

To the Graduate Council:

I am submitting herewith a dissertation written by Peter Angelini entitled "Chemical Vapor Deposition of Silicon Carbide from Methylsilane and Coating of Nuclear Waste Ceramics." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Metallurgical Engineering.

E. E. Stansbury

E. E. Stansbury, Major Professor

We have read this dissertation
and recommend its acceptance:

J. E. Sprinzel
Don T. Oliver

C. R. Brooks

Paul A. Huray

W. J. Lackey

J. Bentley

Accepted for the Council:

Cumink

Vice Provost
and Dean of the Graduate School

CHEMICAL VAPOR DEPOSITION OF SILICON CARBIDE
FROM METHYLSILANE AND COATING OF NUCLEAR WASTE CERAMICS

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Peter Angelini

June 1985

ACKNOWLEDGEMENTS

The author expresses his sincere appreciation to his major professor, Dr. E. E. Stansbury for guidance and encouragement. Special thanks also go to the members of this doctoral committee: Profs. C. R. Brooks, B. F. Oliver, J. E. Spruiell from the Materials Science and Engineering Department, Prof. P. G. Huray from the Physics Department, Dr. J. Bentley from the Oak Ridge National Laboratory (ORNL), and Dr. W. J. Lackey. Special appreciation is also due to the staff of the Materials Science and Engineering Department.

The research presented in this dissertation was performed in the Metals and Ceramics Division of ORNL under contract with Union Carbide Nuclear Division and Martin Marietta Energy Systems, Inc. The research was funded initially by the Exploratory Research Program Office of ORNL and later by the Office of Waste Operations and Technology, and the Division of Materials Sciences, U.S. Department of Energy.

The author is grateful to Dr. J. O. Stiegler, Dr. P. F. Becher, and J. R. Weir for their enthusiastic support of this research. Special thanks go to Dr. R. W. Carpenter formerly at ORNL and now at Arizona State University for introduction into the field of transmission electron microscopy (TEM), and to Dr. P. S. Sklad for many helpful discussions on analytical electron microscopy. Many thanks go to Dr. G. M. Begun of the ORNL Chemistry Division for Raman spectroscopy; O. B. Cavin for x-ray diffraction; T. J. Henson and L. R. Walker for scanning electron microscopy and electron microprobe analyses; N. M. Atchley and G. C. Marsh for optical ceramography;

C.K.H. DuBose, C. P. Haltom, and A. T. Fisher for TEM specimen preparation; H. Livesey for drawings; D. P. Stinton and J. C. McLaughlin for their expert assistance in coating technology; Dr. T. Lindemer and Dr. T. M. Besmann of the ORNL Chemical Technology Division for introduction to and assistance in the use of the SOLGASMIX-PV computer program; Dr. W. D. Bond, W. D. Arnold, and S. M. Robinson of the Chemical Technology Division of ORNL for supplying sol-gel-derived materials and cesium loaded zeolite; R. E. McHenry for introduction of the author to sol-gel materials in both rare earth and actinide oxides.

Special thanks also go to C. E. DeVore for providing support in coating technology and experimental methods and to F. C. Stooksbury for typing and editing the manuscript.

Sincere and loving appreciation goes to the authors children Bibiana, Isabella, and Joseph Angelini for their understanding and especially to his spouse, Suzanne Black Angelini for her continued support during this endeavor.

ABSTRACT

This research evaluated the chemical vapor deposition (CVD) of silicon carbide from methylsilane (CH_3SiH_3) and coating of nuclear waste ceramics. The phase equilibria of the SiC coatings were investigated and compared with thermodynamic equilibrium calculations. The major variables studied were coating temperature, hydrogen content of the diluent gaseous system ($\text{Ar} - \text{H}_2$) or ($\text{N}_2 - \text{H}_2$), and addition of C_2H_2 to the system. Pyrocarbon coated alumina, and nuclear waste ceramic substrate particle were coated with silicon carbide in a fluidized-bed coater.

Most of the thermodynamic calculations were performed with a mole ratio of $\text{CH}_3\text{SiH}_3/\text{diluent} = 5.8 \times 10^{-3}$ and a total system pressure of 1.01×10^5 Pa. The results for the $\text{CH}_3\text{SiH}_3 - \text{Ar}$ system indicate that SiC + Si are codeposited up to a temperature of ≈ 1450 K. Single phase SiC is computed to form above that temperature. The results for the $\text{CH}_3\text{SiH}_3 - \text{H}_2$ system are similar to those mentioned above except SiC + Si is computed to form over the entire 973 to 1600 K temperature range. The silicon content in the condensed phase increases as the temperature decreases or the hydrogen content in the diluent gas increases. Additions of various amounts of C_2H_2 to the $\text{CH}_3\text{SiH}_3 - (\text{Ar} - \text{H}_2)$ system can alter the types and concentration of phases present in the condensed phase (SiC + Si, SiC + C, or SiC). Results for the condensed phases are presented as CVD phase diagrams and those of the gaseous phase as partial pressures of various species.

The coatings were evaluated by x-ray diffraction, Raman spectroscopy, quantitative electron microprobe, and other techniques. Coatings deposited at 1073 K were amorphous and those deposited at 1180 K were crystalline. Annealing of the amorphous SiC coating to 1173 K crystallized the material. The major phase observed is β -SiC, however a small amount of α -SiC is also present and the coatings are isotropic. The SiC crystallite size decreased as the hydrogen content in the diluent gas increased.

Coatings deposited in diluents of high hydrogen content had a silicon content greater than that of stoichiometric SiC by ≈ 2 wt %. The phases and their relative concentration present in the coatings were modified by adding C_2H_2 to the system. The experimental results were in agreement with thermodynamic calculations.

The coated particle concept for solidification of high-radiation-level nuclear waste was also evaluated. Sol-gel derived substrates of high-waste loading, and Cs-loaded zeolite were coated with SiC and pyrolytic carbon in a fluidized-bed coater. Leach testing by standard techniques showed them to be highly leach resistant and possess leach rates lower than other nuclear waste forms.

TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION	1
II. LITERATURE SURVEY	5
Coated Forms	5
Coating of Silicate Substrates	5
Coating of Sol-Gel Derived Substrates	10
Zeolite	15
Chemical Vapor Deposition of SiC	20
Non-halogenated Reactants	21
III. EXPERIMENTAL PROCEDURE	28
Apparatus	28
Fluidized-Bed Coating System	28
Sintering and Annealing Furnaces	34
Materials	35
Specimen Characterization	40
Thermal Analysis	40
Density Determination	41
Defective SiC Coating Measurements	44
Raman Spectroscopy	44
Electron Microprobe	45
X-ray Diffraction	47
IV. RESULTS	50
Thermodynamic Evaluation of the Chemical Vapor Deposition of SiC from Methylsilane	50
Analysis of the $\text{CH}_3\text{SiH}_3 - \text{C}_2\text{H}_2 - (\text{Ar} - \text{H}_2)$ System . . .	53

CHAPTER	PAGE
IV. (Continued)	
Analysis of the $\text{CH}_2\text{SiH}_3 - \text{C}_2\text{H}_2 - (\text{N}_2 - \text{H}_2)$ System . . .	64
CVD of Silicon Carbide	71
Initial Experiments	71
Coating of Pyrocarbon Coated Alumina Substrates	82
Effect of C_2H_2 Addition	99
Coating of Nuclear Waste Ceramics	108
Zeolite Substrates	108
Substrates of High Waste Loading	114
V. DISCUSSION	121
Chemical Vapor Deposition of Silicon Carbide from Methylsilane	122
Coating of Nuclear Waste Ceramics	132
VI. SUMMARY AND CONCLUSIONS	135
REFERENCES	138
APPENDICES	147
APPENDIX A	148
APPENDIX B	150
VITA	153

LIST OF TABLES

TABLE	PAGE
2.1. Various coatings applied to calcine particles	7
2.2. Leach tests of coated supercalcine	9
2.3. Leach test results for uncoated and pyrocarbon coated sol-gel derived particles	14
2.4. Fixation of Cs in fully Cs-loaded zeolites by heat treatment in air	19
2.5. Phases present in fully Cs-loaded natural zeolites after heating in air	20
2.6. Reactant gases for the CVD of SiC	22
3.1. Impurity levels for diluent gases Ar, N ₂ , H ₂	36
3.2. Characteristics of PyC coated alumina substrate particles	38
3.3. Chemical analysis of dried IE-95 zeolite loaded with 5 wt % Cs	40
4.1. Thermodynamic data for CVD calculations in the CH ₃ SiH ₃ - C ₂ H ₂ - (Ar or N ₂ - H ₂) system	51
4.2. Experimental coating parameters and coating property data for initial SiC coating experiments	73
4.3. Open porosity and defective particle fraction of SiC coated particles	81
4.4. Experimental coating parameters and coating property data for SiC coating of pyrocarbon coated alumina substrates . .	84
4.5. Open porosity and defective particle fraction of SiC coated particles	88
4.6. Coating conditions for experiments evaluating the effect of C ₂ H ₂ on the thermal decomposition of CH ₃ SiH ₃	100
4.7. Quantitative electron microprobe analyses of SiC coatings and single crystal SiC	107
4.8. Leach rate results for uncoated and pyrocarbon coated Cs-loaded zeolite	112

TABLE	PAGE
4.9. Leach test results for uncoated and pyrocarbon coated sol-gel derived particles	120
A.1. Composition of simulated SRP waste matrix additives, and product	149
B.1. SiC crystallite size determined by x-ray diffraction . . .	151

LIST OF FIGURES

FIGURE	PAGE
2.1. Microspheres of SYNROC-D formed by the internal gelation process (sintering temperature 1173 K, atmosphere — Ar — 4% H ₂ , density 4.19 g/cm ³)	12
2.2. Pyrocarbon coated gel-derived substrate of the SYNROC-D formulation	13
2.3. Microspheres of high-waste loading (>70 wt %) react with pyrocarbon during coating at 1273 K	16
2.4. Composition of SiC powder synthesized from the thermal decomposition of CH ₃ SiH ₃ in an Ar diluent	27
3.1. Diagram of coating system	29
3.2. Diagram of the fluidization assembly, furnace element, and location of the furnace side sightport	32
3.3. Photograph of fluidized-bed coating system	33
3.4. Cs-loaded zeolite (5 wt % Cs) air dried 400 K	39
4.1. CVD phase diagram based on thermodynamic equilibrium calculations for the system CH ₃ SiH ₃ — C ₂ H ₂ — (Ar — H ₂); mole ratios CH ₃ SiH ₃ /diluent = 5.8×10^{-3} , C ₂ H ₂ /CH ₃ SiH ₃ = 0.0, and total pressure = 1.01×10^5 Pa (≈ 1 atm). Phase boundaries separate range of conditions where single phase SiC, or SiC + Si forms. Contours of constant mole ratio $r_{Si} = \text{Si/SiC}$ are shown	55
4.2. Partial pressure of various gaseous product species versus temperature for the CH ₃ SiH ₃ — C ₂ H ₂ — (Ar — H ₂) system; mole ratios CH ₃ SiH ₃ /diluent = 5.8×10^{-3} , C ₂ H ₂ /CH ₃ SiH ₃ = 0.0, total pressure = 1.01×10^5 Pa (≈ 1 atm), and H ₂ content in the diluent gas = 0.0 mol % (100 mol % Ar)	57
4.3. Partial pressure of various gaseous product species versus temperature for the CH ₃ SiH ₃ — C ₂ H ₂ — (Ar — H ₂) system; mole ratios CH ₃ SiH ₃ /diluent = 5.8×10^{-3} , C ₂ H ₂ /CH ₃ SiH ₃ = 0.0, total pressure = 1.01×10^5 Pa (≈ 1 atm), and H ₂ content in the diluent gas = 100 mol %	58
4.4. CVD phase diagram based on thermodynamic equilibrium calculations for the CH ₃ SiH ₃ — C ₂ H ₂ — (Ar — H ₂) system; mole ratios CH ₃ SiH ₃ /diluent = 5.8×10^{-3} , C ₂ H ₂ /CH ₃ SiH ₃ = 3.4×10^{-4} , and total pressure = 1.01×10^5 Pa (≈ 1 atm) . .	60

FIGURE

PAGE

- 4.5. Content of gaseous product species CH_4 , and condensed phases C(s) and Si(s) versus H_2 content in diluent gas for the $\text{CH}_3\text{SiH}_3 - \text{C}_2\text{H}_2 - (\text{Ar} - \text{H}_2)$ system; mole ratios $\text{CH}_3\text{SiH}_3/\text{diluent} = 5.8 \times 10^{-3}$, $\text{C}_2\text{H}_2/\text{CH}_3\text{SiH}_3 = 3.4 \times 10^{-4}$, total pressure = 1.01×10^5 Pa (≈ 1 atm), and $T = 1600$ K 62
- 4.6. CVD phase diagrams based on thermodynamic equilibrium calculations for the $\text{CH}_3\text{SiH}_3 - \text{C}_2\text{H}_2 - (\text{Ar} - \text{H}_2)$ system; mole ratios $\text{CH}_3\text{SiH}_3/\text{diluent} = 5.8 \times 10^{-3}$, total pressure = 1.01×10^5 Pa (≈ 1 atm) (a) mole ratio $\text{C}_2\text{H}_2/\text{CH}_3\text{SiH}_3 = 3.4 \times 10^{-3}$ and (b) mole ratio $\text{C}_2\text{H}_2/\text{CH}_3\text{SiH}_3 = 3.4 \times 10^{-2}$ 63
- 4.7. CVD phase diagram based on thermodynamic equilibrium for the $\text{CH}_3\text{SiH}_3 - \text{C}_2\text{H}_2 - (\text{Ar} - \text{H}_2)$ system. Phase boundaries separate range of conditions where single phase SiC, and codeposits of SiC + C, or SiC + Si form 65
- 4.8. CVD phase diagram based on thermodynamic equilibrium calculations for the $\text{CH}_3\text{SiH}_3 - \text{C}_2\text{H}_2 - (\text{N}_2 - \text{H}_2)$ system; mole ratios $\text{CH}_3\text{SiH}_3/\text{diluent} = 5.8 \times 10^{-3}$, $\text{C}_2\text{H}_2/\text{CH}_3\text{SiH}_3 = 0.0$, total pressure = 1.01×10^5 Pa (≈ 1 atm). Phase boundaries separate range of conditions where single phase Si_3N_4 , $\text{Si}_3\text{N}_4 + \text{C}$, SiC + Si_3N_4 , or SiC + Si forms. Contours of constant mole ratio of $r_c = \text{C}/\text{Si}_3\text{N}_4$, or $r = \text{Si}_3\text{N}_4/\text{SiC}$ are shown 67
- 4.9. Partial pressure of various gaseous product species versus temperature for the $\text{CH}_3\text{SiH}_3 - \text{C}_2\text{H}_2 - (\text{N}_2 - \text{H}_2)$ system; mole ratios $\text{CH}_3\text{SiH}_3/\text{diluent} = 5.8 \times 10^{-3}$, $\text{C}_2\text{H}_2/\text{CH}_3\text{SiH}_3 = 0.0$, total pressure = 1.01×10^5 Pa (≈ 1 atm), and $T = 1600$ K . . . 69
- 4.10. Mole ratios of C in condensed phase/total C, $\text{CH}_4/\text{total C}$, and $\text{HCN}/\text{total C}$ versus H_2 in diluent gas for the $\text{CH}_3\text{SiH}_3 - \text{C}_2\text{H}_2 - (\text{N}_2 - \text{H}_2)$ system; $\text{CH}_3\text{SiH}_3/\text{diluent} = 5.8 \times 10^{-3}$, $\text{C}_2\text{H}_2/\text{CH}_3\text{SiH}_3 = 0.0$, total pressure = 1.01×10^5 Pa (≈ 1 atm), and $T = 1300$ K 70
- 4.11. SiC deposited onto PyC coated alumina substrate particles, 7 g charge (a) coating efficiency versus coating temperature, and (b) coating density versus coating temperature. (Values at 1483 K determined by tap density measurements.) 75
- 4.12. Secondary electron micrographs of SiC fracture surfaces - 100% Ar diluent (a,b) Run 35, $T = 1280$ K, (c,d) Run 43, $T = 1180$ K, and (e,f) Run 42, $T = 1073$ K 77

FIGURE

PAGE

4.13	Secondary electron micrographs of SiC fracture surfaces - 100% H ₂ diluent (a,b) Run 34, T = 1685 K, and (c,d) Run 38, T = 1280 K	78
4.14	Secondary electron micrographs of SiC surfaces (a,b) Run 34, T = 1685 K, 100% H ₂ diluent, (c,d) Run 35, T = 1280 K, 100% Ar diluent, and (e,f) Run 42, T = 1073 K, 100% Ar diluent	79
4.15	Coating efficiency versus coating temperature (SiC deposited onto PyC coated alumina substrate particles, 20 g charge)	85
4.16	Secondary electron micrographs of SiC fracture surfaces - 100% Ar diluent (a,b) Run 92, T = 1280 K, (c) Run 84, T = 1180 K, (d) Run 84, T = 1180 K, annealed 1180 K, and (e,f) Run 45, T = 1073 K	89
4.17	Secondary electron micrographs of SiC fracture surfaces - 100% H ₂ diluent (a,b) Run 99, T = 1280 K, (c,d) Run 85, T = 1180 K, and (e,f) Run 75, T = 1073 K	90
4.18	Secondary electron micrographs of SiC surfaces (a) Run 82, T = 973 K, 100% Ar diluent, (b) Run 84, T = 1180 K, 100% Ar diluent, (c) Run 85, T = 1180 K, 100% H ₂ diluent, and (d) Run 99, T = 1280 K, 100% H ₂ diluent	92
4.19	Secondary electron micrographs of SiC surfaces (a) Run 82, T = 973 K, annealed 1523 K, and (b) Run 84, T = 1180 K, annealed 1523 K	93
4.20	Secondary electron micrographs of SiC coating fracture surface; Run 82, T = 973 K, annealed 1523 K	93
4.21	Crystallite size of as-produced SiC coatings versus (a) coating temperature, and (b) H ₂ content in the diluent gas	95
4.22	X-ray diffraction spectra for SiC coating deposited at a temperature of 1180 K in 100% Ar diluent (a) annealed 1723 K, 3 h, (b) annealed 1523 K, 3 h, (c) annealed 1173 K, 24 h, and (d) as-produced 1180 K. Al ₂ O ₃ peaks occur from substrate material	96
4.23	X-ray diffraction spectra for SiC coating deposited at a temperature of 1180 K in H ₂ diluent (a) annealed 1723 K, 3 h, (b) annealed 1523 K, 3 h, (c) annealed 1173 K, 24 h, and (d) as-produced 1180 K. Excess Si is present in coating. Al ₂ O ₃ peaks occur from substrate material	98

FIGURE	PAGE
4.24. Raman spectra for SiC coating (Run 84), $T = 1180$ K, diluent gas 100% Ar, $\text{CH}_3\text{SiH}_3/\text{diluent} = 4.4 \times 10^{-3}$ (a) as-produced, and (b) annealed 1523 K, 3 h	101
4.25. Raman spectra for SiC coating (Run 353), $T = 1180$ K, diluent gas 100% Ar, $\text{C}_2\text{H}_2/\text{CH}_3\text{SiH}_3 = 4.2 \times 10^{-2}$, $\text{CH}_3\text{SiH}_3/\text{diluent} = 5.5 \times 10^{-3}$ (a) as-produced, and (b) annealed 1523 K, 3 h	102
4.26. Raman spectra for SiC coating (Run 88), $T = 1180$ K, H_2 content in (Ar - H_2) diluent gas = 77 mol %, $\text{CH}_3\text{SiH}_3/\text{diluent} = 3.6 \times 10^{-3}$ (a) as-produced, and (b) annealed 1523 K, 3 h	104
4.27. Raman spectra for SiC coating (Run 349), $T = 1180$ K, H_2 content in (Ar - H_2) diluent gas = 77 mol %, $\text{C}_2\text{H}_2/\text{CH}_3\text{SiH}_3 = 4 \times 10^{-2}$, $\text{CH}_3\text{SiH}_3/\text{diluent} = 3.6 \times 10^{-3}$ (a) as-produced, and (b) annealed 1523 K, 3 h	105
4.28. Thermal analyses of Cs-loaded zeolite (≈ 5 wt % Cs) (a) thermal gravimetric data to 1300 K in air and Ar - 4% H_2 , and (b) mass spectrometric data to 1023 K . .	110
4.29. Optical micrographs of silicon carbide coated zeolite (a) polished section, and (b) macrograph of surface . . .	113
4.30. Gel-derived substrate particle of 70/30 (70 wt % simulated Savannah River Plant waste, 30 wt % additives) coated with low density buffer layer of SiC and a dense outer layer of SiC; the polished section shown is of a coated particle after being heat-treated in Ar - 4% H_2 to 1373 K to evaluate substrate-coating compatibility . .	116
4.31. Micrographs of 90/10 (90 wt % simulated Savannah River Plant waste, 10 wt % ZrO_2) microspheres (a) sintered, (b), (c), and (d) SiC coated microspheres	117
4.32. SiC and pyrocarbon coatings were applied to gel-derived substrates of 90/10 (90 wt % simulated Savannah River Plant waste, 10 wt % ZrO_2); nonflammable mixtures; SiC coating from $\text{CH}_3\text{SiH}_3 - \text{N}_2$; and pyrocarbon coating from propylene and N_2	118

CHAPTER I

INTRODUCTION

The solidification of high-radiation-level nuclear waste material, in preparation for its long-term storage, is a significant and important subject. The future of nuclear energy may very well depend on the resolution of this topic.¹ Although there are many different types of nuclear materials to be disposed, the high-level waste can be grouped into two sets: defense or commercial. These materials differ in radioisotope content, inert components content, and chemical form. It is of interest to further categorize these nuclear waste materials into three types: (1) cesium bearing, (2) materials containing the remaining species other than cesium, and (3) those containing the transuranium elements. The primary waste form developed to immobilize these wastes has been borosilicate glass.^{2,3} However, high-temperature leach tests that show the leach properties of borosilicate glass can be degraded⁴ has lead to increased efforts in research and development of alternative waste forms to minimize the risk of radioactive release from a repository. Some of the alternative waste forms evaluated include crystalline ceramic materials such as supercalcline,^{5,6} SYNROC,^{4,7} tailored ceramic,^{8,9} and monazite.¹⁰⁻¹³ The radiation stability of natural minerals as analogues to radioactive waste forms is being studied.¹⁴ Multiple barriers such as container, overpack, and repository conditions are also being evaluated to increase the integrity of the solidified materials.

