatings of SiC were deposited from $Si(CH_3)_4$ over the temperature range 1025 to 1525°C in beds of particles fluidized with either H_2 or Ar. The densest coatings were deposited at 1025°C, but none approached the theoretical density of SiC. A SiC coating was also deposited at 800°C from a mixture of SiH_4, C_2H_4, and H_2.

INTRODUCTION

The purpose of the silicon carbide (SiC) coating on High-Temperature Gas-Cooled Reactor (HTGR) nuclear fuel particles is to prevent diffusion of fission products to the surface of the particle during service at high temperatures. The coating is typically deposited in a fluidized bed of particles using methyltrichlorosilane (CH_3SiCl_3, or MTS) as the source gas and hydrogen as the fluidizing gas.[1] This source gas is easily vaporized (bp 66.4°C), contains silicon and carbon in stoichiometric proportion for SiC, and decomposes readily in the presence of hydrogen to form SiC. The disadvantages with MTS are the large amount and corrosive nature of the HCl and other chlorine-containing by-products. A commercial coating operation would require scrubbers and neutralizers to treat the exhaust gases, adding considerably to capital and maintenance

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[1] J. I. Federer, *Fluidized Bed Deposition and Evaluation of Silicon Carbide Coatings on Microspheres*, ORNL/TM-5152 (January 1977).

costs. A source compound containing less chlorine than MTS would alleviate this if the SiC coating were comparable in quality to that deposited from MTS.

Compounds that might be used to deposit SiC are shown in Table 1, wherein MTS is also included for comparison. No compounds containing oxygen or fluorine are included. The presence of oxygen might result in deposition of oxides, while the presence of fluorine would result in formation of by-products more corrosive than those formed by compounds containing chlorine. The compounds in Table 1 offer a variety of volatilities, C/Si ratios, and Cl/Si ratios. The most interesting of these are SiH_4, SiH_3CH_3, $SiH_2(CH_3)_2$, $Si_2(CH_3)_6$, $Si(CH_3)_4$, CH_3SiH_2Cl, and $(CH_3)_3SiCH_2Cl$. Five of these contain no chlorine, while two have a Cl/Si ratio of one compared with a ratio of three for MTS. Except for SiH_4, all contain carbon, although not always in stoichiometric proportion for SiC.

Table 1. Possible Source Compounds for Deposition of SiC

Compound	Boiling Point (°C)	C/Si Ratio	Cl/Si Ratio
Silicon tetrachloride, $SiCl_4$	57.6	0	4
Dichlorosilane, H_2SiCl_2	8.2	0	2
Silane, SiH_4	−111.8	0	0
Methyltrichlorosilane, CH_3SiCl_3	66.4	1	3
Methyldichlorosilane, CH_3SiHCl_2	41.5	1	2
Methychlorosilane, CH_3SiH_2Cl	/	1	1
Methylsilane, SiH_3CH_3	31	1	0
Dimethyldichlorosilane, $(CH_3)_2SiCl_2$	70.5	2	2
Dimethylsilane, $SiH_2(CH_3)_2$	−20.1	2	0
Methylvinyldichlorosilane, $CH_3(C_2H_3)SiCl_2$	92.9	3	2
Hexamethylsilane, $Si_2(CH_3)_6$	112.5	3	0
Trimethylchloromethylsilane, $(CH_3)_3SiCH_2Cl$	97.1	4	1
Tetramethylsilane, $Si(CH_3)_4$	26.5	4	0

Commercial sources for some of these compounds could not be found. Two compounds, silane (SiH_4) and tetramethylsilane [$Si(CH_3)_4$], were available for use in this study. Others would have been used had time permitted. The feasibility of depositing SiC using SiH_4 and $Si(CH_3)_4$ has been assessed by conducting deposition experiments over a range of temperatures. The resulting deposits were evaluated principally by x-ray diffraction and ceramographic examination.