Another of the alternative nuclear waste forms evaluated is the coated particle concept. Previous work on coating of calcine,¹⁵⁻²⁰ supercalcine,¹⁵⁻²⁰ and glass²¹ has been reported. The anticipated low leach rates for coated particles, however, were not achieved.¹⁹ This was due mainly to difficulties encountered with the thermal stability of the substrate and its interaction with coating process variables such as temperature, halogenated reactants, and reduction by the pyrocarbon coating.

Sol-gel technology developed for reactor fuel fabrication²²⁻²⁴ can be applied directly to the solidification of radioactive waste in crystalline ceramics. The chemical vapor deposition (CVD) fluidized-bed coating process, developed for coating High-Temperature Gas-Cooled Reactor (HTGR) fuel,²⁵⁻³³ should also be applicable.³⁴ For reactor fuels, radiation resistant coatings of pyrocarbon and silicon carbide are applied on gel-derived fissile microspheres to retain fission products. The coating process offers mechanical simplicity and, in addition, a large amount of background information exists related to substrate formation, quality assurance, processing of radioactive materials, and radiation testing of both pyrolytic carbon and of silicon carbide coatings. Thus it would be advantageous to evaluate both pyrolytic carbon and silicon carbide as coatings for nuclear waste. However, current chemical vapor deposition of SiC in the HTGR Program is performed near 1823 K with the halogenated reactant methyltrichlorosilane (CH_3SiCl_3) and hydrogen diluent gas. As related to high-level waste, the coating development needs are (1) the coating must be applied at low temperature (<1273 K) to minimize fission

product vaporization, and (2) substrate — coating gas compatibility must be maintained.

Methylsilane³⁵⁻⁴⁵ CH_3SiH_3 is a reactant which contains equimolar amounts of carbon and silicon, does not contain chlorine, and should decompose to form SiC ^{35,38,42} at temperatures lower than 1273 K. The chemical vapor deposition of SiC from methylsilane was thus evaluated and is reported in this dissertation. The variables included in the evaluation are the reactant gas flow rate, diluent gas type (argon or nitrogen) and flow rate, hydrogen content in the diluent gas, additive C_2H_2 gas flow rate, coating temperature, and type of substrate particle. Coating of pyrolytic carbon coated alumina substrate particles enabled a more complete evaluation of the SiC coating. Both low density buffer coatings as well as dense SiC coatings were synthesized and evaluated. The low density buffer coatings are necessary to prevent fracture of the dense SiC layer due to thermal expansion differences between the coating and the substrate. The ability to change the phases and their relative content in the SiC coating was evaluated. This was performed by varying (1) the composition or concentration of the gaseous additives (C_2H_2), and diluent gases, and (2) the coating temperature.

The coating process has been studied by evaluating coating efficiency, density, defective particle fraction, phase content, elemental composition, crystallite size, microstructure, and annealing behavior. Thermodynamic equilibrium calculations were performed for both the $\text{CH}_3\text{SiH}_3 - \text{C}_2\text{H}_2 - (\text{Ar} - \text{H}_2)$, and $\text{CH}_3\text{SiH}_3 - \text{C}_2\text{H}_2 - (\text{N}_2 - \text{H}_2)$ systems. The partial pressure of gaseous product species and the type and content of condensed phases were predicted and compared with

experiment. The comparison of experimental results with those of the thermodynamic evaluation points to the importance and significance of the free energy concept.

Examples of coated simulated nuclear waste forms are also presented. These are related to the development of a generic cesium bearing waste form and the coating of substrate particles with high waste loading. The research reported is the first performed with methylsilane in a fluidized-bed coating system. The subsequent application of the ideas developed in this dissertation has lead to two U.S. patents related to the low temperature chemical vapor deposition of SiC coatings.^{46,47}

CHAPTER II

LITERATURE SURVEY

Coated Forms

The coated particle concept for the solidification of nuclear waste materials can result in waste forms possessing excellent leach-resistant characteristics. The coating method which has received the greatest attention is the chemical vapor deposition process and various types of coaters have been evaluated including fluidized bed, drum, auger, and agitated bed. The properties of the substrate material (the material which contains the nuclear waste) have been shown to be very important in being able to produce acceptable coated forms.

Coating of Silicate Substrates

One of the earliest substrates evaluated was "calcine."¹⁵⁻²⁰ Calcine is the solid which forms when a slurry is introduced into an externally heated chamber. The volatiles are removed from the slurry resulting in a material composed of metal oxides, H_2O , and traces of nitrates and carbonates. The actual composition depends on the initial slurry. The particle size of calcine produced in spray-calciners can range from submicrometer to tens of micrometers. The particle size for the spheroid materials produced in fluid-bed calciners can range from submicrometers to millimeters. This substrate concept did not include the formation of specific phases or production of a substrate with special properties. Although the material was not an optimal substrate for CVD coating processes, it did provide a beginning for the coating

of nuclear waste forms and valuable information was obtained about the properties of substrates most important in the coating process. The calcine materials were found to be volatile and to possess a relatively low thermal stability with liquid phases present often at temperatures less than 1123 K. Initial coating experiments were performed with $\approx 200\text{ }\mu\text{m}$ substrates of irregular shape using a fluidized-bed coater. The coating chamber was a quartz tube of 55 mm diameter with a conical gas inlet distributor. Approximately 10 or 20 g of particles were coated per experiment. Volatile species such as cesium vaporized and the substrate particles tended to agglomerate when substrates were coated with pyrolytic carbon (PyC) at 1373 K. Initial efforts using acetylene for PyC deposition seemed successful in that PyC was deposited at temperatures as low as 1123 K. However even in those experiments the PyC coated particles were often broken and not of high physical integrity. Additional types of coating materials, such as metallic Fe, Si, Cr, or Ni as well as ceramic Al_2O_3 and SiC compounds were also evaluated. Both non-halogenated as well as halogenated reactants were tested and coating temperatures usually maintained near or below 1123 K. A list of some of the systems evaluated is shown in Table 2.1.

Some of the difficulties encountered were related to the thermal instability of the substrate, substrate porosity, thermal expansion mismatch between the substrate and coating, reactions between reactant or gaseous products and substrate, and use of halogenated reactants. The coated particles were evaluated by optical metallography, oxidation testing to at least 1023 K in air, and cursory leach tests. However,

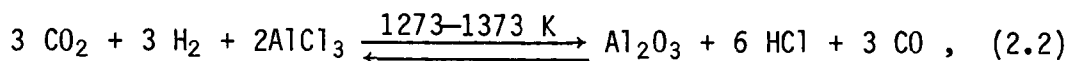
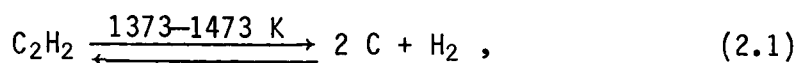
Table 2.1. Various coatings applied to calcine particles

Coating	Reactant	Coating temperature (K)
Ni	Ni(CO) ₄	443-503
PyC	C ₂ H ₂	1073-1223
Si	SiHCl ₃ + H ₂	773-1073
Cr ₇ C ₃	Cr(C ₉ H ₁₂) ₂	773
SiO ₂	SiCl ₄ + H ₂ O + H ₂	973-1073
SiC	CH ₃ SiCl ₃ + H ₂	1373
Al ₂ O ₃	AlCl ₃ + H ₂ O + H ₂	873-1173

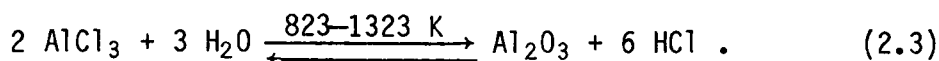
Source: R. W. Kidd, M. F. Browning, and J. M. Rusin, "Chemically Vapor Deposited Coatings for Multibarrier Waste," pp. 563-77 in Proceedings of the Seventh International Conference on Chemical Vapor Deposition 1979, T. O. Sedgwick and H. Lydtin, eds., Los Angeles, CA (October 1979).

it was felt that the quality of all coatings could have been improved if the substrate were modified or the coating processes optimized.

The multibarrier program goals were later changed to evaluate coated particles where the average size of the substrate particles was at least in the 1 to 10 mm range.¹⁵⁻²⁰ Both a rotating drum coater and a vibratory-bed coater were used to coat these larger particles. Some of the reactions considered were



and



All PyC coatings were deposited in fluidized-bed coaters with ZrO_2 diluent particles of ≈ 0.5 mm. The Al_2O_3 coatings were deposited in either drum or agitated-bed coaters with no diluent particles. Substrate materials for these experiments consisted of the supercalcine^{5,6,48} formulation. These particles were still quite heavily loaded with waste (70 wt % waste and 30 wt % additives). However, additives were included in an effort to produce specific phases in the final material. In this way the nuclear waste would be incorporated in a crystalline phase assemblage. Leach testing [Table 2.2] of coated particles produced in this manner indicated only a one-order-of-magnitude improvement over the leach rate of uncoated supercalcine particles.¹⁹ Cesium was also shown to be included in the coating layer. Indications are that the coatings may have been porous, defective, or cracked. Other work showed that supercalcine particles reacted with PyC at coating temperatures as low as 900°C leading to localized pitting in the coating. Other efforts included the coating of glass beads.^{19,21} Pyrolytic carbon was produced as a coating at 803 K. The coating rate was extremely low and highly toxic nickel carbonyl was necessary to catalyze the decomposition of C_2H_2 . Glass beads coated with PyC using this process yielded unsatisfactory results with the coating spalling at a low temperature of a few hundred degrees celsius.

Table 2.2. Leach tests of coated supercalcine^a

Substrate	Coating	Normalized Elemental Loss, [g/(m ² · d)]											
		Si		Ba		Ca		Mo		Sr		Cs	
		DIW ^b	NaCl ^c	DIW	NaCl	DIW	NaCl	DIW	NaCl	DIW	NaCl	DIW	NaCl
SPC-2	None	6.0	6.1	24	33	2.2	3.9	17	20	20	24	3.1	0.9
SPC-2	PyC	0.04	0.14	0.3	0.4	0.3	1.7	0	0.2	0.9	1.0	3.8	1.9
SPC-4	None	6.0	5.5	6.9	18	1.7	5.9	8.9	14	6.0	9.9	4.8	1.2
SPC-4	Al ₂ O ₃	0.09	0.18	0.05	0.05	0.7	3.7	0.02	0.12	0.005	0.05	0.28	0.31
SPC-4	PyC/Al ₂ O ₃	0.09	0.17	0.01	0.05	0.7	4.4	0	0.2	0.01	0.15	0.12	0.28

Source: J. M. Rusin, J. W. Shade, R. W. Kidd, and M. F. Browning, "Chemically Vapor Deposited Coatings for Multibarrier Containment of Nuclear Wastes," pp. 248-61 in Alternate Nuclear Waste Forms and Interactions in Geologic Media, L. A. Boatner and G. C. Battle, Jr., eds., CONF-8005107, U.S. Department of Energy, Washington, D.C. (1980).

^a363 K — 28 days, SA/SV + 10 m⁻¹.

^bDeionized water.

^c0.5 M NaCl.

Coating of Sol-Gel Derived Substrates

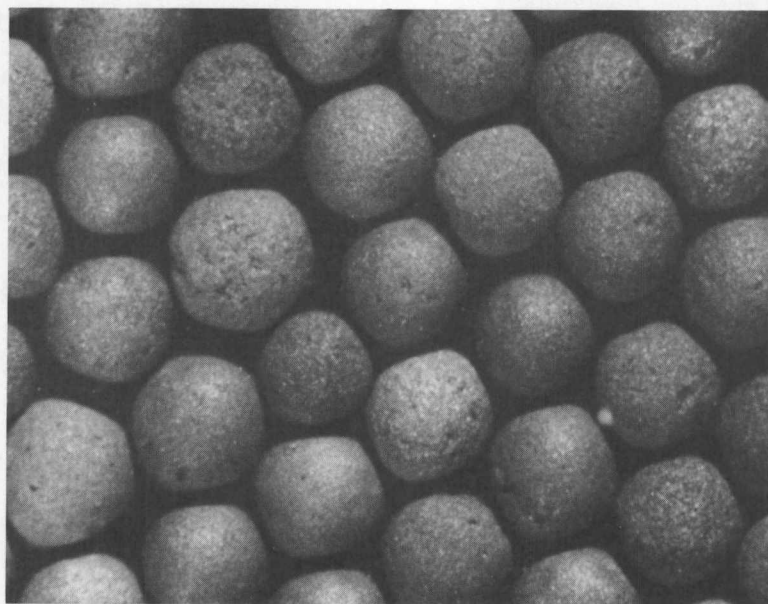
Much emphasis has recently been placed on crystalline ceramic substrates, since high-temperature high-pressure leach tests have shown that the leach properties of glass can degrade. SYNROC is a titanate-based ceramic waste form developed by Ringwood.^{4,7,49} This concept seeks to immobilize radioactive species by incorporating them in a solid solution crystalline phase assemblage and was unique in that (1) a titanate based mineral system was chosen which possesses low leach rates and (2) the radioactive waste components were added in dilute solution. The composition with little or no nuclear waste is SYNROC-B and the composition which deals with commercial nuclear materials solidification is SYNROC-C.⁵⁰ This material contains as its final phases Hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$), zirconolite ($\text{CaZrTi}_2\text{O}_7$), and perovskite (CaTiO_3). Defense related nuclear waste poses a different set of conditions on the final waste form and process.^{51,52} One of the crystalline waste forms for the solidification of defense-related nuclear materials is SYNROC-D^{53,54} (Table A.1) which is an assemblage of nepheline ($\text{NaAlSi}_3\text{O}_8$), zirconolite, perovskite, spinel [$\text{MN}_2\text{O}_4 - \text{M}_2\text{TO}_4$ (M = divalent cation, N = trivalent cation, T = tetravalent cation)]. The various SYNROC alternative waste forms are thermally stable to a temperature of at least 1273 K which makes them excellent candidates as coating substrates.

Sol-gel technology has been used to produce tons of reactor fuel for the HTGR Program by the external gelation and water extraction process.^{22,23} Initial research and development on its application for the solidification of nuclear waste has been placed on the internal

gelation process to maintain system flexibility. Microspheres of the SYNROC-B, SYNROC-C, and SYNROC-D formulations were produced.⁵⁵ Microspheres of the SYNROC-D formulation sintered to a density of 4.19 g/cm^3 in an Ar — 4% H₂ atmosphere at a temperature of 1173 K are shown in Fig. 2.1.

Chemical vapor deposited coatings of pyrolytic carbon and SiC in fluidized-bed coaters have been evaluated and used for coating HTGR fuel for many years. Pyrolytic carbon coatings of HTGR fuel were applied at 1573 K to obtain isotropic and impermeable coatings. In addition carbon has been shown to be highly leach resistant in aqueous media.⁵⁶ However, since the alternative waste form substrates are not stable at this temperature, pyrocarbon coatings were applied to SYNROC microspheres at $\approx 1273 \text{ K}$. Initially thermal expansion differences between the substrate and the dense pyrocarbon layer resulted in cracked coatings. Cracking was eliminated by depositing a low-density pyrocarbon coating between the substrate and the dense pyrocarbon coating (Fig. 2.2). Characterization by mercury porosimetry, immersion density, gaseous chlorine leach at 1273 K, and aqueous leaching proved them to be of high quality.⁵⁷⁻⁶⁰ Results of aqueous leach tests by the MCC-1 procedure⁶¹ for both uncoated and pyrocarbon coated SYNROC-B and SYNROC-D (defense simulated waste) are presented in Table 2.3. The leach results for all species of the pyrocarbon-coated substrates were below the detection limit of the inductively coupled plasma technique used to measure the concentration of each species. The leach results were calculated from the equation

ORNL-DWG 81-10207



1000 μm

Fig. 2.1. Microspheres of SYNROC-D formed by the internal gelation process (sintering temperature 1173 K, atmosphere — Ar — 4% H₂, density 4.19 g/cm³).

ORNL-PHOTO 2703-81

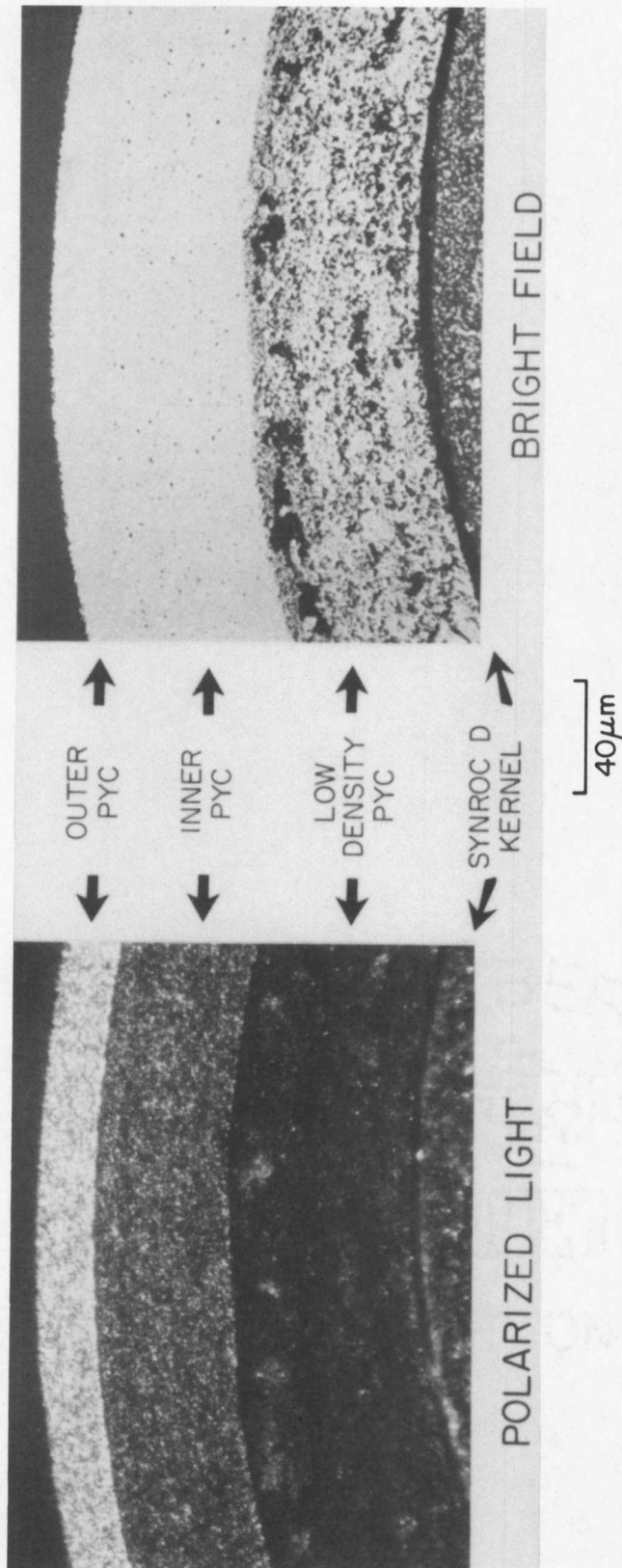


Fig. 2.2. Pyrocarbon coated gel-derived substrate of the SYNROC-D formulation.

Table 2.3. Leach test results for uncoated and pyrocarbon coated sol-gel derived particles^a

Element	Leach rate [g/(m ² · d)]				
	Detection limit (5 d)	Uncoated SYNROC-B (3 d)	PyC-coated SYNROC-B (1 d)	Uncoated SYNROC-D (3 d)	PyC-coated SYNROC-D ^b (3, 7, or 28 d)
Fe	3×10^{-5}	3×10^{-4}	c	6×10^{-3}	c
Al	1×10^{-4}		c	2×10^{-2}	c
Mn	2×10^{-5}	d	c	1×10^{-3}	c
U	1×10^{-5}	d	c	4×10^{-3}	c
Ca	2×10^{-4}	2×10^{-2}	c	4×10^{-1}	c
Ni	4×10^{-5}	d	c	3×10^{-3}	c
Si	1×10^{-4}	d	c	7×10^{-2}	c
Na	6×10^{-4}	d	c	1×10^{-2}	c
Zr	2×10^{-5}	9×10^{-5}	c	3×10^{-3}	c
Ti	5×10^{-6}	3×10^{-4}	c	2×10^{-4}	c
Ba	2×10^{-4}	4×10^{-3}	c	d	
Mo	1×10^{-3}	c	c		c
Ce	4×10^{-4}	c	c	5×10^{-3}	c
Nd	1×10^{-3}	d	c		c
Sr	1×10^{-5}	4×10^{-4}	c	5×10^{-1}	c
Cs	4×10^{-5}	d	d	d	d

^aLeach rate — $M_i/(f_i SA \Delta t)$; M_i = mass of element in solution (g); f_i = fraction of element in kernel; SA = surface area of sample (m²); Δt = time period of leach (d). Leach test MCC-1; deionized H₂O; 363 K. detection limit determined by averaging blanks submitted during test (V_{sol} = 20 cm³, Δt = 5 d, SA = 75×10^{-4} m²).

^bDetection limit for 28 d samples is a factor of 5 lower than limit listed.

^cBelow detection limit.

^dElement not present in waste form.

$$\text{Leach rate} = M_i / (f_i SA \Delta t) \quad (2.4)$$

where

M_i — mass of element in solution (g),

f_i — fraction of element in specimen,

SA — surface area of the specimen (m^2), and

Δt — the period of the leach test (d).

The composition of alternative nuclear waste ceramics can also be defined by other parameters such as (1) the ease of their processing by the gelation process or (2) maximizing the waste loading. However phases which form may not be as thermally stable as those present in the SYNROC materials. Substrates of higher waste loading (from 70 to 90 wt % waste) were found to react with pyrocarbon⁶¹ at either 1273 or 1573 K. An example of reactions which can occur when using substrates with a high Savannah River Plant (SRP) waste loading (>70 wt %) are shown in Fig. 2.3. Other coating materials may be required to prevent or minimize reactions during coating.

Zeolite

Cesium is one of the species in radioactive waste which is difficult to immobilize in waste forms such as glass, calcine, supercalcine, and the various types of SYNROC formulations. These alternative waste form processes seek to incorporate all the species in radioactive waste into one ceramic materials system. This proves to be a difficult task which can compromise the chemical stability and mechanical properties of the ceramic waste form. High leach rates

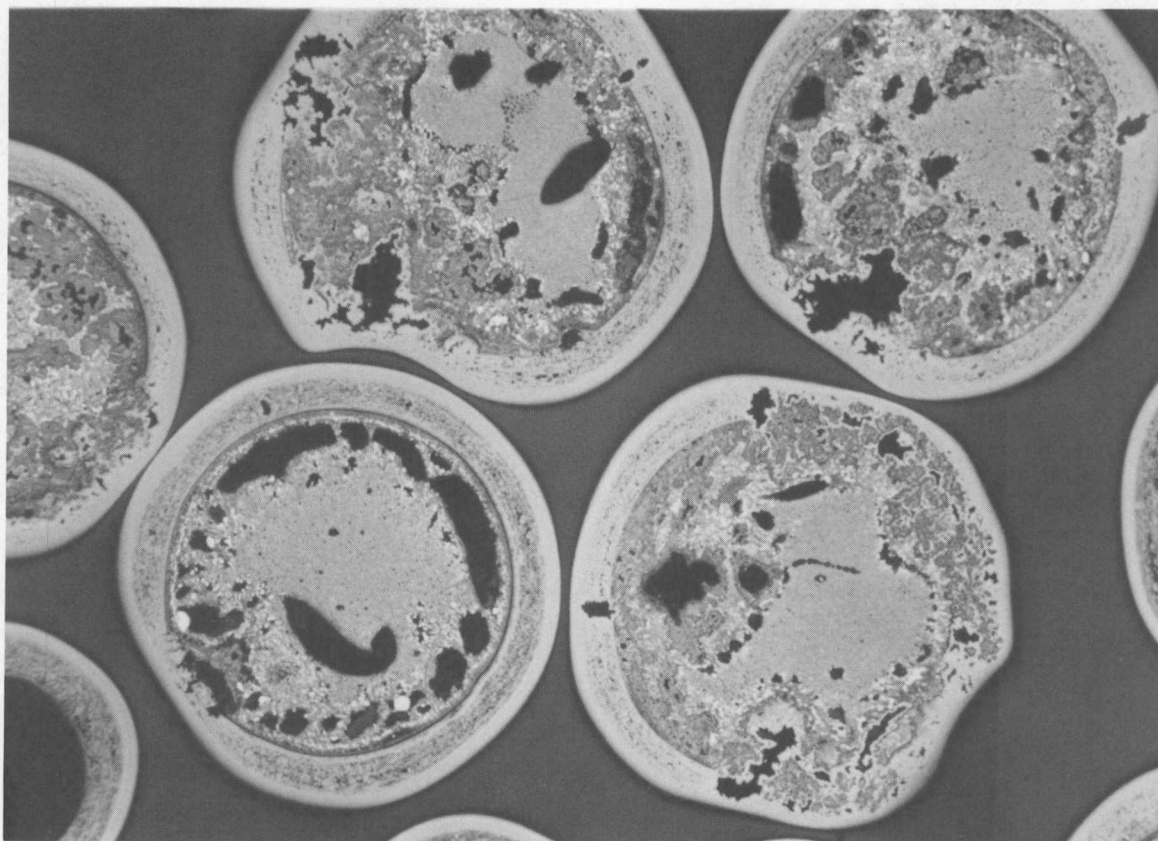


Fig. 2.3. Microspheres of high-waste loading (>70 wt %) react with pyrocarbon during coating at 1273 K.

can result since some species have an inherently high solubility or tendency to partition into leachable phases.

In processing of defense waste, cesium is frequently removed from the waste stream and loaded onto zeolite granules. This has been reported by Wiley and Wallace⁵² for removal of cesium from the Savannah River Plant waste supernate. Cesium and strontium have also been removed from high-level defense waste at Hanford, Washington, by adsorption onto zeolite as reported by Nelson and Mercer,⁶² and Buckingham.⁶³ Storage of strontium and cesium loaded zeolite for future recovery has been evaluated. Several laboratory and pilot plant scale projects have been performed where zeolite was loaded with radioactive strontium or cesium. Radiolytic decomposition of the H₂O component in the zeolite to hydrogen and oxygen can occur leading to pressurization of the container. In some cases zeolite loaded with strontium was dried to 873 K before being sealed in containers for a period of 2 years. The material was heated to remove most of the H₂O component from the zeolite and thereby minimize the products of radiolytic decomposition. The sealed container was later opened and the adsorption-desorption properties of the zeolite evaluated. It was found that it was possible to elute strontium from the zeolite even after irradiation to very high doses of $>10^{11}$ rads. However, the partitioning of cesium and strontium for long-term storage in zeolites has received little attention. Zeolite was also used as a medium to transport radioactive cesium between sites. More recently a synthetic zeolite, Ionsiv IE-95 (Linde Division, Union Carbide Corporation, New York, N.Y.) was used at Three Mile Island Nuclear

Facility for removal of cesium from the containment building sump water and reactor system water.⁶⁴

Komarneni and Roy evaluated various zeolites for fixation of cesium and strontium by thermal and hydrothermal treatments.⁶⁵ Natural zeolites were used but the composition of each type was not determined. The fixation, defined as the difference between the total cesium loaded onto the zeolite and the amount released after a 24 h exposure in 0.1 N KCl, was determined for each zeolite. Seven zeolites were evaluated in the fully loaded condition and two types of zeolites were evaluated in the partially loaded condition. A partial listing of their results is presented in Table 2.4. The lower fixation of cesium, at intermediate temperatures (~ 1073 K), for the mordenite and chabazite zeolites was attributed to their high thermal stability. These results indicate that the phillipsites and analcite fix the most cesium at the lowest temperatures. The differences in the fixation percent for the two phillipsite zeolites was attributed to differences in their composition even though their compositions or microstructures were not evaluated. Evaluation of partially loaded phillipsites and analcite zeolites showed that higher heat treating temperatures were required to achieve the same level of fixation.

Most zeolites fixed a large fraction of the cesium when heated to 1273 K in air. The mechanism of cesium fixation was evaluated by analyzing x-ray diffraction patterns of the various cesium loaded zeolites. Results of some of the zeolites are summarized in Table 2.5. Fixation in analcite was attributed to dehydration of the structure (transformation to pollucite). In phillipsite, fixation was also

Table 2.4. Fixation of Cs in fully Cs-loaded zeolites by heat treatment in air

Zeolite	Mass of Cs loaded per 100 g of zeolite	Cs Fixation (%)				
		298 K	623 K	873 K	1073 K	1273 K
Mordenite $\text{Na}_8\text{Al}_8\text{Si}_4\text{O}_{96} \cdot 24\text{H}_2\text{O}$	18	15.6	15.6	16.7	22.6	67.7
Chabazite $\text{Ca}_6\text{Al}_{12}\text{Si}_{24}\text{O}_{77} \cdot 40\text{H}_2\text{O}$	22	16.5	17.6	17.0	25.9	89.3
Phillipsite (1) $(\text{K}, \text{Na})_{10}\text{Al}_{10}\text{Si}_{22}\text{O}_{64} \cdot \text{ZOH}_2\text{O}$	26	12.8	13.1	87.0	91.2	99.9
Phillipsite (2)	29	10.5		72.3	88.5	99.8
Analcite $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$	0.8	0	98.5 ^a	99.5	99.8	b

Source: Komarneni, S., R. Roy, "Zeolites for Fixation of Cesium and Strontium from Radwastes by Thermal and Hydrothermal Treatment," Nucl. Chem. Waste Management, 2[4], 259-64 (1981).

^aHeated to 693 K.

^bNot reported.

Table 2.5. Phases present in fully Cs-loaded natural zeolites after heating in air

Zeolite	Phases present after heat treatment	
	873 K	1273 K
Mordenite	Mordenite	CsAlSiO ₄ + Cristobalite
Chabazite	Chabazite	a + b
Phillipsite (1)	Cs-feldspar ^c + pollucite	Cs-feldspar ^c + pollucite
Phillipsite (2)	Cs-feldspar ^c + pollucite	Cs-feldspar ^c + pollucite
Analcite	Analcite ^c + pollucite	Cs-feldspar ^c + pollucite

Source: Komarneni, S., R. Roy, "Zeolites for Fixation of Cesium and Solutions from Radwastes by Thermal and Hydrothermal Treatment," Nucl. Chem. Waste Management, 2[4], 259-64 (1981).

^aUnidentified phases.

^bAmorphous background.

^cPreliminary result.

attributed to dehydration and the subsequent formation of a new mineral phase tentatively identified as Cs-feldspar (CsAlSi₃O₈). Fixation in the mordenite, chabazite was attributed to recrystallization. However, no Cs partitioning studies were reported.

The results of these previous studies show that Cs can be incorporated in zeolites. In addition the Cs-loaded zeolites can be heat treated to minimize radiolytic decomposition effects, and to minimize leaching effects.⁶⁶ The data show that zeolite may be a suitable substrate for the coated particle concept if it can be coated at a sufficiently low temperature.

Chemical Vapor Deposition of SiC

Silicon carbide is a material which is used in many segments of our society.^{67,68} One method of obtaining SiC, especially as a

coating, is by the use of CVD. Currently the chemical vapor deposition process is used for coating of HTGR nuclear fuel particles with SiC to prevent the escape of fission products. The SiC is deposited at temperatures near 1823 K in fluidized-bed coaters, hydrogen-diluent gas, and methyltrichlorosilane (CH_3SiCl_3) reactant gas. Since CH_3SiCl_3 contains chlorine, various chloride compounds can form; with HCl being one of the most pronounced and corrosive. For HTGR applications these coating conditions are acceptable. However, for other applications, these conditions can lead to extensive process-substrate interactions such as chlorine corrosion, melting, or hydrogen reduction. As related to high-level waste, the basic requirements for coating development are the following: a coating must be applied at low temperature to prevent or minimize vaporization, substrate-coating-gas compatibility must be maintained, the oxygen fugacity during coating must be within certain limits to prevent reduction of phases in the substrate, and the coating must be leach resistant.

Non-Halogenated Reactants

The deposition of SiC by the chemical vapor deposition process has been evaluated by many researchers.^{27,29,30,33,44,69} The experiments and results can be grouped in various sets depending on the type of reactant gases, carrier gas, temperature, total system pressure, substrate, furnace type, growth rate, and gas flow rates. Each of these conditions can change the microstructure, composition, or properties of the material which is produced. An article by Schlichting⁴⁴ reviews recent papers on this subject. The various

reactant gases can be grouped into halogenated or non-halogenated compounds. A list of some of the gases is presented in Table 2.6.

Table 2.6. Reactant gases for the CVD of SiC

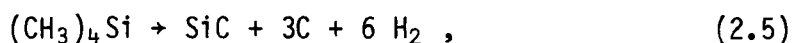
Halogenated		Non-halogenated
CH_3SiCl_3	SiCl_4	CH_3SiH_3
$\text{CH}_3\text{SiCl}_3 + \text{CH}_4$	$\text{SiHCl}_3 + \text{CHCl}_2$	$\text{CH}_3\text{Si}(\text{CH}_3\text{O})$
$\text{CH}_3\text{SiCl}_3 + \text{CF}_4$	$\text{SiHCl}_3 + \text{CCl}_4$	$(\text{CH}_3)_4\text{Si}$
$(\text{C}_2\text{H}_5)\text{SiCl}_3$	$\text{SiHCl}_3 + \text{C}_5\text{H}_{12}$	$\text{SiH}_4 + \text{C}_3\text{H}_8$
$\text{CH}_3\text{SiHCl}_2$	$\text{SiCl}_4 + \text{C}_x\text{H}_y$	$\text{SiH}_4 + \text{CH}_4$
$(\text{CH}_3)_2\text{SiCl}_2$	$\text{SiCl}_4 + \text{CCl}_4$	CH_4
$(\text{C}_2\text{H}_5)_2\text{SiCl}_2$		
$(\text{C}_2\text{H}_5)_2\text{SiCl}_2 + \text{CH}_3\text{SiHCl}_2$		
$(\text{CH}_3)_3\text{SiCl}$		

Diluent gases have consisted of H_2 , Ar, N_2 , He, HCl. In cases where nitrogen was used as a carrier or diluent gas the reactant gas was a halogenated compound, the substrate heated by direct means, and the temperature range evaluated was between 1473 and 1673 K. Formation of SiC was reported in two cases and $\text{Si}_3\text{N}_4 - \text{SiC}$ in a third. The codeposition of $\text{Si}_3\text{N}_4 - \text{SiC}$ was reported in a fluidized-bed coating system.²⁹

Gareis⁷⁰ has reported the formation of a β -SiC coating on inorganic substrates. The main objective of that work was to evaluate SiC for wear resistant coating, and semiconductor applications. The reactants evaluated were $(\text{CH}_3)_4\text{Si}$, and a mixture of $\text{SiH}_4 - \text{CH}_4$. The reactions were carried out in a system pressure range of 13 to 26 Pa and a temperature as low as 1023 K. The total system pressure was found to be a critical variable. No SiC deposit was apparent for pressures below 13 Pa. Also flakes of SiC formed at pressures greater

than 26 Pa. Many side reactions were noted to occur at temperatures greater than 1673 K.

Deposition of SiC in a fluidized bed coater using the non-halogenated reactants $(\text{CH}_3)_4\text{Si}$ or SiH_4 has been evaluated by Federer.⁷¹ The main variables in that study were deposition temperature, reactant gas type, and fluidizing gas. The substrate particles coated were PyC coated ThO_2 spheres of $\sim 475 \mu\text{m}$ diameter, and 2.44 g/cm^3 density. Either 10 or 20 g particle batches were coated with SiC. The SiC coated particle were evaluated by metallography, density and x-ray diffraction. In the $(\text{CH}_3)_4\text{Si}$ experiments, the reactant liquid was placed in a vaporizer and transported to the furnace with hydrogen carrier gas. When hydrogen was used as the fluidizing gas the coating density decreased with increasing temperature. There was no mass gain at a deposition temperature of 1098 K although a coating was formed at 1248 K which had broad SiC x-ray diffraction lines. Experiments were performed at temperatures up to 1800 K. Coating density was found to decrease with increasing temperature. It had been thought that hydrogen would suppress the decomposition reaction



however, it was speculated that excess carbon was present in the coatings. Coatings deposited at 1298 K contained radial cracks and, after oxidation of the coating at 1273 K, a white residue, later identified as SiO_2 by x-ray diffraction, was found. Coatings deposited at 1498 and 1798 K appeared to be completely oxidized. Oxidation experiments of SiC coatings deposited with argon as the fluidizing gas

gave similar results. Particle fluidization stopped shortly after coating experiments began when argon was the fluidization gas. Fluidization with hydrogen suppressed the reaction and adherent porous coatings were obtained.