EXPERIMENTAL PROCEDURE

The apparatus used in previous work[1] to deposit SiC coatings from MTS is shown in Fig. 1. This apparatus, modified as described below, was also used in the present study. When used in previous work, the reservoir was heated to vaporize MTS, and the vapor was carried by a stream of hydrogen into the fluidized bed. In the present work the reservoir was filled with $Si(CH_3)_4$ instead of MTS, and the vapor was transported in the same manner as for MTS. When using SiH_4 from a cylinder of compressed gas (not shown in Fig. 1), the vapor generator

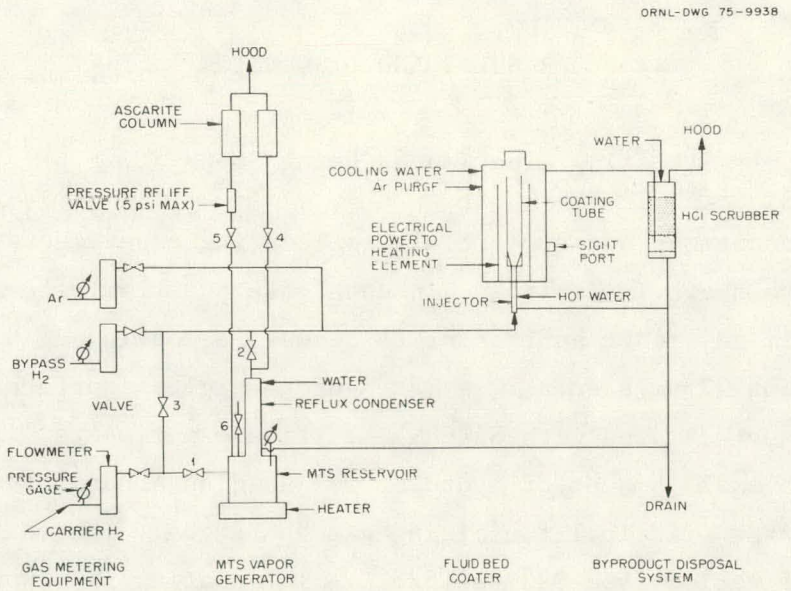

Fig. 1. Fluidized Bed Coating System. The system was slightly modified for depositing SiC from $Si(CH_3)_4$ and SiH_4 instead of MTS.

was simply bypassed. The HCl scrubber, which is required for MTS, was not used for either SiH_4 or $Si(CH_3)_4$. Instead, the exhaust gases bypassed the scrubber (bypass not shown in Fig. 1) and were burned in a hood.

Fluidized beds were obtained in a 25-mm-ID graphite tube with a 36°-included-angle cone. The particles to be coated, which consisted of ThO_2 kernels with two layers of pyrocarbon (PyC), had an average diameter of about 475 μm, a density of about 2.44 Mg/m^3, and a specific surface area of about 5.2 m^2/kg. Either 10 or 20-g batches were coated. All coating experiments were conducted at a system pressure of about 0.1 MPa. The temperature was measured by an optical pyrometer sighted on the coating tube wall at about the junction of tube and cone. The pyrometer reading was corrected for the silica glass sight port.

The SiH_4 was metered with a rotameter-type flowmeter. Since the flowmeter was calibrated for air at about 25°C, a correction factor based on the density of SiH_4 was applied to the flowmeter reading. The $Si(CH_3)_4$ was transferred in a metered stream of H_2, the flow rate of $Si(CH_3)_4$ having been previously determined by condensing and weighing the vapor.

RESULTS AND DISCUSSION

Coating Experiments Using $Si(CH_3)_4$

The conditions and some results of coating experiments using $Si(CH_3)_4$ are shown in Table 2. In each case the flow rate of $Si(CH_3)_4$ was 13 mg/s, an amount sufficient to deposit a coating at a theoretical rate of about 17 nm/s on a 20-g batch of particles (surface area ≈0.104 m^2). Only hydrogen was used with $Si(CH_3)_4$ in five experiments. In the other four only a small amount of hydrogen was used as a carrier for $Si(CH_3)_4$ vapor, and the principal fluidizing gas was argon. The coating temperature varied from 825 to 1525°C. The coating time was 1.8 ks in each case.

Table 2. Conditions and Results of Coating Experiments Using $Si(CH_3)_4$[a]

Flow Rate, cm^3/s		Temperature (°C)	Particle Density, Mg/m^3		Coating Weight (g)	X-Ray Intensity[b]	
H_2	Ar		Before Coating	After Coating		PyC[c]	β-SiC[d]
50	0	825	2.41	2.41	0		
50	0	1025	2.41	2.41	3.94	S	W[c]
50	0	1125	2.41	1.97	9.85	M+	S[c]
50	0	1225	2.44	1.61	7.48	M	S[c]
50	0	1525	2.44	1.17	14.50	M	S
2	25	1025	2.39	2.42	5.35		W-[c]
2	25	1125	2.43	2.06	11.95	W	S[c]
2	25	1225	2.44	1.50	16.85	M	S[c]
2	25	1525	2.44	1.70	12.58	S	S

[a] In all cases, the $Si(CH_3)_4$ flow rate was 13 mg/s and the surface area of the particles being coated was 0.104 m^2.