Results reported by Wacker-Chemie G.M.B.H.³⁵ show that SiC can be produced from alkyl-silanes such as CH_3SiCl_3 and CH_3SiH_3 . The main objective of their work was to produce pure or doped SiC crystals suitable for semiconductor applications. Using a reactant with equal amounts of silicon and carbon also simplified the process in that only one reactant gas needs to be monitored. Crystals of SiC were grown on a carbon substrate which was inductively heated within a cold wall furnace. Powder was produced when CH_3SiH_3 was decomposed at atmospheric pressure in the 873 to 1373 K temperature range. Heating the powder to 1873 or 2273 K in an inert atmosphere or vacuum was reported to produce coarse crystalline SiC. The size of the as-produced material was dependent on the total system pressure and type of diluent gas. Possible diluent gases included the rare gases, H_2 , N_2 , CO or a mixture of these. The diluent gas volume fraction varied from 99 to 30%. The reaction was also carried out at low pressure without diluent gas at 973 to 2773 K. Large crystals up to 10 mm in size were obtained by performing the reaction at a temperature of 2073 K and large dilution factors. Crystals of 3 mm in size were produced at temperatures as low as 1673 K and at even lower temperatures if carried out at lower pressure. High reactant gas flow rates resulted in fine crystals and low flow rates in coarser materials.

Spielmann³⁸ evaluated the epitaxial growth of SiC onto <0001> oriented hexagonal single crystal SiC by decomposing CH_3SiH_3 or $\text{SiH}_4 + \text{C}_3\text{H}_8$ in vacuum. These non-halogen containing systems were studied to avoid the formation of HCl, and any reactions which could occur with HCl during the epitaxial growth process. A single crystal α -SiC was placed on an inductively-heated graphite rod which was placed vertically in a water cooled quartz reaction tube. The reactant gas flow was directed down onto the SiC-crystal resting on the graphite rod. Methylsilane was diluted with H_2 by a factor of 1 to 1000, the total pressure maintained at 1.01×10^5 Pa, and the α -SiC crystal heated to 2073 K. A fraction of the CH_3SiH_3 decomposed prior to contacting the substrate resulting in particulates impinging on the single crystal. These particles were believed to be nucleation sites where polycrystalline growth occurred. In order to avoid the thermal decomposition of CH_3SiH_3 prior to contacting the SiC single crystal, methylsilane without any hydrogen diluent gas was flowed over the SiC single crystal at a total system pressure of ≈ 1.3 Pa. A SiC growth rate of approximately 60 to 80 $\mu\text{m}/\text{min}$ was achieved. In both of these experiments the deposited SiC was polycrystalline. This was explained in the following manner. Since silicon has a high vapor pressure in this temperature range, a codeposition of SiC + C can take place. This could lead to polycrystalline growth since the excess carbon can act as nucleation sites where SiC grain growth can occur.

The second system evaluated by Spielmann³⁸ was that of $\text{SiH}_4 + \text{C}_3\text{H}_6$. The gas flow rate of each reactant gas was regulated, the total pressure maintained at ≈ 1.3 Pa, and no diluent gases were

used. Epitaxial growth was obtained at a Si/C mole ratio in the reactant gas phase of 1/2. Silicon carbide of either β -cubic or 6H-hexagonal crystal modification was obtained in the 1873 to 2173 K temperature range. The 6H polytype formed at lower growth rates and β -cubic at higher growth rates. The SiC growth rate was controlled by changing the respective reactant gas flow rates which implies that the total system pressure would change.

Böcker and Hausner⁴² synthesized silicon carbide powder from the gas phase thermal decomposition of CH_3SiH_3 . The powder reaction chamber consisted of an inductively heated graphite tube connected to a powder collection and filtering system. Argon was used as a diluent gas and the experiments were carried out in the 1273 to 2073 K temperature range. The yield or efficiency of the process was always greater than 80% and approached 98% at a temperature of 2073 K. Crystalline SiC material was produced over this entire range. The crystallite size of the SiC was determined from X-ray diffraction analyses by the Scherrer method. The crystallite size increased from 5 to 20 nm as the thermal decomposition temperature increased from 1273 to 2073 K. The powder was reported as β -SiC. Quantitative analyses of the composition were also performed and results shown in Fig. 2.4. Powder produced at 1473 K was rich in silicon by ≈ 4 wt % absolute. The silicon concentration was found to decrease as the decomposition temperature increased. The composition of the powder produced at 1873 K and above was constant although the carbon content was ≈ 0.5 wt % higher than the theoretical value for stoichiometric SiC.

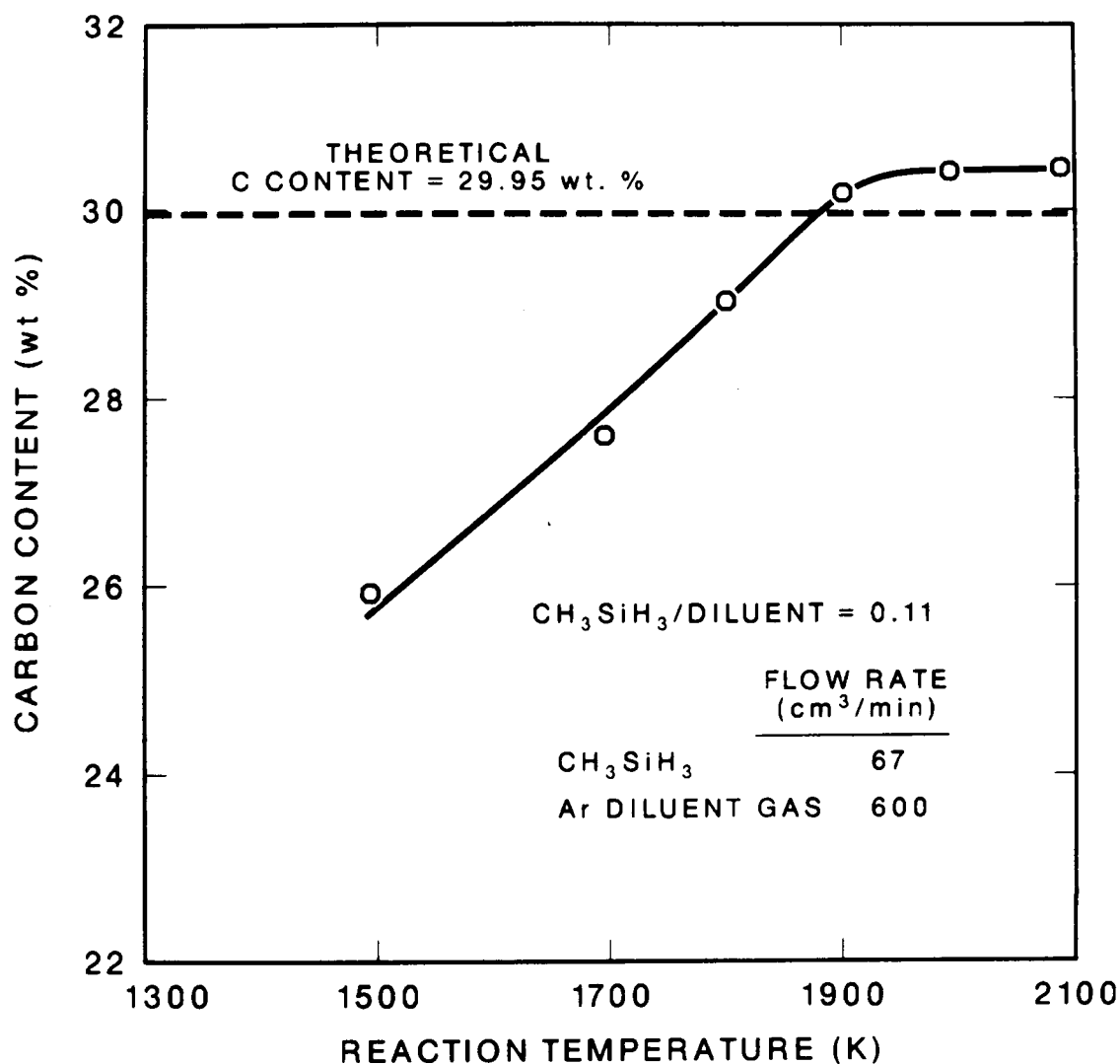


Fig. 2.4. Composition of SiC powder synthesized from the thermal decomposition of CH₃SiH₃ in an Ar diluent.

Source: W. Böcker and H. Hausner, "Verfahren zur Herstellung von Siliciumcarbidpulvern aus der Gasphase," Ber. Dt. Keram. Ges., 55(4), pp. 233-37 (1978).

CHAPTER III

EXPERIMENTAL PROCEDURE

Apparatus

Fluidized-Bed Coating System

The CVD coating system constructed for this research is similar in design to those used for pyrocarbon and silicon carbide coating of nuclear fuel particles.⁷¹ Various changes were made but the system was kept versatile so that it could be used for a variety of CVD processes. Most earlier studies of the CVD of SiC on nuclear fuel were performed with the reactant methyltrichlorosilane (CH_3SiCl_3) and hydrogen carrier gas. A reaction product for that case is HCl which can be very corrosive to the equipment. Thus it was necessary in those coaters to pass the gaseous products through a scrubber which either neutralized or diluted the HCl component. In addition a vaporizer was required to produce gaseous CH_3SiCl_3 from the liquid. The CH_3SiCl_3 vapor saturated a carrier gas, normally hydrogen, and was introduced into the coating furnace. The scrubber and vaporizer components of the CVD system are not necessary for CVD of SiC from CH_3SiH_3 but were constructed in case chloride or fluoride based reactants were used.

A diagram of the present coating system is shown in Fig. 3.1. One major difference from previous systems is the CH_3SiH_3 supply. The CH_3SiH_3 supply cylinder and regulator were installed on a Mettler P11N scale. The scale has a 10 kg capacity, 0.05 g sensitivity. The outlet pressure of the regulator was maintained at a constant 6.7×10^4 Pa

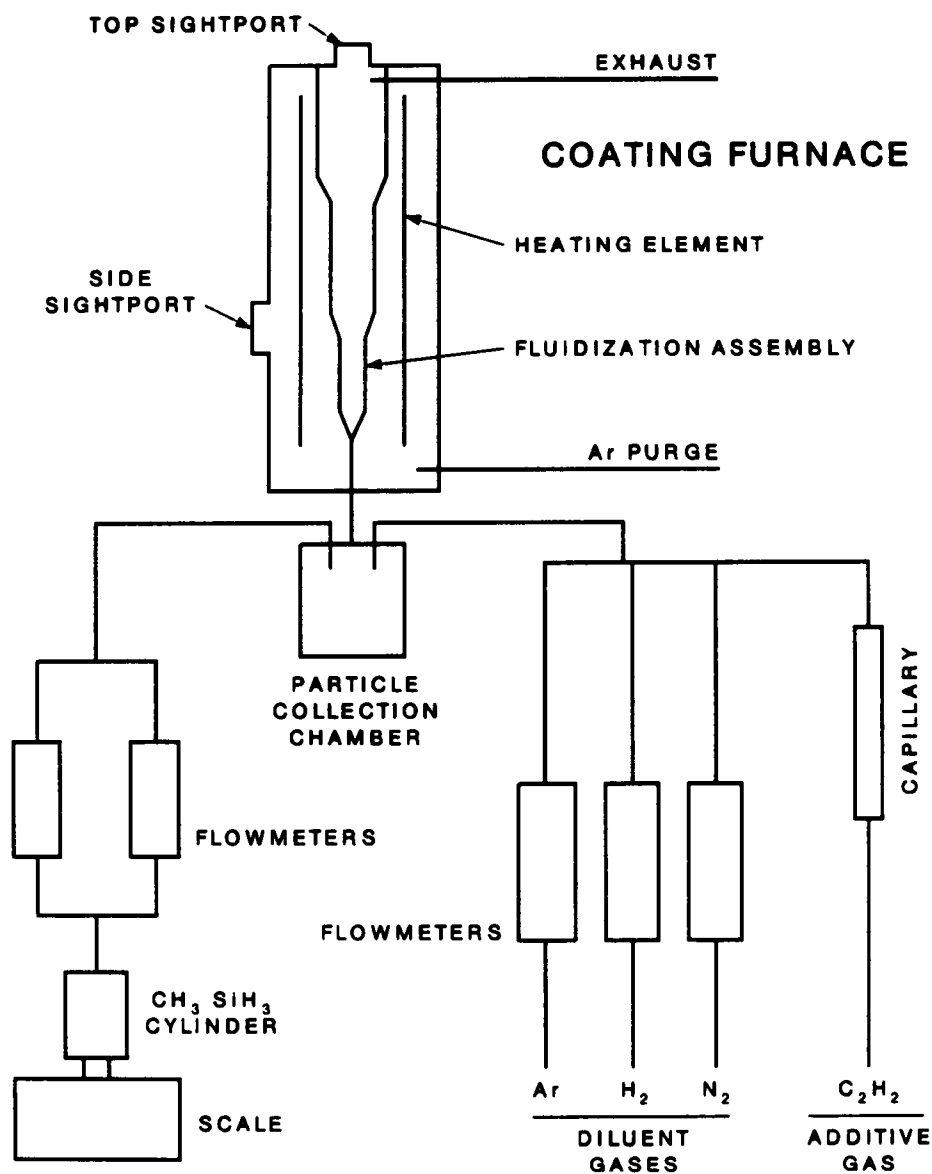


Fig. 3.1. Diagram of coating system.

(≈ 10 psi) for all coating experiments. Since CH_3SiH_3 is highly reactive if exposed to air or moisture it was decided to calibrate the flowmeters by measuring the mass of the CH_3SiH_3 cylinder and regulator before and after each coating experiment. Connection between the regulator and the flowmeters was made with polyethylene tubing. Two float-type flowmeters metered CH_3SiH_3 in two flow rate regimes. A Brooks flowmeter with R-2-15-D tube and sapphire float was used for flow rates up to $500 \text{ cm}^3/\text{min}$ and a Brooks flowmeter with R-2-15-AA tube and pyrex float for flowrates as low as $20 \text{ cm}^3/\text{min}$. The flow rate in each case was set by adjusting a valve on the exit side of the respective flowmeter. The CH_3SiH_3 flowmeters are connected with polyethylene tubing to the particle collection chamber located at the bottom of the coating furnace.

Each of the diluent gases Ar, N_2 , H_2 and additive gas C_2H_2 supplies have independently controlled metering systems. The backing pressure to each gas metering system was held constant at $6.7 \times 10^4 \text{ Pa}$. Brooks float-type flowmeters with R-2-15-C tube were used for Ar, N_2 , and H_2 , whereas a capillary was used to control the C_2H_2 additive flow rate. The flowmeters in the argon and nitrogen supplies used carboloy floats but the hydrogen flowmeter used a pyrex float. The argon and hydrogen flowmeters were calibrated with a wet test meter. The nitrogen flow rate was related to the argon calibration by using standard correction tables. The C_2H_2 additive capillary was calibrated by recording the volume of water displaced in a specified time period.

The coating furnace was designed to accept fluidization tubes with various diameters and cone angles. The fluidization tube provides a

controlled volume where CVD reactions may take place. Particles are fluidized and coated within the reaction cone section. The top of the fluidization tube is in contact with the furnace thereby assuring that particles are not lost during a coating experiment. All experiments related to the present research were performed with a fluidization tube of design shown in Fig. 3.2. The three piece graphite assembly has a 2.5 cm inner diameter and 30° included angle reaction cone. A disentrainment chamber is connected to the reaction cone and provides an upper limit to the fluidization of particles. The top graphite tube is of larger diameter and connects the disentrainment chamber to the top section of the coating furnace to prevent any loss of particles and to route the product gases out of the furnace. A resistance-heated graphite heating element surrounds the fluidization tube.

A photograph of the coating system is shown in Fig. 3.3. The furnace outer jacket is made from aluminum and is water cooled. The furnace power supply provides a maximum of 25 kW (500 A, 50 V) with 4 kW typically required for a 1300 K experiment (200 A, 20 V). The coating furnace is operated with an argon atmosphere surrounding the heating element and fluidization assembly to prevent oxidation of the graphite parts. A side sightport is located at a level corresponding to the reaction cone fluidization region. This port is used for temperature measurement of the reaction cone's outer surface. A second sightport located at the top of the furnace permits observation of the fluidized particles during a coating run. Temperature measurements were made with a micro-optical pyrometer of the disappearing filament type manufactured by the Pyrometer Instruments Company. The pyrometer

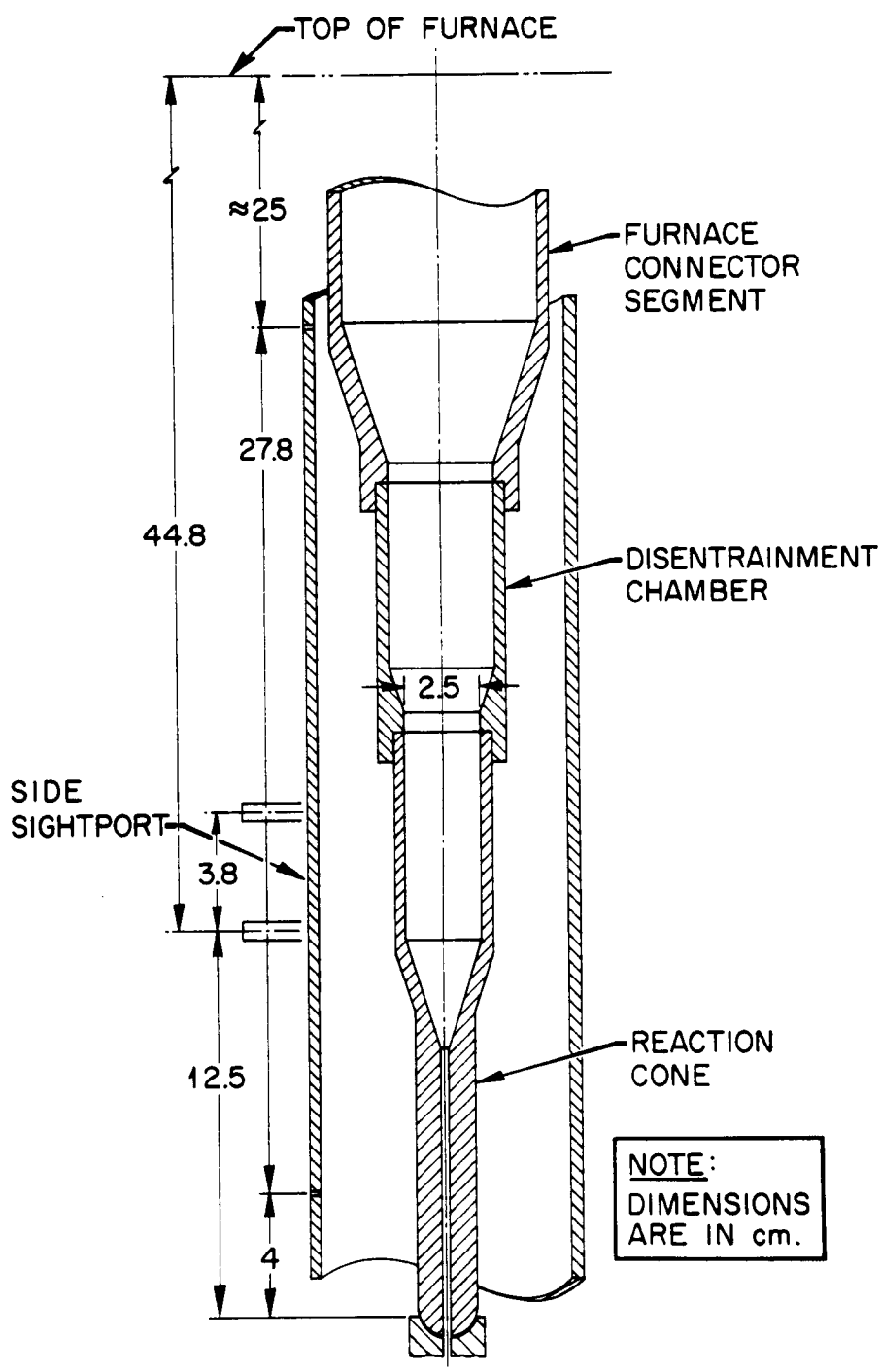


Fig. 3.2. Diagram of the fluidization assembly, furnace element, and location of the furnace side sightport.

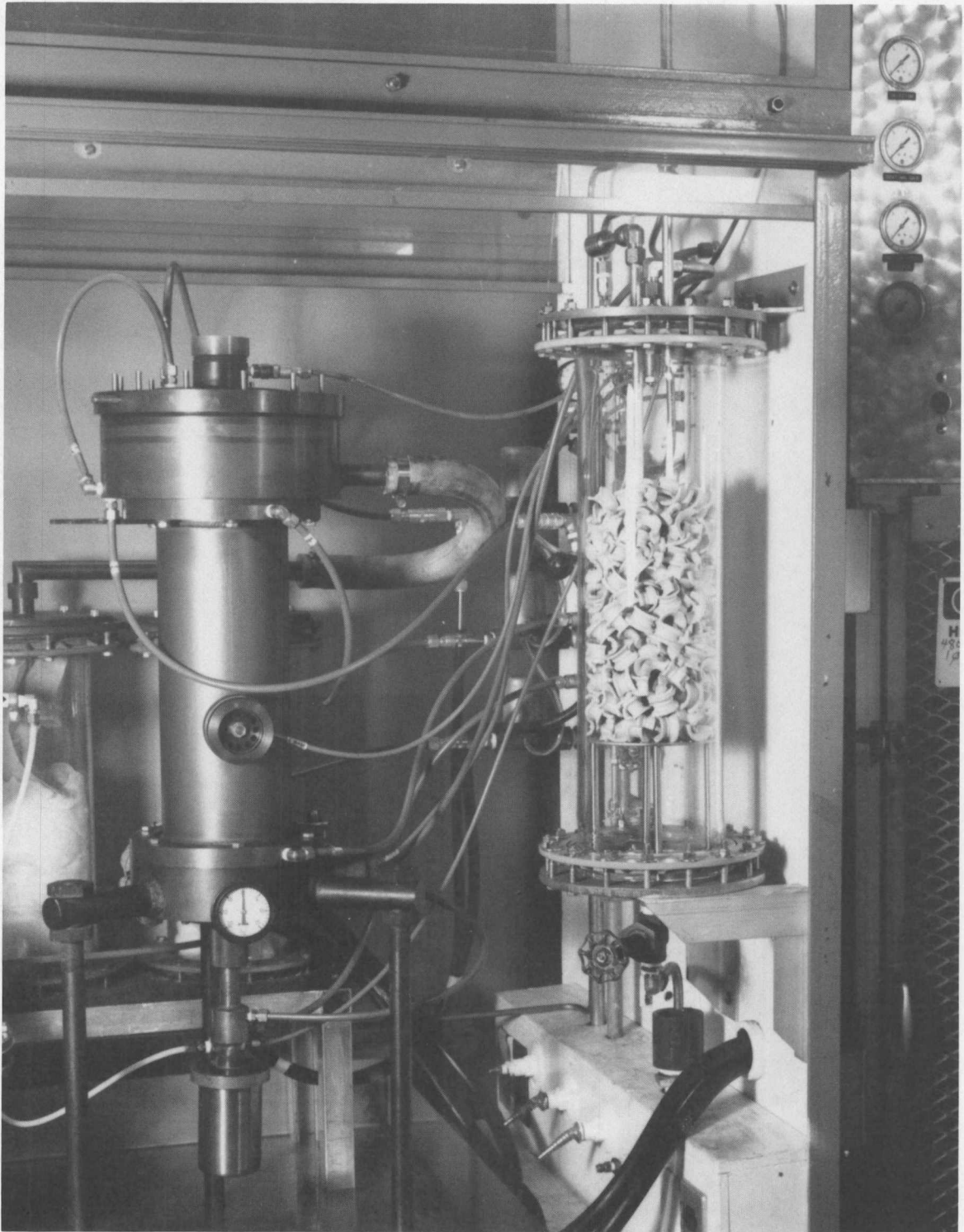


Fig. 3.3. Photograph of fluidized-bed coating system.

was calibrated and temperature measurements were corrected for sight glass absorption effects. These corrections were less than 10 K for temperatures less than 1273 K. The coating temperature for the 873, 973, and 1073 K experiments were measured with a thermocouple positioned into the fluidized bed.

Sintering and Annealing Furnaces

Two controlled atmosphere furnaces were used to calcine and sinter specimens which could later be coated. Controlled atmospheres of Ar, Ar — 4% H₂, N₂, or air can be maintained within the specimen tubes. The furnaces are each controlled by individual power supplies and both have alumina specimen tubes. One furnace is an Astro model A725S which has a 3.8 cm diameter specimen tube. A wire wound Pt-50% Rh heating element enables long-term operation of the furnace in air to temperatures of 1973 K. A Pt-6% Rh vs Pt-30% Rh temperature control thermocouple is located near the center of the furnace hot-zone but outside of the alumina specimen tube. A second furnace, also manufactured by Astro, has a 7.6 cm diameter specimen tube with a similar heating element and thermocouple as described above. Controlled atmospheres were maintained in the specimen tubes by sealing the ends with flanges that contained the appropriate gas inlet and exhaust lines. Low density alumina insulators were placed within and near each end of the specimen tubes to prevent the tubes from fracturing due to large thermal gradients. The gas flow was monitored by passing the gas through an oil bubbler on the exhaust side of each furnace to prevent back diffusion of gases into the furnace specimen tube.

The SiC coated particles were annealed to various temperatures and hold times in a Brew model 920-B furnace. The furnace has a digital power control system and W-5% Re vs W-26 Re thermocouple for temperature measurement. The thermocouple is sheathed with alumina for most of its length but the junction is exposed. It monitors the temperature within the central plane of the hot-zone approximately 1 cm from the heating element. The working space in the hot-zone is ≈ 7.5 cm diameter $\times$ 15 cm high. The unit is a top loading furnace with a resistance heated graphite heating element and carbon felt insulation. A water cooled copper hearth surrounds the heating element and insulation. The furnace can be operated between 700 and 2800 K in vacuum (≈ 1.3 Pa) or at atmospheric pressure with an inert gas. The procedure was to load the SiC coated particles in a graphite crucible. The crucible was then loaded into the furnace and covered with a graphite plate to prevent cross-contamination between specimens in case any SiC coatings fragmented. The furnace was evacuated to ≈ 6.5 Pa and backfilled with argon. An argon flow of ≈ 1 l/min was maintained during the complete annealing cycle. The furnace temperature was increased to the required hold temperature usually in less than 15 min. At completion of the hold time at temperature the furnace power was decreased and the specimen allowed to furnace cool.

Materials

The reactant CH_3SiH_3 was purchased from Petrarch Systems, Inc. Approximately 500 g was supplied per 1 l compressed gas cylinder. The CH_3SiH_3 is synthesized by reacting $\text{LiAlH}_4(\text{s})$ with $\text{CH}_3\text{SiCl}_3(\text{l})$ at 273 K

in a diethylether medium. It is a distilled product with purity level of $\approx 97\%$ minimum as determined by gas chromatography by the supplier. Typical impurities can include N_2 , CO_2 , and Cl. The Cl-content is ≈ 100 ppm which can be in the form of CH_3ClSiH_2 , HCl or $SiCl_4$ resulting from an incomplete reduction during the synthesis of CH_3SiH_3 . Existing supply lines routed the argon gas from a large holding tank located outside the building to the CVD laboratory. The other gases used in this study were N_2 , H_2 , C_2H_2 . All were obtained commercially and supplied from compressed gas cylinders. The impurity levels for the diluent gases Ar, N_2 , and H_2 are presented in Table 3.1.

Table 3.1. Impurity levels for diluent gases Ar, N_2 , H_2

Diluent	Impurity species (ppm by volume)					Total impurity level not to exceed
	O_2	N_2	H_2	H_2O	Hydrocarbons	
Ar	5	20	5	5	5	30
N_2	5		0.5	0.5	5	a
H_2	<5000	<2000	a	a	a	a

^aNot available.

SiC coatings were applied to various types of substrate materials. These included sol-gel derived Al_2O_3 microspheres, pyrocarbon coated α -alumina microspheres, simulated Cs-loaded IE-95 zeolite irregular particles, 70/30 (70 wt % Savannah River Plant waste, 30% additive) sol-gel derived microspheres, and 90/10 (90 wt % simulated Savannah River Plant waste, 10 wt % ZrO_2) sol-gel derived microspheres. Most of the SiC deposition studies reported in this work are from experiments

conducted with pyrocarbon coated Al_2O_3 substrate particles. The characteristics of the PyC coated alumina particles are presented in Table 3.2. More than one batch of starting materials was used since at the time the experiments began only ≈ 30 g of PyC coated particles could be produced per coating experiment. The initial set of SiC coating experiments were conducted with ≈ 7 g of substrate particles. Thus only four SiC coating experiments could be performed per batch of PyC coated Al_2O_3 . At the completion of the initial SiC coating experiments it was decided to increase the amount of charge to ≈ 20 g of PyC particles per SiC coating experiment. Thus a large batch of alumina microspheres was coated with PyC. This was performed in a 12.7 cm diameter fluidized-bed coater. All subsequent substrates for SiC coating experiments using PyC coated alumina microspheres came from this batch. The alumina microspheres were coated with pyrocarbon to produce substrate particles of ≈ 720 μm diameter. This was the approximate size of the sol-gel — derived alternative waste form microspheres. The typical density of the PyC coated particles was ≈ 2.3 g/cm^3 and their geometric surface area per unit mass was ≈ 35 cm^2/g . It is also important to comment on the particle size distribution of both the alumina and PyC coated alumina microspheres. The standard deviation for the alumina spheres is ≈ 12 μm and that of the PyC coated alumina microspheres is ≈ 20 μm . The particle size distributions are narrow and show the excellent control capabilities for producing gel-derived microspheres and ceramic coatings. This type of control enhances the qualification of the process and minimizes variables which could conceivably influence the coating characteristics and processing procedures.

Table 3.2. Characteristics of PyC coated alumina substrate particles

Run number	Particle			Geometric surface area/mass (cm ² /g)
	Average ^a diameter (μm)	Density ^b (g/cm ³)	PyC thickness ^c (μm)	
12	704	2.369	105	40.6
36	740	2.352	120	34.9
44	752	2.352	128	33.9
54	753	2.354	129	33.9
55	745	2.332	124	34.5
74	743	2.390	123	33.8
A977	756	2.156	131	36.8
J1123 ^d	500	3.796	e	31.6

^aMeasurements from microradiographs; number of particles measured =50; standard deviation for coated particles ≈20 μm; standard deviation for uncoated alumina substrate particles J1123 ~12 μm.

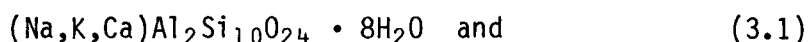
^bParticle density determined from mercury pycnometry (1.7 MPa measurement).

^cMeasurements from microradiographs; number of particles measured =50.

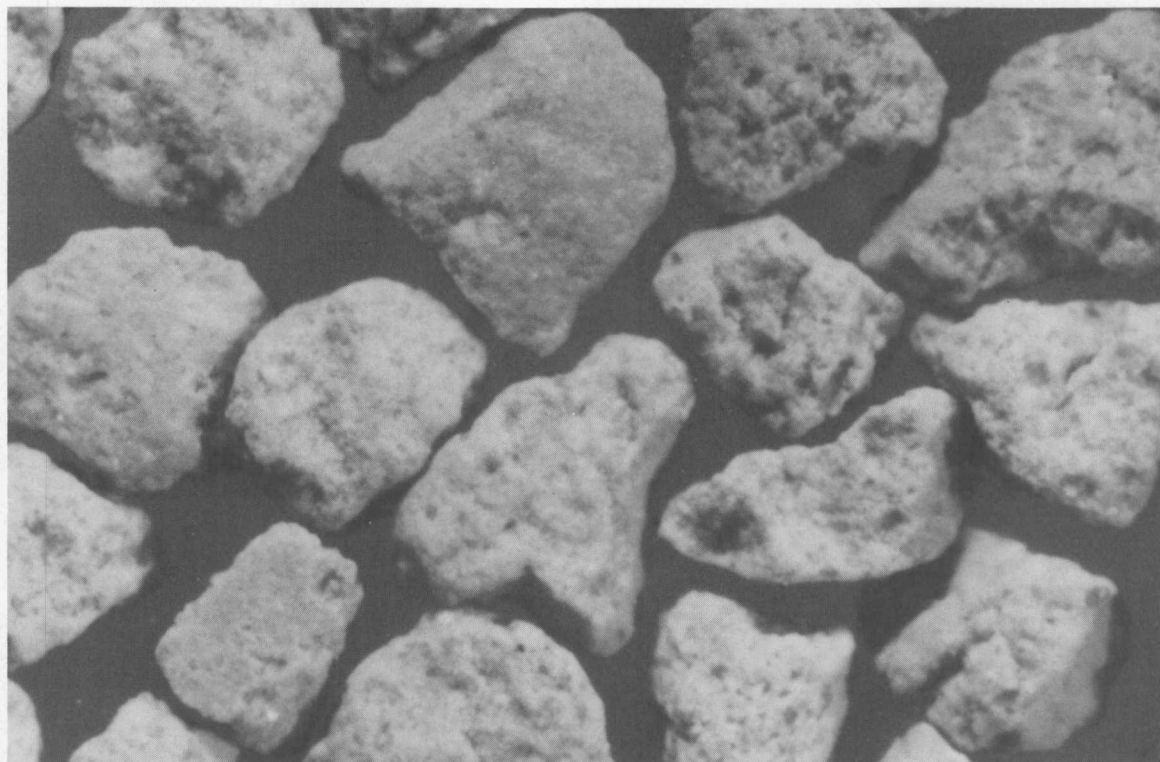
^dUncoated alumina microspheres.

^eNot applicable.

The substrate used to incorporate cesium was a commercially available zeolite IE-95 (Fig. 3.4).⁵⁵ The composition of the zeolite as reported by the manufacturer is given as a mixture of



The chemical procedure for loading the zeolite with cesium to a level of 5 wt % cesium is reported by Arnold and coworkers.⁵⁵ Previous work by Arnold recommended zeolite IE-95 for cesium loading and it was found to be the most effective adsorbant tested in that work.



0.5 μm

Fig. 3.4. Cs-loaded zeolite (5 wt % Cs) air dried 400 K.

The bulk of the zeolite particles are brown in color but a small fraction (less than 0.05) of white particles are also present. A specimen of cesium loaded zeolite was submitted for chemical analysis with the white particles removed to obtain a better estimate of the elemental composition of the (Na,K,Ca) $\text{Al}_2\text{Si}_{10}\text{O}_{24} \cdot 8 \text{H}_2\text{O}$ phase which forms the bulk of the zeolite. The results are presented in Table 3.3 and are given in terms of elemental oxides as well as in at. % cations.

Table 3.3. Chemical analysis of dried IE-95 zeolite loaded with 5 wt % Cs

Species	Mole percent ^a	Species	at. % ^b
Cs ₂ O	1.4	Cs	2.3
Na ₂	5.2	Na	8.5
MgO	1.8	Mg	1.5
CaO	3.8	Ca	3.1
Al ₂ O ₃	14.7	Al	24.3
SiO ₂	73.1	Si	60.3

^aBased on oxides.

^bBased on cations.

Specimen Characterization

Thermal Analysis

Mass spectrometric analyses of gaseous species evolved during calcining or sintering of simulated nuclear materials were made with a CVC Ma-2 mass spectrometer.⁷² The unit is a time of flight instrument with a 1 m flight tube and model CSI 260I readout system. Spectra were taken at an electron ionization energy of 70 eV and ion energy of 2.7 keV. Two furnaces are available for connection to the unit where specimens can be heated either in vacuum or in a controlled

atmosphere. Temperatures of 1673 K can be attained with the Pt wound furnace and Al_2O_3 specimen tube. A second furnace with an inconel specimen tube is available for analyses up to 1200 K. The mass spectrometer system allows computer control of parameters such as the time period or temperature interval between measurements and signal level above which a species is recorded. The data from the mass spectrometer and furnace thermocouple temperature measurements are stored on-line with a PDP-11/40 computer. Data can later be retrieved, analyzed and plots or numerical tables produced.

Thermogravimetric (TGA) and differential thermal analyses (DTA) were made with a DuPont 990 thermal analyzer, 951 thermogravimetric analyzer, and 1473 K differential thermal analyzer attachment. The data output was directed to chart recorders or a computer.

Density Determination

Three techniques were used to obtain coating density measurements.⁷³ In the first method the coating density is calculated from particle density and coating thickness measurements. The mass of the SiC coating can be expressed as

$$\rho_C V_C = \rho_f (V_C + V_i) - \rho_i V_i \quad (3.3)$$

where

ρ_C = SiC coating density,

V_C = volume of SiC coating,

ρ_f = density of SiC coated particle,

V_f = volume of SiC coated particle,

ρ_i = density of initial pre-SiC coated particle, and

V_i = volume of initial pre-SiC coated particle.

Since $V_c = V_f - V_i$ the expression can be rewritten as

$$\rho_c(V_f - V_i) = \rho_f V_f - \rho_i V_i \quad (3.4)$$

$$\rho_c = \frac{\rho_f R - \rho_i}{R - 1} \quad (3.5)$$

where

$$R = \frac{V_f}{V_i} = \left(\frac{d_f}{d_i} \right)^3 \quad (3.6)$$

where

d_f = diameter of SiC coated particle and

d_i = diameter of initial pre-SiC coated particle.

The particle density data were determined with a mercury pycnometer and the particle diameter was obtained from x-ray microradiographs. The microradiographs are made by placing a monolayer of particles on a plastic holder and radiographing the holder. The inner and outer diameter of the coating are measured with an optical microscope equipped with a calibrated reticle eyepiece. The position of the reticle can be adjusted with a micrometer. A potentiometer connected to the micrometer provides an output proportional to position and is calibrated using NBS standard templates.

Coating density can also be obtained from particle density and the mass gained by the particles during coating. The coating density can be expressed

$$\rho_c = \frac{\text{mass gain}}{\text{volume gain}} \quad (3.7)$$

$$\rho_c = \frac{\frac{M_f - M_i}{\rho_f - \rho_i}}{\frac{M_f}{\rho_f} - \frac{M_i}{\rho_i}} \quad (3.8)$$

where

M_f = mass of SiC coated particle

M_i = mass of initial particles

and ρ_c , ρ_f , ρ_i are defined as in the previous case.

The third technique for determining coating density was a sink-float type method. This technique uses a density gradient column. The density of the liquid varies nearly linearly with height along the column. Density gradient columns can be prepared to cover density ranges over which there are two miscible liquids corresponding to the high and low densities. A particle immersed in the column will reach a level where its density is equal to the density of the liquid and remain suspended in that position. The column is calibrated by standards of known density and the position along the column measured. Columns useful for measurements of particles with densities ranging from 0.9 to 2.95 g/cm³ were prepared from benzene and 1,1,2,2-tetrabromoethane. Columns used to measure particle densities in the range 2.9 to 3.3 g/cm³ range were prepared from di-iodomethane (CH₂I₂)

and 1,1,2,2-tetrabromoethane. SiC coating fragments were obtained by crushing the SiC coated particles. The fragments normally consisted of SiC coatings bonded to the pyrocarbon substrate and the largest fragments were oxidized at 1173 K in flowing oxygen for 15 min to remove the pyrocarbon. The SiO₂ layer that forms on the SiC coating was removed by immersing the fragments in an acid solution of HNO₃ and HF. The fragment was then washed in water and acetone, and allowed to dry prior to being immersed in the column.

Defective SiC Coating Measurements

The physical integrity of SiC coatings is evaluated by a mercury intrusion method.⁷⁴ This test evaluates only those pores or cracks which are connected to the outside surface, and penetrable by mercury. A mercury pycnometer is used to force mercury at a pressure of 102 MPa through defects in the SiC coating. If the coating is defective, a layer of mercury usually forms between the substrate particle and the SiC coatings or agglomerates in voids beneath the SiC coating. Particles are then microradiographed and the number of defective particles recorded. Since there are large atomic number and density differences between mercury and the SiC or substrate materials, there is a clear indication if the SiC coatings are defective.