[b] Intensity estimated from diffractometer traces: S-strong, M-medium, W-weak.

[c] PyC in the SiC coating, if present, could not be distinguished from the underlying layer of PyC.

[d] Broad peaks.

The particle densities shown in Table 2 were calculated from the weight and "tapped" volume.[2] The tapped volume was adjusted to the true volume by using the packing fraction for spheres of 0.62. In the five experiments using hydrogen as the fluidizing gas, the particle density after coating decreased with increasing deposition temperature, indicating that the coating was less dense than the original particle ($\sim$2.4 Mg/m^3) and, therefore, much less dense than SiC (theoretical density 3.210 Mg/m^3). Coatings deposited with argon as the fluidizing gas behaved similarly to those deposited with hydrogen.

Table 2 indicates that the weights of coatings deposited with hydrogen varied somewhat erratically with increasing temperature, whereas those of coatings deposited with argon exhibited a maximum as a function of deposition temperature. Deposition of all the silicon as SiC in the metered $Si(CH_3)_4$ would have resulted in a coating weight of 10.9 g. Since the weight of some coatings exceeded 10.9 g, and since $Si(CH_3)_4$

[2] The "tapped" volume was obtained by tapping a graduated cylinder containing the particles with a commercially obtained device until closest packing of the particles was achieved.

contains excess carbon over that required for stoichiometric SiC, the coatings probably contained excess carbon. Decomposition of $Si(CH_3)_4$ to SiC and by-products requires that C-H bonds be broken. Hydrogen would be expected to suppress breaking of C-H bonds, thereby suppressing carbon deposition. Decomposition of $Si(CH_3)_4$ in an argon atomosphere should be less likely to suppress deposition of carbon; however, essentially the same results were obtained with either hydrogen or argon used as the principal fluidizing gas.

The presence of excess carbon in some of the coatings was inferred from the coating weights, but was not proven by x-ray diffraction of either whole particles or coating fragments. In the case of whole particles, x-ray diffraction cannot distinguish between PyC in the SiC coating and the underlying layers of PyC, which were part of the original particle. On the other hand, when coating fragments were heated in air to burn away adhering PyC layers, x-ray diffraction revealed only SiC and SiO_2. Of course, any PyC in the coating might also have burned away, so x-ray evidence of PyC could not be expected, and none was obtained. Table 2 shows that β-SiC was deposited at each temperature. The x-ray diffractometer patterns of coatings deposited at 1025°C had very broad peaks, indicating either an amorphous character or small crystallites. Broad peaks persisted to 1225°C, but the crystalline perfection was better at 1525°C. Nevertheless, these experiments have demonstrated the feasibility of depositing SiC from $Si(CH_3)_4$ at temperatures as low as 1025°C.

Polished sections of the coatings are shown in Fig. 2. The outer coatings deposited from either carrier gas at 1025°C appear to be single phase and denser than the underlying PyC layer; however, these coatings always contained radial cracks. At higher deposition temperatures the outer coatings are much thicker relative to the coating deposited at 1025°C and appear to contain more than one phase and/or porosity. Gross porosity is shown in most cases by intrusion of the ceramographic mounting material into the coatings.

The density of coatings is usually determined with a liquid density gradient column by procedures described elsewhere.[1] The coating fragments for determination of density are obtained by breaking the coated

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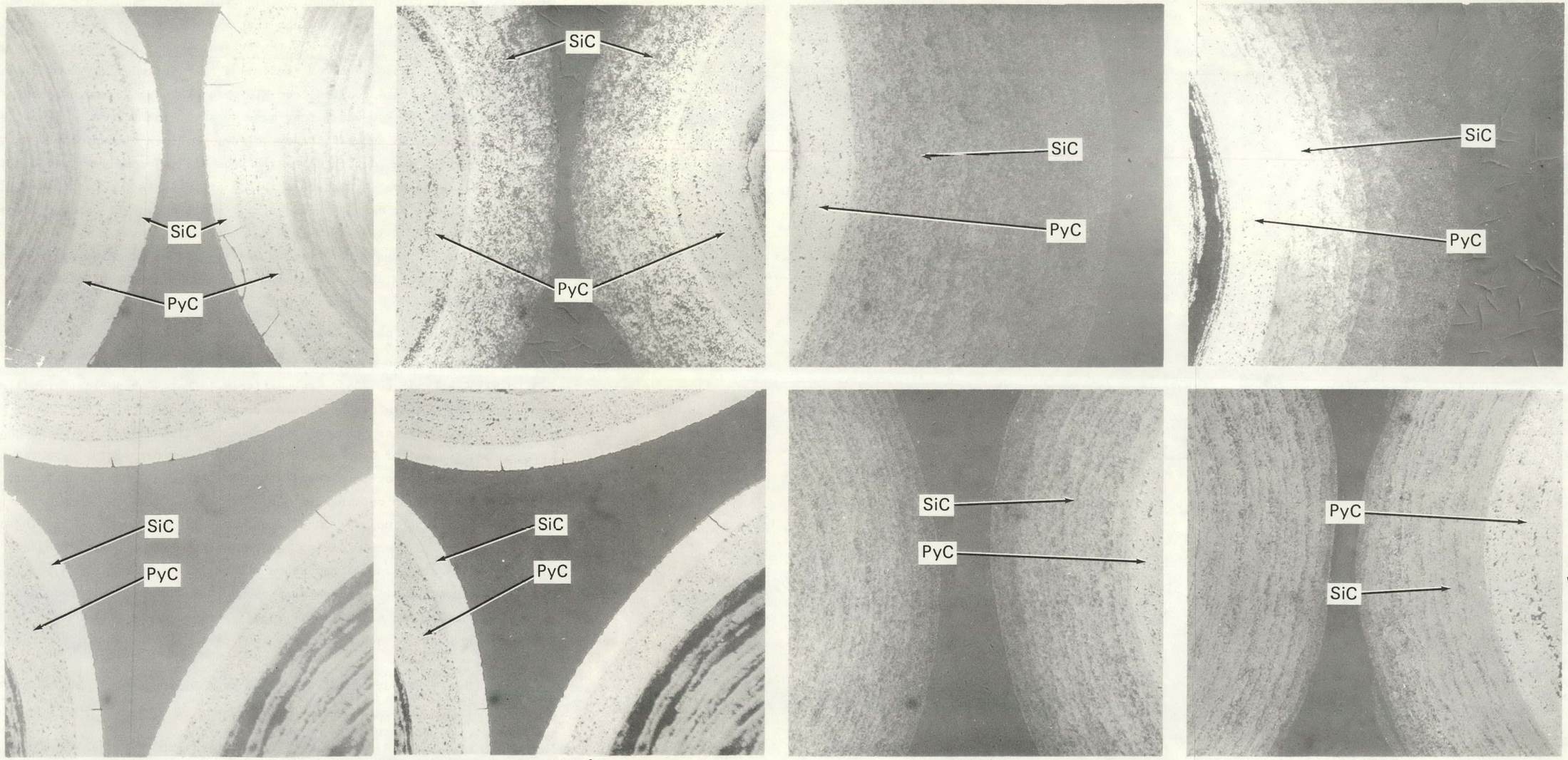
SiC
PyC
SiC
PyC
SiC
PyC
SiC
PyC
FLUIDIZED WITH H_2
SiC
PyC
SiC
PyC
SiC
PyC
PyC
SiC
FLUIDIZED WITH Ar
1125°C
1225°C
1525°C

microspheres, collecting fragments, and burning away adhering PyC layers. Figure 3 shows fragments of coatings that had been heated in air at 1000°C to burn away adhering PyC layers. The fragments in the top row, which were deposited from MTS under optimum conditions, are included for comparison. The coating fragments deposited from MTS were translucent and uniformly green after adhering PyC was burned away in air. The fragments deposited from $Si(CH_3)_4$ at 1025 and 1125°C were black, or black and white, after burning. Whereas the coating deposited from MTS was completely stable in air at 1000°C, the coatings deposited from $Si(CH_3)_4$ were subject to oxidation, as evidenced by a white residue, and the tendency to oxidize increased with increasing deposition temperature (decreasing density). The white residue in the coatings after burning was identified by x-ray diffraction as SiO_2. The coating deposited at 1225 and 1525°C appeared to be completely oxidized to SiO_2.