Raman Spectroscopy

The Raman spectra were recorded with a Romanor HG-2S manufactured by Jobin Yvon-Instruments.⁷⁵ The instrument has a double monochromator with curved holographic gratings, a cooled photoelectric detector, and pulse counting electronics. The light intensity from an argon-ion

laser (514.5 nm line) focused on the specimen ranged between 0.2 and 0.5 W. The outer surface of the SiC coated spheres was analyzed. Specimens were placed on the tip of a hypodermic needle and held there by suction. The laser light was then focused on the equator of the sphere and the sphere translated to give the maximum Raman scattering. The measurements were made with the take-off angle 90° with respect to the incident laser light. The monochromator slits were parallel to the horizontal plane formed by the illuminating and the scattered light and the spectrometer slit openings at 514.5 nm corresponded to 4 to 7 cm^{-1} . Spectra of SiC fracture surfaces were also made. In these cases the incident exciting laser light was focused on the fracture surface by passing it through an optical microscope.

Electron Microprobe

Quantitative electron microprobe analyses for the Si content of SiC coatings and single crystal SiC were performed on a Cameca MBX electron microprobe equipped with a Tracor Northern TN5500 control system. An electron beam accelerating voltage of 10 kV and beam current of ≈ 30 nA were used. The quantitative data acquisition was performed with x-ray wavelength dispersive spectrometers (WDS) with the elements analyzed being silicon and carbon. The K x-ray lines of each element were analyzed. One set of measurements was standardized on elemental silicon and graphite for carbon, and another set on the SiC single crystal specimen. Once the elements in each specimen were identified, the silicon content was quantified by (1) correcting its background subtracted peak intensity due to matrix effects including

mean atomic number (Z), absorption (A), and secondary x-ray fluorescence (F), and determining the ratio of the modified intensity in the specimen to its standard. The carbon contents were obtained by difference since the ZAF correction was inordinately large. At least five 20 s measurements were made on each SiC coating. Measurements were made in the spot mode in areas free of contamination from the mounting material. X-ray energy dispersive spectroscopy was used to detect the presence of elements with atomic numbers greater than 11. The beam current during an EDS analyses was typically less than 1 nA. The EDS analyses were performed either before or after the quantitative analyses by WDS had been completed. The oxygen content of single crystal SiC, and SiC coated particles was determined. The specimens for these analyses were prepared in a special manner to remove ambiguities which could occur due to the polishing procedure. Since the elements of interest were silicon and carbon, a low melting Sn-Bi mounting alloy was used. This provided an electrically conducting mount whose elemental species would not interfere with WDS analyses of silicon or carbon or with EDS analyses. An Al_2O_3 final polishing medium was used instead of the usual SiC or diamond (C). The specimens were polished in H_2O rather than kerosene since carbon contamination was to be minimized. Oxidation of the SiC coating, which can occur as a result of grinding in an aqueous media, was evaluated on the microprobe by analyzing the SiC single crystal and the SiC coated particles for oxygen. The oxygen content of the specimens was less than 0.5 wt.

X-ray Diffraction

The x-ray diffraction analyses of the SiC coated particles were performed on two instruments. The first system consists of a Siemens diffractometer, type F goniometer, NaI scintillation detector, and recorder output. A copper target x-ray tube was typically operated at 35 kV and 35 mA. No filters were placed in the beam. A three degree divergence slit and a one degree acceptance slit were used. The diffractometer scan speed for most analyses was one degree per minute and the total scan time was ≈ 60 min. Special specimen holders were used which have different cut-out depths depending on the amount of specimen available for analysis. This allowed the top surface of the particle bed to be in the same alignment position for each run. A ≈ 2 μm -thick mylar film was placed over the particles to keep them within the specimen holder which was rotated while measurements were made.

The second system consists of a Philips automated powder diffractometer (APD) 3600-02 x-ray diffraction unit, XRG 3100 x-ray generator, NaI scintillation detector, and Data General NOVA 4x computer. The diffractometer scan is computer controlled and is step-scanned by means of a stepping motor. The data is stored by the computer. A copper target x-ray tube was operated at 40 kV and 40 mA and no filters were placed in the beam. A diffracted beam monochromator with graphite crystal was utilized to increase the peak to background ratio by preventing sample fluorescence from reaching the detector. The divergence slit is continuously variable and maintains a 15 mm wide $\times$ 13 mm high sampling area during an analysis. These data

correspond to a divergence angle of $\approx 2^\circ$ when $2\theta = 35^\circ$, and $\approx 4^\circ$ when $2\theta = 70^\circ$. The scan time was varied from ≈ 2 to 16 h depending on the amount of specimen available for analyses. A few measurements were made with common specimens and specimen holder design similar to the one described earlier so that data from the two x-ray systems could be compared. Most analyses were then made with a low-background holder. Specimen particles were placed in a holder (again with cut-out depth depending on the amount of specimen available) which has a silicon single crystal at its base oriented $\approx 15^\circ$ from (111). Double-sided tape kept the particles on the holder. In this way the contribution from the holder is only general background with no peaks present and since silicon has a low atomic number the background scatter is quite low. The present holder design was quite useful for the experiments reported in this dissertation. Peak finding and fitting, and spectra matching algorithms are available for analyzing data.

Crystallite-size determinations of the SiC coatings were calculated by the Scherrer method where

$$D = \frac{0.94 \lambda}{\beta_{1/2} \cos \theta} \quad , \quad (3.9)$$

D = average dimension of crystallites normal to the diffracting planes,

λ = wavelength of the x-ray beam,

θ = $1/2$ of the 2θ diffraction angle (radians), and

$\beta_{1/2}$ = full-width-half max of the diffracted peak (radians).

The $\beta_{1/2}$ used in the above equation was obtained by

$$\beta_{\text{crystallite size}}^2 = \beta_{\text{measured}}^2 - \beta_{\text{instrumental}}^2. \quad (3.8)$$

All x-ray diffraction spectra of SiC coatings which were applied onto PyC coated alumina spheres had an internal standard ($\alpha\text{-Al}_2\text{O}_3$). The

$\beta_{\text{instrumental}}^2$ was typically obtained using the data for the most significant nearby but nonoverlapping $\alpha\text{-Al}_2\text{O}_3$ diffraction peak.

Measurements were calculated from (111), (220), and (311) $\beta\text{-SiC}$ peaks.

Residual stresses can also affect the full width at half-maximum of the diffracted peak and can affect the above crystallite-size analyses. In more precise analyses the contributions from both residual stress and crystallite size can be separated by Fourier transform techniques.

CHAPTER IV

RESULTS

Thermodynamic Evaluation of the Chemical Vapor Deposition of SiC from Methylsilane

Equilibrium thermodynamic calculations were performed with the computer program SOLGASMIX-PV which was written by Eriksson⁷⁶ and modified by Besmann.⁷⁷ The program is based on a procedure developed by White⁷⁸ involving the calculation of a system's composition which results in the minimum free energy. The program calculates equilibria in systems containing gaseous phases, condensed phase solid solutions, and condensed phases of invariant or variant stoichiometry.⁷⁹⁻⁸¹ The input to the program includes the species present, coefficients for the elements in the molecular formula for the species, free energy of each species as a function of temperature, total pressure, initial content for each element, and temperature. The output includes the amount and partial pressure of gaseous species, and the amount of each condensed phase present at equilibrium.

The species included in the calculations and the corresponding thermodynamic data are presented in Table 4.1. The free energy data for all of the species except CH_3SiH_3 were obtained from the JANAF Tables.⁸² The free energy of formation data for CH_3SiH_3 was estimated from the free energy function reported by Spangenberg and Kriegsmann,³⁶ ΔH_{298}° reported by O'Neal and Ring,⁴⁰ and the free energy function of

Table 4.1. Thermodynamic data for CVD calculations in the $\text{CH}_3\text{SiH}_3 - \text{C}_2\text{H}_2 - (\text{Ar or N}_2 - \text{H}_2)$ system

	A ^a (J/mol)	B ^a [J/(mol · K)]
<u>Gaseous species</u>		
Ar	0.0	0.0
C	7.16×10^5	-157
CH_3	1.33×10^5	25.3
CH_3SiH_3	-2.46×10^4	202
CH_4	-9.26×10^4	112
CN	4.32×10^5	-99.2
CN_2	4.77×10^5	-35.4
C_2H_2	2.01×10^5	-51.8
C_2H_4	3.53×10^4	83.2
C_4N_2	5.39×10^5	-89
H	2.27×10^5	-59.8
H_2	0.0	0.0
HCN	1.32×10^5	-31.1
HN	3.76×10^5	-19.9
H_2N	1.85×10^5	41.7
H_2N_2	2.07×10^5	117
H_4N_2	9.07×10^4	230
N	4.78×10^5	-65.8
N_2	0.0	0.0
Si	4.46×10^5	-144
SiH	3.68×10^5	-103
SiH_4	2.33×10^4	90.4
SiN	3.65×10^5	-93
Si_2C	5.20×10^5	-181
Si_2N	3.88×10^5	-112
<u>Condensed phases</u>		
C	0.0	0.0
Si	0.0	0.0
$\text{Si}_{\text{,l}}$	5.06×10^4	-30.0
SiC, α	-7.12×10^4	7.7
SiC, β	-7.29×10^4	7.5
Si_3N_4	-7.37×10^5	325.0

^aCoefficients in the expression for the Free Energy of Formation of each species: $\Delta G^\circ \text{ (J/mol)} = A + B \cdot \text{Temperature (K)}$.

the elements C, Si, H₂ from the JANAF Tables.⁸² The values of the coefficients in the expression for the free energy of formation

$$\Delta G^\circ = A + BT \quad (4.1)$$

were obtained for each species by least square fitting a function of the form shown in Eq. 4.1 to numerical data typically in the 1100 to 1500 K temperature range. The condensed phases included in the calculations were C (graphite), Si (l)-liquid, Si(s)-crystalline, β -SiC, α -SiC, and Si₃N₄(s). The total system pressure was maintained constant at 1.01×10^5 Pa (≈ 1 atm). The initial elemental contents of the system were chosen to closely match the experimental requirements necessary to properly fluidize particles in the CVD coating system. In this way the calculated results could be compared directly with experimental data.

The effects of two types of gaseous diluents, (1) (Ar — H₂) and (2) (N₂ — H₂), and one type of additive gas, C₂H₂, were evaluated. The results of the calculations are summarized in the form of CVD phase diagrams. Phase boundaries are determined which define a range of conditions where single phase or codeposited phases can form. Contours of constant mole ratios of the species in the condensed phase are also shown on the CVD phase diagrams. Plots of the equilibrium partial pressure of various gaseous product species in the system are also presented. The partial pressure data are useful in understanding reaction mechanisms, determining gaseous additions which can change the range of conditions defining the condensed phase fields, and indicating which gaseous species should be monitored during a coating experiment.

Analysis of the $\text{CH}_3\text{SiH}_3 - \text{C}_2\text{H}_2 - (\text{Ar} - \text{H}_2)$ System

The range of input parameters evaluated in the calculations and termed as the standard conditions are listed below.

Temperature — 900 to 1600 K (100 K increment)

Pressure — $1.01 \times 10^5 \text{ Pa}$ ($\approx 1 \text{ atm}$)

CH_3SiH_3 flow rate — $29 \text{ cm}^3/\text{min}$

Diluent gas species — Ar, H_2

Total diluent gas flow rate — $5000 \text{ cm}^3/\text{min}$

$\frac{\text{H}_2 \text{ diluent}}{\text{Total diluent}} = \frac{\text{H}_2}{\text{diluent}} - \frac{0 \text{ to } 100 \text{ mol } \% (10 \text{ mol } \% \text{ increment})}{\text{and } 95 \text{ mol } \%}$

These conditions lead to the following mole ratios

$$\frac{\text{CH}_3\text{SiH}_3}{\text{diluent}} = 5.8 \times 10^{-3} \quad (4.2)$$

$$\frac{\text{C}_2\text{H}_2}{\text{CH}_3\text{SiH}_3} = 0.0 \quad (4.3)$$

The additive gas, C_2H_2 was chosen to evaluate its affect on the type and relative concentration of condensed species computed to be present at equilibrium. Thus additional calculations were made with the following conditions:

C_2H_2 additive flow rate — 0.01, 0.1, 0.3, 0.6, and $1.0 \text{ cm}^3/\text{min}$

which lead to mole ratios of

$$\frac{C_2H_2}{CH_3SiH_3} = 3.4 \times 10^{-4}, 3.4 \times 10^{-3}, 10^{-2}, 2 \times 10^{-2}, \quad (4.4)$$

and 3.4×10^{-2}

Note that the H_2 /diluent term does not include the hydrogen contribution from either CH_3SiH_3 or C_2H_2 . It is a term based solely on the diluent gases.

The case where $C_2H_2/CH_3SiH_3 = 0.0$ evaluates the $CH_3SiH_3 - C_2H_2 - (Ar - H_2)$ system in essentially its simplest condition and will be considered first. A calculated CVD phase diagram for initial conditions of CH_3SiH_3 /diluent = 5.8×10^{-3} and $C_2H_2/CH_3SiH_3 = 0.0$ is presented in Fig. 4.1. The condensed phases computed to form are β -SiC and Si(s). The diagram is divided into two regions, one of single phase SiC and another of codeposited SiC + Si. The conditions resulting in single phase SiC are for temperatures greater than ≈ 1450 K and hydrogen content in the diluent gas of less than ≈ 5 mol %. The remainder of the diagram defines conditions where SiC + Si codeposit. Contours of constant mole ratio $r_{Si} = Si/SiC$ are also shown in Fig. 4.1. A general result from this set of calculations is that the concentration of solid silicon is calculated to increase as the H_2 /diluent mole ratio increases or as the temperature decreases.

When the diluent gas consists solely of argon (H_2 /diluent = 0.0 mol %), r_{Si} increases from $\approx 8 \times 10^{-7}$ to 3×10^{-6} as the temperature decreases from 1400 to 900 K. Such concentrations of silicon are relatively small and may be difficult to detect experimentally. As the hydrogen content in the $(Ar + H_2)$ diluent is increased, r_{Si} also increases as shown by the contours in Fig. 4.1. When hydrogen is the

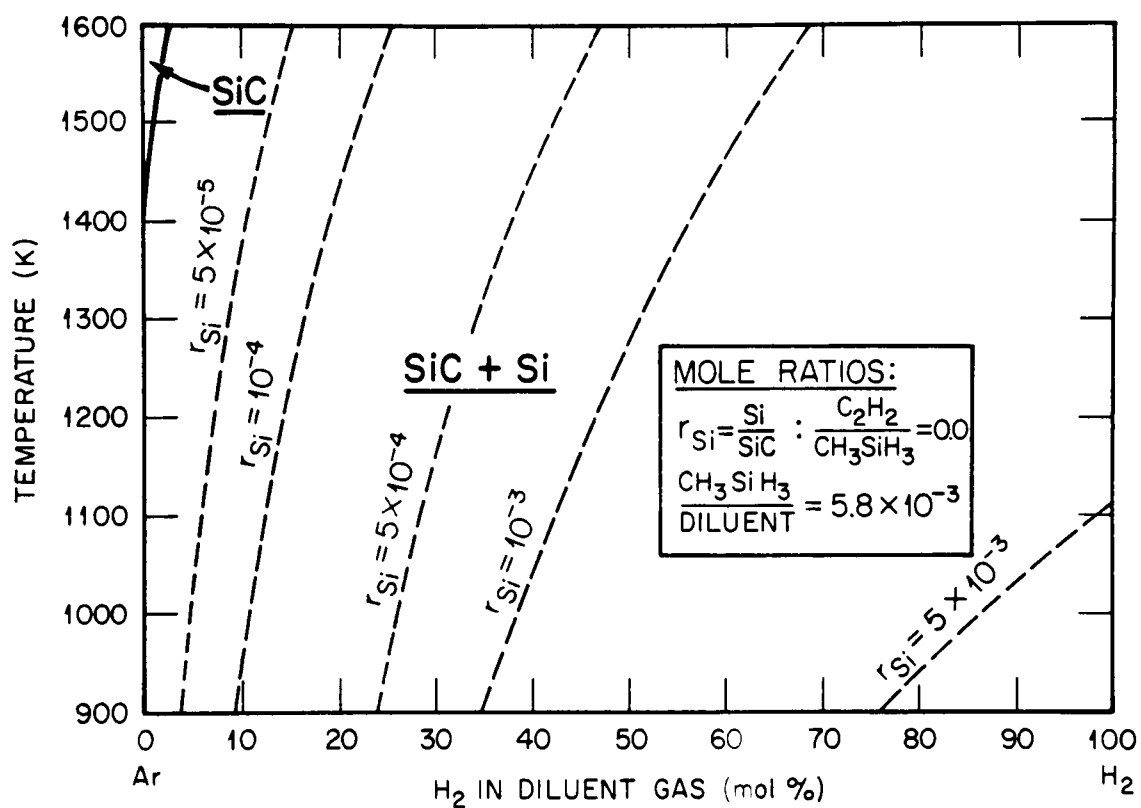


Fig. 4.1. CVD phase diagram based on thermodynamic equilibrium calculations for the system $CH_3SiH_3 - C_2H_2 - (Ar - H_2)$; mole ratios $CH_3SiH_3/diluent = 5.8 \times 10^{-3}$, $C_2H_2/CH_3SiH_3 = 0.0$, and total pressure = 1.01×10^5 Pa (≈ 1 atm). Phase boundaries separate range of conditions where single phase SiC, or SiC + Si forms. Contours of constant mole ratio $r_{Si} = Si/SiC$ are shown.

only diluent gas ($H_2/\text{diluent} = 100 \text{ mol } \%$), r_{Si} increases from $\approx 3 \times 10^{-3}$ to 9×10^{-3} as the temperature decreases from 1600 to 900 K. Also the deposition efficiency, defined as the SiC mole content in the condensed phase divided by the total silicon mole content, is always greater than 99.6% over the entire range of conditions evaluated.

The most plentiful gaseous product species are argon and hydrogen. The reason for this, of course, is that argon does not take part in the chemical reactions, and all other hydrogen bearing gases are highly unstable under the conditions evaluated in this study. The next set of most abundant gaseous product species include CH_4 , SiH_4 , H , SiH , C_2H_2 , CH_3 , Si_2C , and C_2H_4 . The calculated partial pressures of these species for initial conditions of $CH_3SiH_3/\text{diluent} = 5.8 \times 10^{-3}$, $H_2/\text{diluent} = 0.0 \text{ mol } \%$ (100% argon), and 900 to 1600 K temperature range, is shown in Fig. 4.2. Methane is the carbon bearing species with the highest partial pressure and the species SiH_4 and SiH are the most significant silicon bearing gases. The partial pressure of these same species for an hydrogen content in the diluent gas of 100 mol % is shown in Fig. 4.3. The partial pressure of each species has increased nearly four orders of magnitude. The species CH_4 and SiH_4 are again the carbon and silicon bearing gases with the highest partial pressures.