Coating Experiments Using SiH_4

Silane has been used to deposit Si_3N_4 and SiO_2 coatings on wafers at 675 to 825°C and 475 to 725°C, respectively.[3] Barry[4] reports that silicon can be deposited on wafers by thermal decomposition of SiH_4 at 1000 to 1050°C. Since hydrogen tends to retard decomposition of SiH_4, an inert carrier gas instead of hydrogen should allow lower deposition temperatures to be used, and, in fact, this was demonstrated by Richman and Arlett,[5] who deposited silicon coatings at 800°C using helium as the carrier gas.

The conditions and some results of coating experiments using SiH_4 are shown in Table 3. The fluidizing gas was either hydrogen or argon, and the source of carbon was either propene (C_3H_6) or acetylene (C_2H_2). In three experiments a silicon coating was desired, so no hydrocarbon gas was used. A 10-g bed of particles with a surface area of about 0.052 m^2 was used in each case. The flow rates of SiH_4 and hydrocarbons

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[3]G. Wahl, "Hydrodynamic Description of CVD Processes," *Thin Solid Films* 40: 13–26 (1977).

[4]B. E. Barry, "Vapour Phase Growth of Semiconducting Layers," *Thin Solid Films* 39: 35–53 (1977).

[5]D. Richman and R. H. Arlett, "Low-Temperature Epitaxial Growth of Single Crystalline Silicon From Silane," *J. Electrochem. Soc.* 116: 872–873 (1969).