The results of a limited set of calculations, where the mole ratio of CH_3SiH_3 in the initial reactants was decreased to $CH_3SiH_3/\text{diluent} = 2.9 \times 10^{-3}$, show no major changes in the phase boundaries. However, the r_{Si} mole ratio decreases by a factor of ≈ 2 for $H_2/\text{diluent} = 0.0$ and increases by approximately the same factor for both $H_2/\text{diluent} = 0.5$

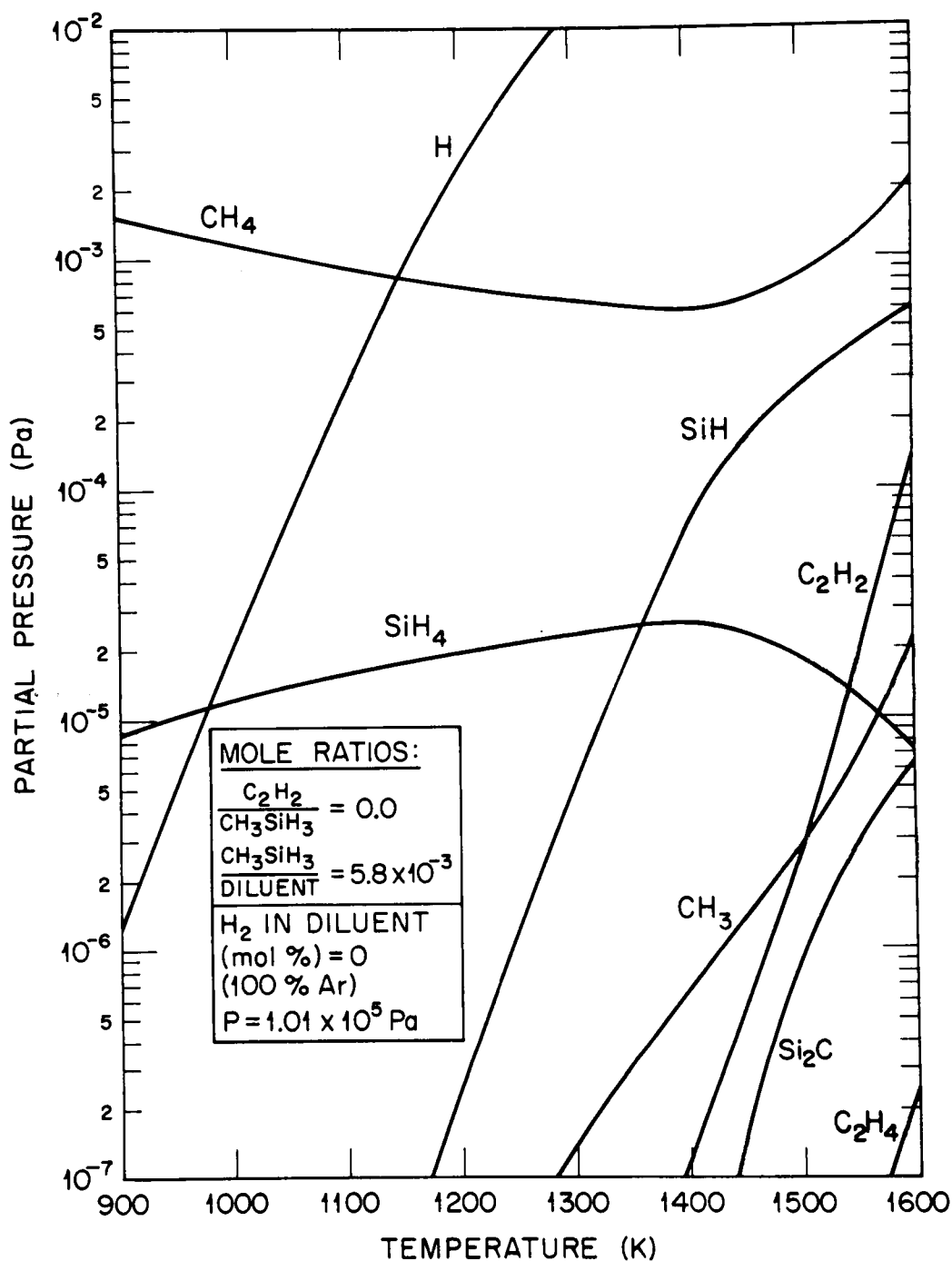


Fig. 4.2. Partial pressure of various gaseous product species versus temperature for the $CH_3SiH_3 - C_2H_2 - (Ar - H_2)$ system; mole ratios $CH_3SiH_3/diluent = 5.8 \times 10^{-3}$, $C_2H_2/CH_3SiH_3 = 0.0$, total pressure = 1.01×10^5 Pa (≈ 1 atm), and H_2 content in the diluent gas = 0.0 mol % (100 mol % Ar).

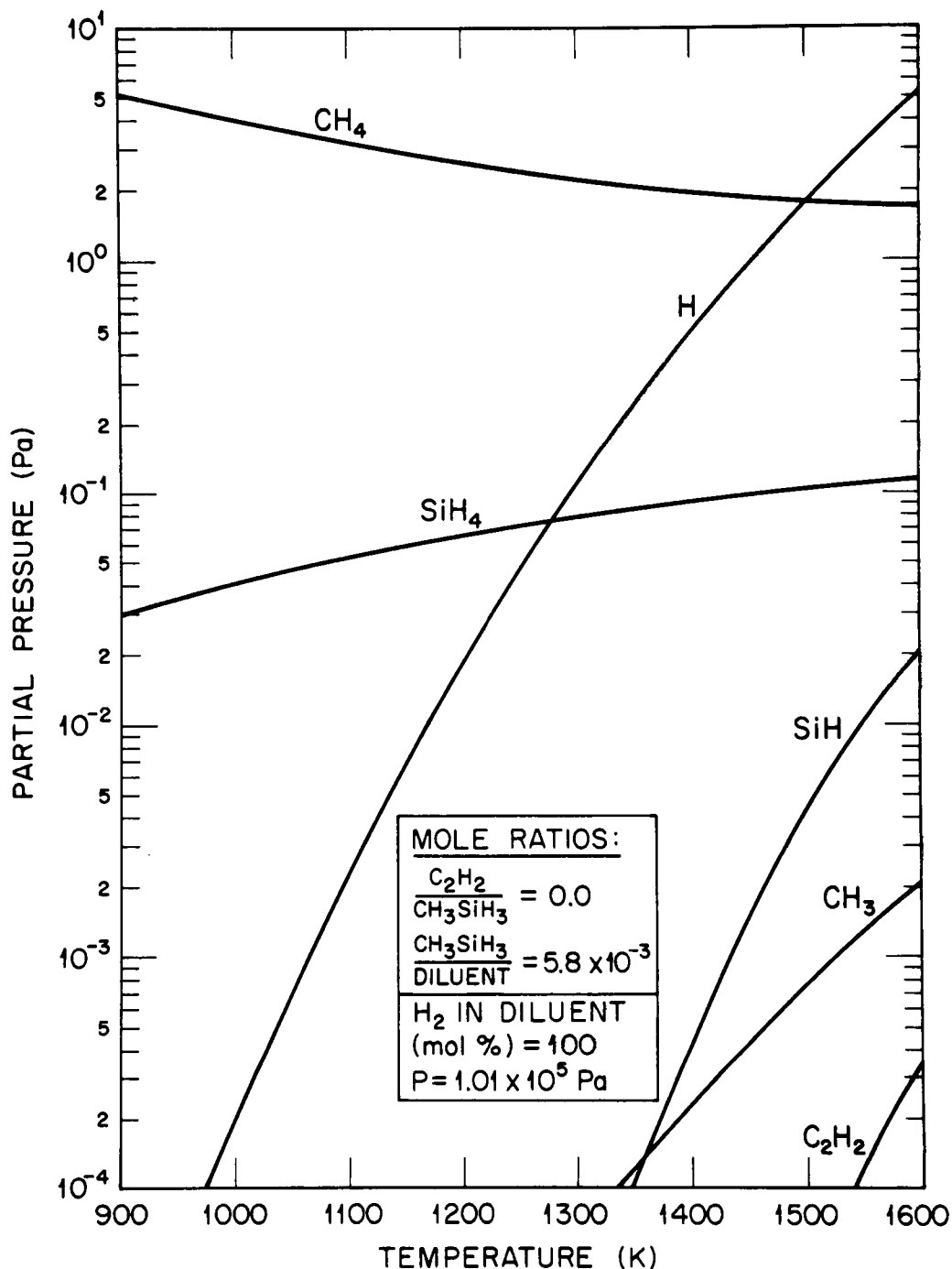


Fig. 4.3. Partial pressure of various gaseous product species versus temperature for the $CH_3SiH_3 - C_2H_2 - (Ar - H_2)$ system; mole ratios $CH_3SiH_3/diluent = 5.8 \times 10^{-3}$, $C_2H_2/CH_3SiH_3 = 0.0$, total pressure = 1.01×10^5 Pa (≈ 1 atm), and H_2 content in the diluent gas = 100 mol %.

and 1.0. The deposition efficiency is also greater than 99.6% over the complete range of conditions.

The influence of the addition of a carbon bearing gaseous species to the initial reactants was also evaluated. Acetylene, C_2H_2 , was chosen as an additive since it is known to decompose at temperatures less than 1273 K, and is commercially available in practically any desired quantity. A calculated CVD phase diagram for initial conditions of $C_2H_2/CH_3SiH_3 = 3.4 \times 10^{-4}$ and $CH_3SiH_3/\text{diluent} = 5.8 \times 10^{-3}$ is shown in Fig. 4.4. The region where single phase SiC is computed to form has greatly expanded under these conditions. It occurs for temperatures lower than ≈ 1200 K when hydrogen content in the diluent gas is = 0.0, and extends over nearly the entire 900 to 1600 K temperature range as the hydrogen content in the diluent gas is increased to ≈ 40 mol %. Regions defining conditions where codeposits of SiC + C, and SiC + Si form are also present. A region where SiC + C are computed to codeposit occurs for temperatures greater than ≈ 1200 K and low $H_2/\text{diluent}$ ratios. The region of SiC + Si occurs throughout the 900 to 1600 K temperature range when the hydrogen content in the diluent gas is greater than ≈ 40 mol %. Contours of constant mole ratio $r_{Si} = Si/SiC$, within the SiC + Si region, show that the silicon concentration increases as the hydrogen content in the diluent gas increases or temperature decreases. Again the coating efficiency is very high, being greater than 99.3 %, over the entire set of conditions shown in Fig. 4.4. Consider now the behavior of gaseous CH_4 and the condensed species carbon and silicon as the hydrogen content of the diluent gas is varied from 0 to 100 mol % at a constant temperature

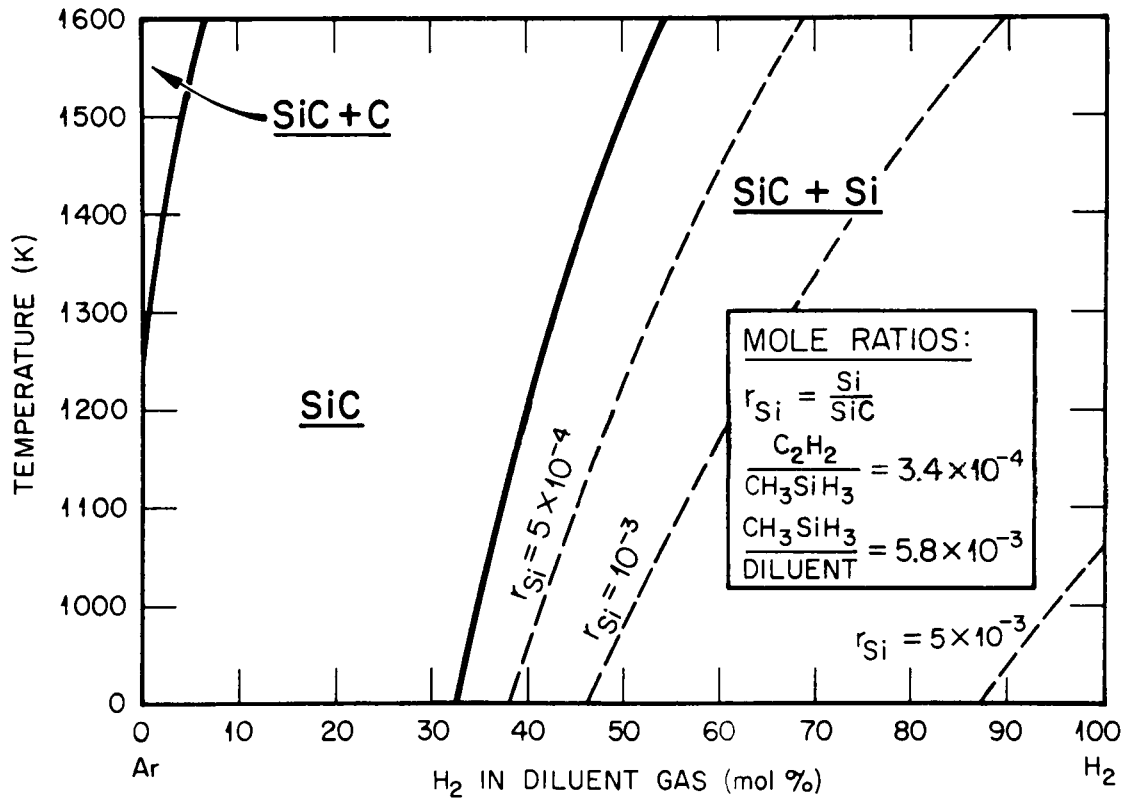


Fig. 4.4. CVD phase diagram based on thermodynamic equilibrium calculations for the $\text{CH}_3\text{SiH}_3 - \text{C}_2\text{H}_2 - (\text{Ar} - \text{H}_2)$ system; mole ratios $\text{CH}_3\text{SiH}_3/\text{diluent} = 5.8 \times 10^{-3}$, $\text{C}_2\text{H}_2/\text{CH}_3\text{SiH}_3 = 3.4 \times 10^{-4}$, and total pressure = 1.01×10^5 Pa (≈ 1 atm).

of 1600 K. Under these conditions the results from Fig. 4.4 show the following phase fields will be transversed SiC + C, SiC, and SiC + Si. A plot of the CH₄, C(s), and Si(s) contents versus the hydrogen content in the diluent gas is shown in Fig. 4.5. In the SiC + C phase field, the sum of the C(s) and CH₄ contents accounts for nearly all of the carbon supplied by the C₂H₂ gaseous additive. When the hydrogen content in the diluent gas is between ≈5 and 55 mol %, single phase SiC forms. The CH₄ content remains nearly constant throughout this range and accounts for nearly all of the carbon supplied by the C₂H₂ additive. As the hydrogen concentration in the diluent gas is increased above ≈55 mol %, SiC + Si are codeposited. Both the CH₄ and Si(s) contents increase as the SiC and SiC + Si phase boundary is passed. The deposition of Si(s) in this region occurs basically at the expense of SiC. Thus an equimolar amount of carbon becomes available as Si(s) forms. Most of the carbon which becomes available reacts to form CH₄ resulting in an increase in the CH₄ partial pressure. This behavior occurs since CH₄ is the most stable gaseous carbon bearing species in the calculations, and the system is constrained by the principle of conservation of mass.

The results in Fig. 4.6(a) show that the region where SiC + Si codeposit is nearly removed when $C_2H_2/CH_3SiH_3 = 3.4 \times 10^{-3}$. The SiC + Si two phase region occurs only for temperatures lower than ≈1000 K and hydrogen content in the diluent gas of greater than ≈85 mol %. The conditions defining the deposition of single phase SiC occur over most of the CVD phase diagram [Fig. 4.6(a)]. A two phase SiC + C region exists in the 900 to 1600 K temperature range when the

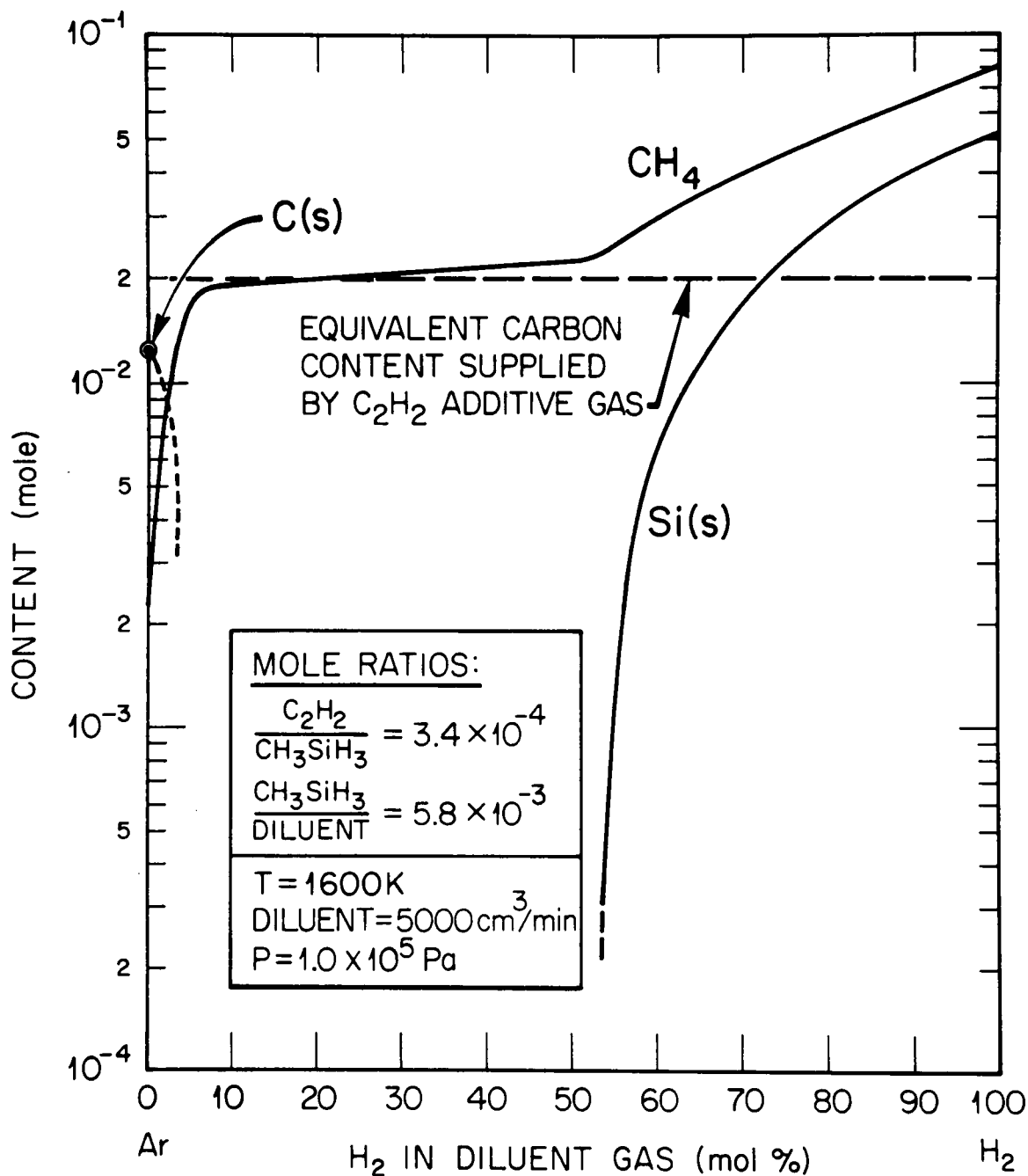


Fig. 4.5. Content of gaseous product species CH₄, and condensed phases C(s) and Si(s) versus H₂ content in diluent gas for the CH₃SiH₃ - C₂H₂ - (Ar - H₂) system; mole ratios CH₃SiH₃/diluent = 5.8 × 10⁻³, C₂H₂/CH₃SiH₃ = 3.4 × 10⁻⁴, total pressure = 1.01 × 10⁵ Pa (≈1 atm), and T = 1600 K.