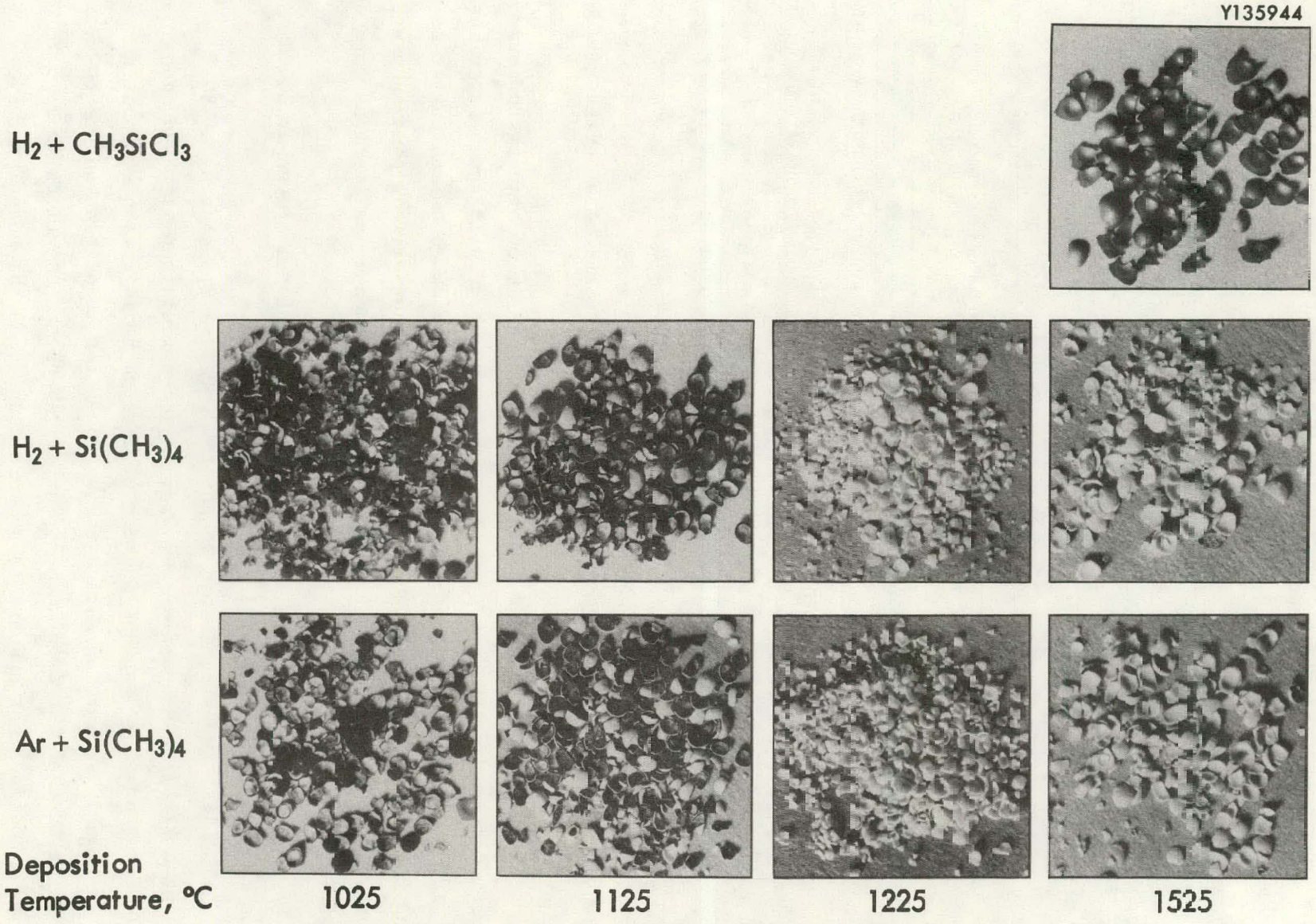

Fig. 3. Fragments of Coatings Deposited from $Si(CH_3)_4$ after Heating in Air at 1000°C for 2 hr.

Table 3. Conditions and Results of Coating Experiments Using SiH_4

Flow Rate, cm^3/s				Temperature (°C)	Results
SiH_4	H_2	Ar	Hydrocarbon		
1.5	0	7	0.5[a]	1300	Fluidization stopped in <60 s.
1.5	0	7	0.5[a]	1200	Fluidization stopped in <60 s.
0.5	0	7	0.5[a]	1300	Fluidization stopped in <60 s.
0.5	25	0	0	1000	Brown, powdery coating identified as silicon by x-ray diffraction.
0.5	35	0	0	800	Adherent coating on particles identified as silicon by x-ray diffraction.
0.5	0	25	0	800	Fluidization stopped in ∿900 s.
0.5	35	0	0.3[b]	800	Fluidization stopped in <30 s.
0.5	60	0	0.3[b]	800	Adherent coating on particles shown by x-ray diffraction to be SiC.

[a] Propene (C_3H_6).

[b] Acetylene (C_2H_2).

were sufficient to deposit SiC at theoretical rates of about 5 to 17 nm/s if all the silicon were deposited as stoichiometric SiC.

The first three experiments shown in Table 3 used 3:1 and 1:1 mixtures of SiH_4 and C_3H_6 in beds fluidized with argon at 1200 and 1300°C. Each time fluidization stopped within 60 s of admission of SiH_4 and C_3H_6. The SiH_4 apparently decomposed so rapidly that a solid mass formed at the entrance to the fluidized bed.

Hydrogen was then used as the fluidizing gas in an attempt to retard decomposition of SiH_4. A hydrocarbon gas was not used in these experiments. At 1000°C a brown, powdery silicon coating was obtained on the particles and the coating tube wall, but at 800°C an adherent silicon coating was obtained on the particles. Figure 4 shows polished cross sections through several particles coated at 800°C. A metallic-like coating with a rough surface is revealed. When argon was substituted for hydrogen at 800°C the bed ceased to be fluidized after about 900 s.

The last two experiments sought to deposit a SiC coating at 800°C using a 2:1 mixture of SiH_4 and C_2H_2 in a bed fluidized with hydrogen. The first of these was not successful because fluidization stopped in less than 30 s, but increasing the hydrogen resulted in an adherent coating in the last experiment. The polished cross sections in Fig. 5 show a coating that appears to be more dense than the underlying PyC

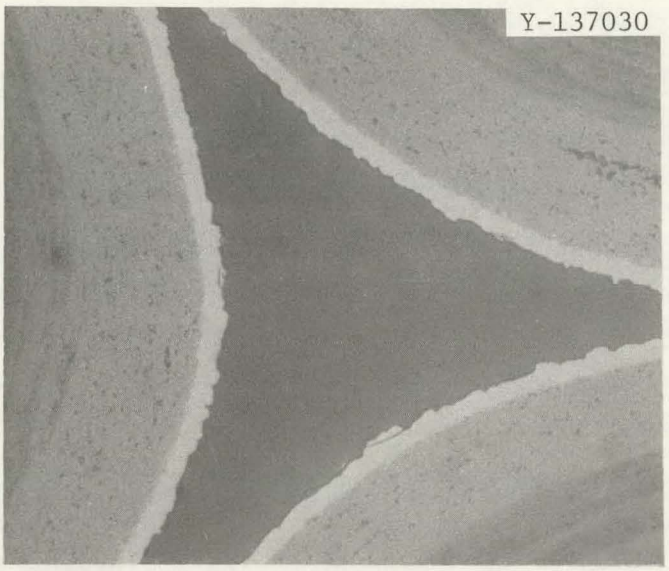

Fig. 4. Silicon Coating Deposited at 800°C from a Mixture of SiH_4 and H_2. As polished. 400×.

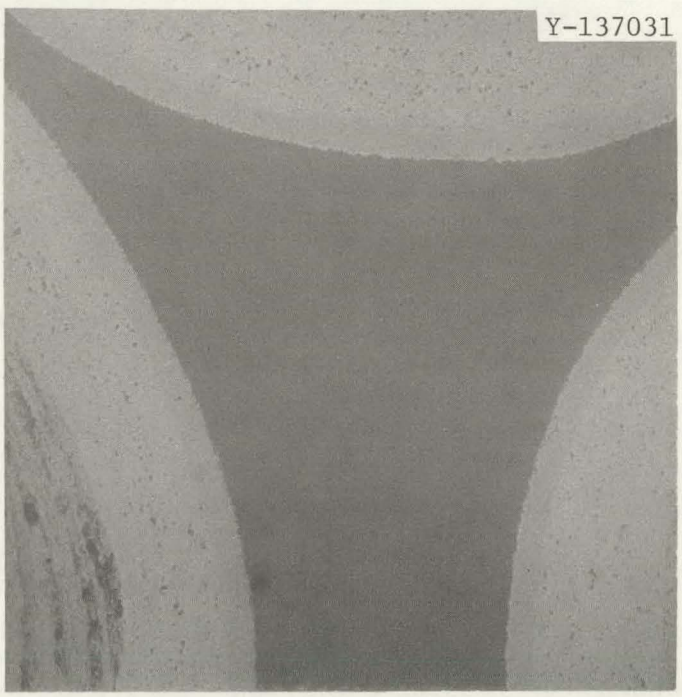

Fig. 5. SiC Coating Deposited at 800°C from a Mixture of SiH_4, C_2H_2 and H_2. As polished. 400×.

layer; however, the coating contains porosity and has a rough surface. The coating was identified as β-SiC by x-ray diffraction. The x-ray pattern had very broad peaks, indicating either an amorphous character or small crystallites.

SUMMARY

Coatings Deposited Using $Si(CH_3)_4$

1. When hydrogen was used as the fluidizing gas, the amount of deposited material varied erratically with increasing temperature in the range 800 to 1500°C. With argon the deposited weight exhibited a maximum in the same temperature range.

2. The density of particles after coating was the same as or lower than the density before coating, indicating that the coating density never exceeded 2.4 Mg/m^3, the density of the original particles. The density of the coatings never approached the theoretical density of SiC (3.210 Mg/m^3).

3. Fragments of coatings heated at 1000°C in air oxidized partly or completely to SiO_2.

4. Ceramographic examination showed that the densest coatings, deposited at 1025°C with either hydrogen or argon, contained radial cracks, while the less dense coatings contained gross porosity.

5. X-ray diffraction revealed that each coating was at least partly SiC; however, the coatings were poorly crystalline, as evidenced by line broadening on the diffraction patterns. The crystallinity of coatings deposited at 1525°C was best.

Coatings Deposited Using SiH_4

The few experiments that have been performed indicate that a large amount of hydrogen is required to suppress the decomposition of SiH_4 to silicon and hydrogen in a fluidized bed. A SiC coating was deposited with a mixture of SiH_4 and C_2H_2 at 800°C. Deposition from SiH_4 and C_3H_6 in beds fluidized with argon at 1200 and 1300°C was unsuccessful because of formation of a solid mass at the entrance to the fluidized

bed within only 60 s. Better success with SiH_4 and C_3H_6 might have been obtained at lower temperatures but no such tests were tried.

CONCLUSIONS

This study has shown the feasibility of depositing SiC coatings on particles in a fluidized bed from either tetramethylsilane [$Si(CH_3)_4$] or silane (SiH_4), thereby avoiding the corrosive by-product gases associated with coatings deposited from such compounds as methyltrichlorosilane (CH_3SiCl_3 or MTS). However, no coatings were deposited that had both high density and structural integrity. Much additional work would be required to achieve highly dense, stoichiometric coatings. This work shows that a potential advantage in using compounds such as $Si(CH_3)_4$ and SiH_4 is the deposition of SiC coatings at temperatures of 800 to 1000°C rather than about 1500°C, as often used for MTS.

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