ORNL-DWG 85-9813

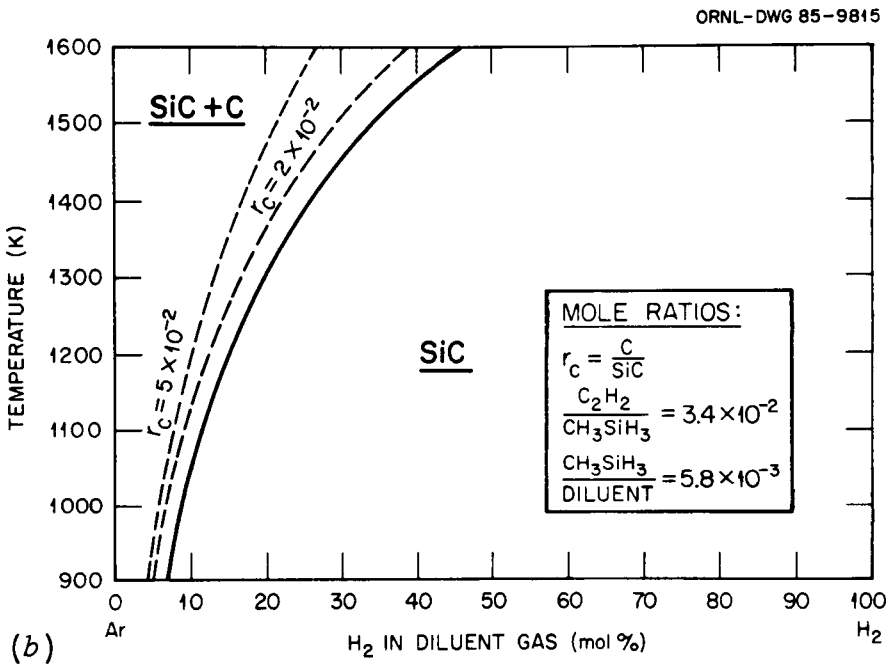
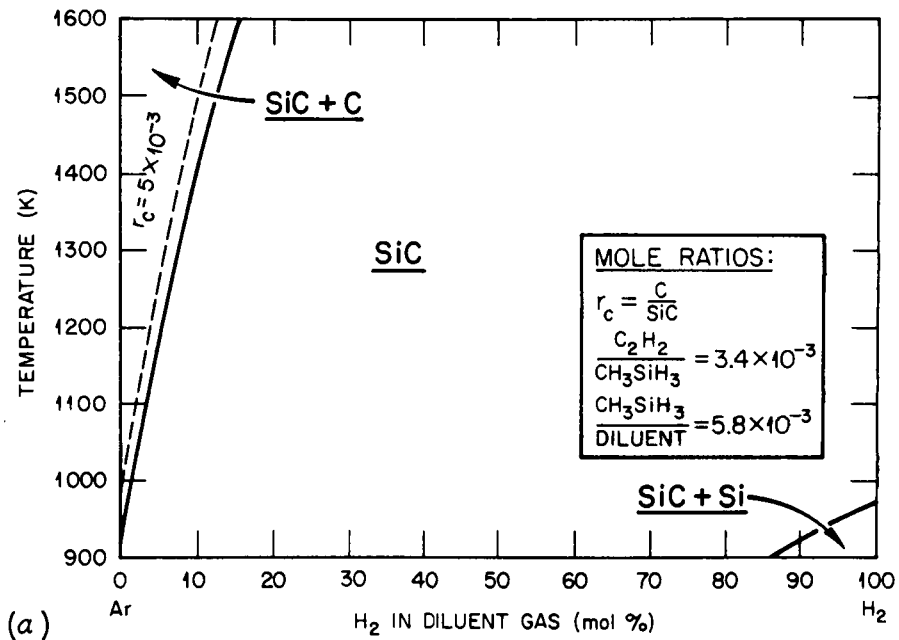


Fig. 4.6. CVD phase diagrams based on thermodynamic equilibrium calculations for the $CH_3SiH_3 - C_2H_2 - (Ar - H_2)$ system; mole ratios $CH_3SiH_3/diluent = 5.8 \times 10^{-3}$, total pressure = 1.01×10^5 Pa (≈ 1 atm) (a) mole ratio $C_2H_2/CH_3SiH_3 = 3.4 \times 10^{-3}$ and (b) mole ratio $C_2H_2/CH_3SiH_3 = 3.4 \times 10^{-2}$.

hydrogen content in the diluent gas is less than ≈ 15 mol %. The two phase SiC + C region increases as additional C_2H_2 is introduced in the system [Fig. 4.6(b)]. Most of the carbon component introduced via C_2H_2 addition at a level of $C_2H_2/CH_3SiH_3 = 3.4 \times 10^{-2}$ exists in the form of condensed carbon when conditions are maintained in the SiC + C two phase field. Single phase SiC is computed to form over the remainder of the diagram shown in Fig. 4.6(b). The results of the CVD phase diagram calculations are summarized in Fig. 4.7. The results indicate that the type and relative concentration of condensed phases in the system $CH_3SiH_3 - C_2H_2 - (Ar - H_2)$ may be changed by varying temperature, H_2 content of the diluent gas, or by introducing a gaseous additive to the initial gaseous mixture.

Analysis of the $CH_3SiH_3 - C_2H_2 - (N_2 - H_2)$ System

A second system was evaluated in which the argon diluent gas was replaced by nitrogen. The species considered in the equilibrium calculations are listed in Table 4.1. The range of input parameters was the same as the standard conditions as for the (Ar - H_2) case except the argon was replaced by nitrogen. Additions of C_2H_2 and CH_4 were also considered at mole ratios

$$\frac{C_2H_2}{CH_3SiH_3} - 0, 3.4 \times 10^{-2} \quad (4.5)$$

$$\frac{CH_4}{CH_3SiH_3} - 0, 3.4 \times 10^{-2} \quad (4.6)$$

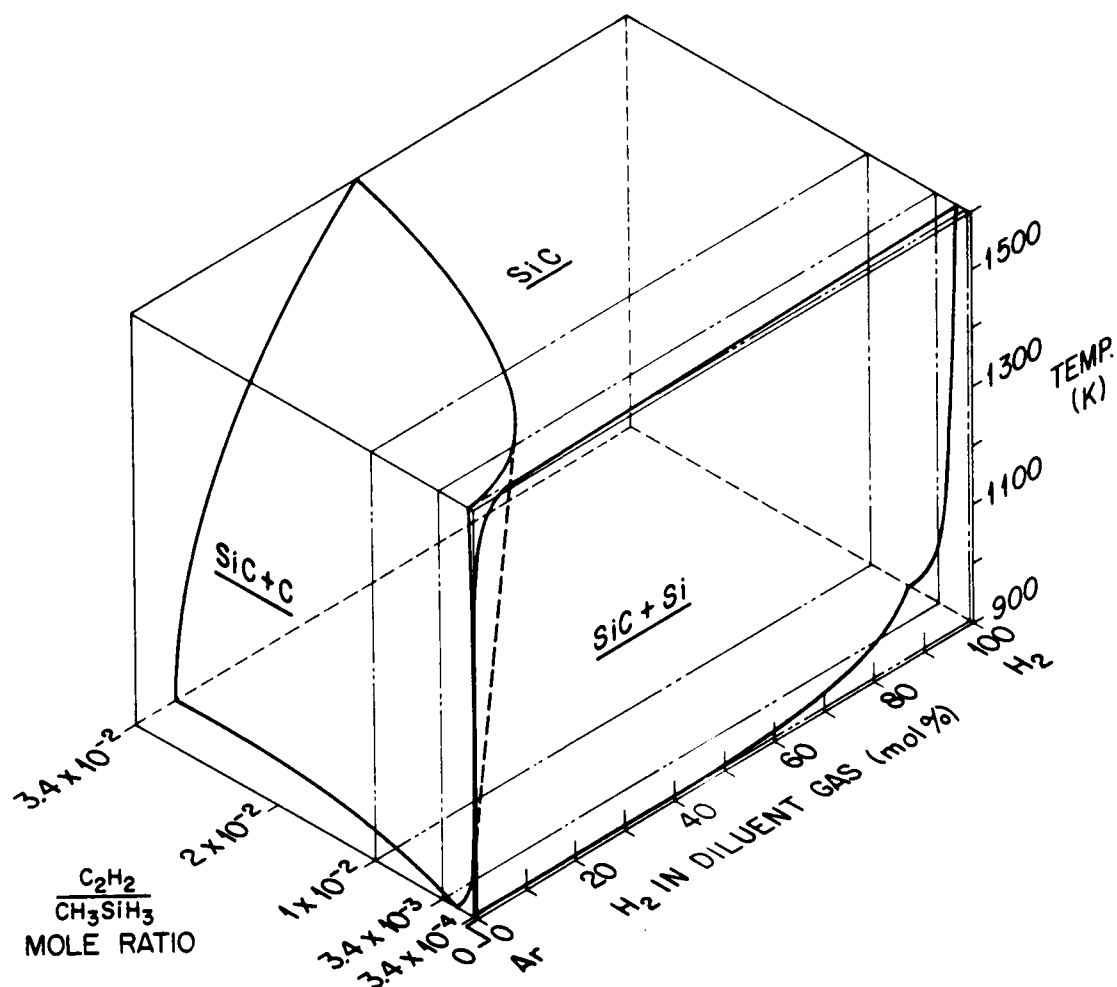


Fig. 4.7. CVD phase diagram based on thermodynamic equilibrium for the $\text{CH}_3\text{SiH}_3 - \text{C}_2\text{H}_2 - (\text{Ar} - \text{H}_2)$ system. Phase boundaries separate range of conditions where single phase SiC , and codeposits of $\text{SiC} + \text{C}$, or $\text{SiC} + \text{Si}$ form.

to evaluate their effect on condensed phase fields and partial pressure of gaseous species. The standard conditions define the case when no additive gas (C_2H_2 or CH_4) is present in the system. A computed CVD phase diagram for the standard input conditions is shown in Fig. 4.8. Phase boundaries separate regions where $Si_3N_4 + C$, Si_3N_4 , $\beta-SiC + Si_3N_4$, and $\beta-SiC + Si$ are computed to form. When no hydrogen is present in the diluent gas the condensed phases computed to occur are $Si_3N_4 + C$ for the entire 900 to 1600 K temperature range. Nearly all of the available carbon present in the system is computed to form in the condensed phase. The $Si_3N_4 + C$ two phase field occurs over a wide range of conditions. At 900 K the two phase field extends to an hydrogen content in the diluent gas of ≈ 15 mol % but, at 1400 K it extends to a hydrogen content in the diluent of ≈ 98 mol %. Contours of constant mole ratio $r_C = C/Si_3N_4$ are also shown in Fig. 4.8. At constant temperature the carbon concentration, r_C , in the $Si_3N_4 + C$ two phase field decreases slowly as the hydrogen content in the diluent is increased. However when either the $Si_3N_4 + C$ and Si_3N_4 , or the $Si_3N_4 + C$ and $SiC + Si_3N_4$ phase boundaries are approached, r_C decreases rapidly to very low values. Single phase Si_3N_4 is also computed to form over a wide set of conditions. The range of conditions where $SiC + Si_3N_4$ are computed to form occurs at temperatures greater than 1400 K and high hydrogen concentration in the diluent gas. The variation of the mole ratio $r = SiC/Si_3N_4$ is also shown on the diagram. At a constant temperature the Si_3N_4 concentration in the $SiC + Si_3N_4$ two phase field decreases as the hydrogen content in the diluent gas increases.

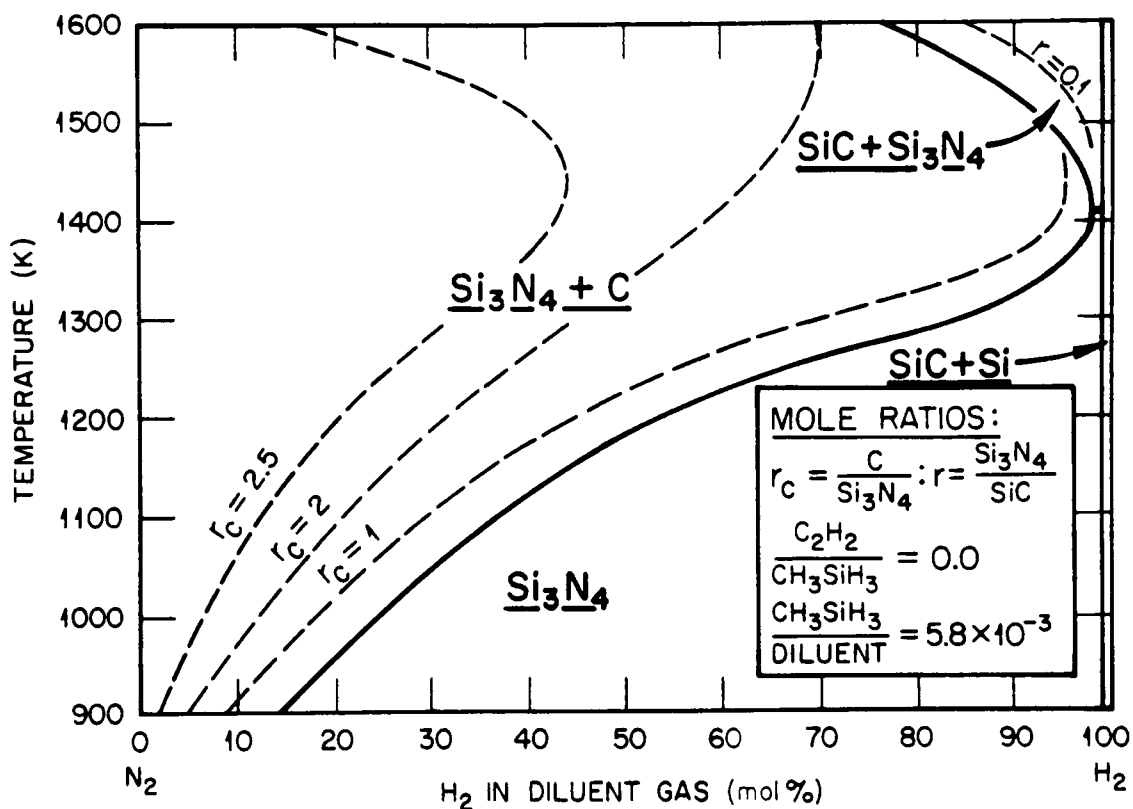


Fig. 4.8. CVD phase diagram based on thermodynamic equilibrium calculations for the $CH_3SiH_3 - C_2H_2 - (N_2 - H_2)$ system; mole ratios $CH_3SiH_3/diluent = 5.8 \times 10^{-3}$, $C_2H_2/CH_3SiH_3 = 0.0$, total pressure = 1.01×10^5 Pa (≈ 1 atm). Phase boundaries separate range of conditions where single phase Si_3N_4 , $Si_3N_4 + C$, $SiC + Si_3N_4$, or $SiC + Si$ forms. Contours of constant mole ratio of $r_c = C/Si_3N_4$, or $r = Si_3N_4/SiC$ are shown.

The gaseous species with the highest partial pressure in the product gas are hydrogen and nitrogen. The next set of most abundant gases are HCN, CH_4 , H, C_2H_2 , C_2H_4 , CH_3 and SiH_4 . The calculated partial pressures of these species for initial conditions of $\text{CH}_3\text{SiH}_3/\text{diluent} = 5.8 \times 10^{-3}$ and standard conditions, at a constant temperature of 1600 K versus hydrogen content in the ($\text{N}_2 + \text{H}_2$) diluent gas are plotted in Fig. 4.9. Also shown on the figure is the range over which $\text{Si}_3\text{N}_4 + \text{C}$, or $\text{SiC} + \text{Si}_3\text{N}_4$, or $\text{SiC} + \text{Si}$ form as the hydrogen content in the diluent gas increases at a constant temperature of 1600 K. The most abundant of the nitrogen bearing species is HCN, and of the carbon bearing species is again CH_4 . The partial pressure of SiH_4 is quite small and is the smallest of these gases for this set of conditions.

Plotted in Fig. 4.10 are the mole ratios C in condensed phase/total C, $\text{CH}_4/\text{total C}$, and $\text{HCN}/\text{total C}$ at a temperature of 1300 K versus the hydrogen content in the diluent gas. Also shown in the figure are the ranges over which condensed phases $\text{Si}_3\text{N}_4 + \text{C}$, Si_3N_4 , and $\text{SiC} + \text{Si}$ form at a temperature of 1300 K. The mole ratio of C in condensed phase/total C is near unity at a hydrogen content in the diluent = 0 % (100 mol % N_2). As the hydrogen content in the diluent gas is increased the C/total C decreases and the CH_4 concentration increases. The increase in CH_4 nearly matches the decrease of condensed C. The HCN concentration is, for most conditions, less than that of CH_4 .

Consider the coating efficiency as two terms, one of C in the condensed phase/total C, and another of total Si in condensed phase/total

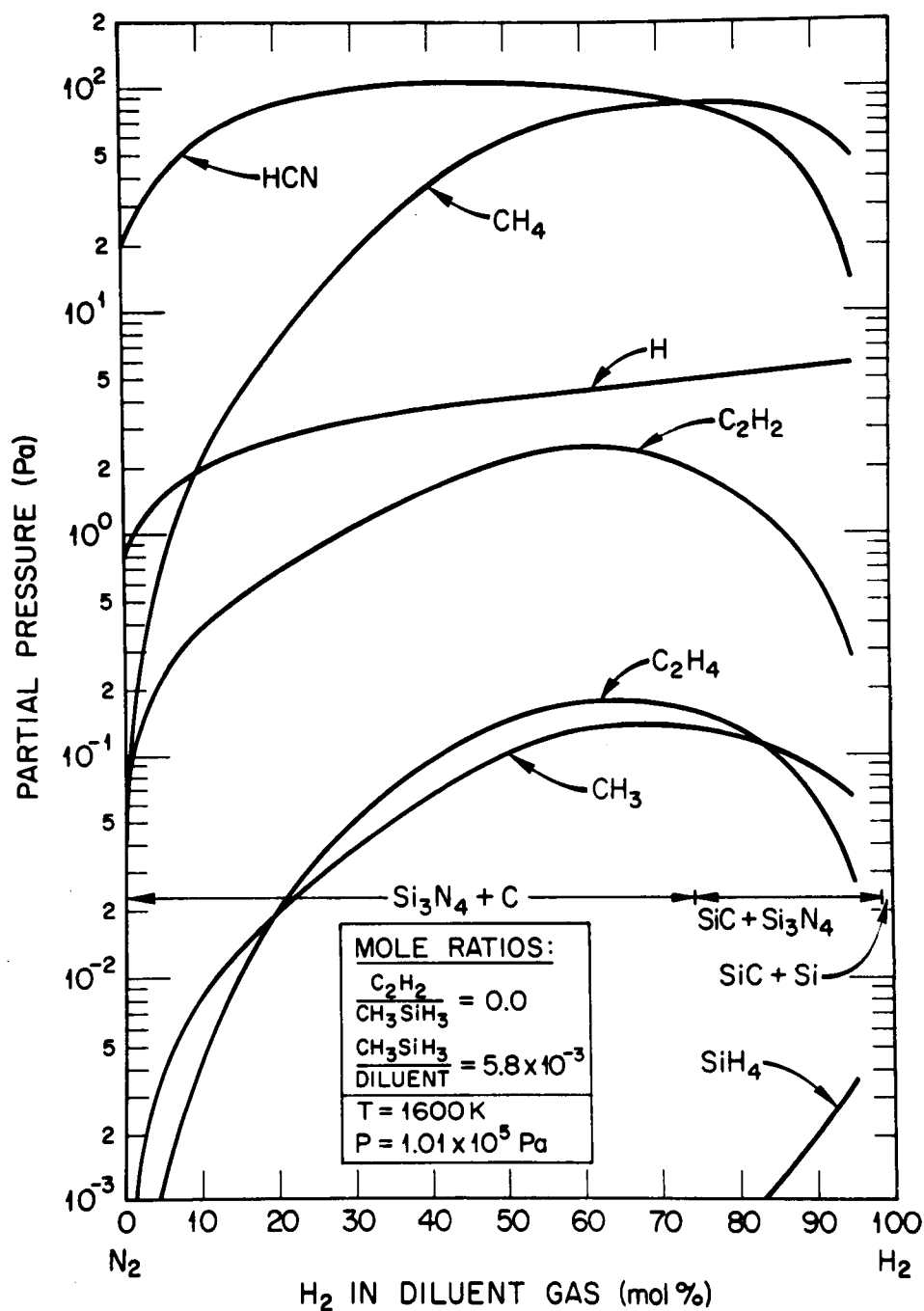


Fig. 4.9. Partial pressure of various gaseous product species versus temperature for the $CH_3SiH_3 - C_2H_2 - (N_2 - H_2)$ system; mole ratios $CH_3SiH_3/diluent = 5.8 \times 10^{-3}$, $C_2H_2/CH_3SiH_3 = 0.0$, total pressure = 1.01×10^5 Pa (≈ 1 atm), and $T = 1600$ K.

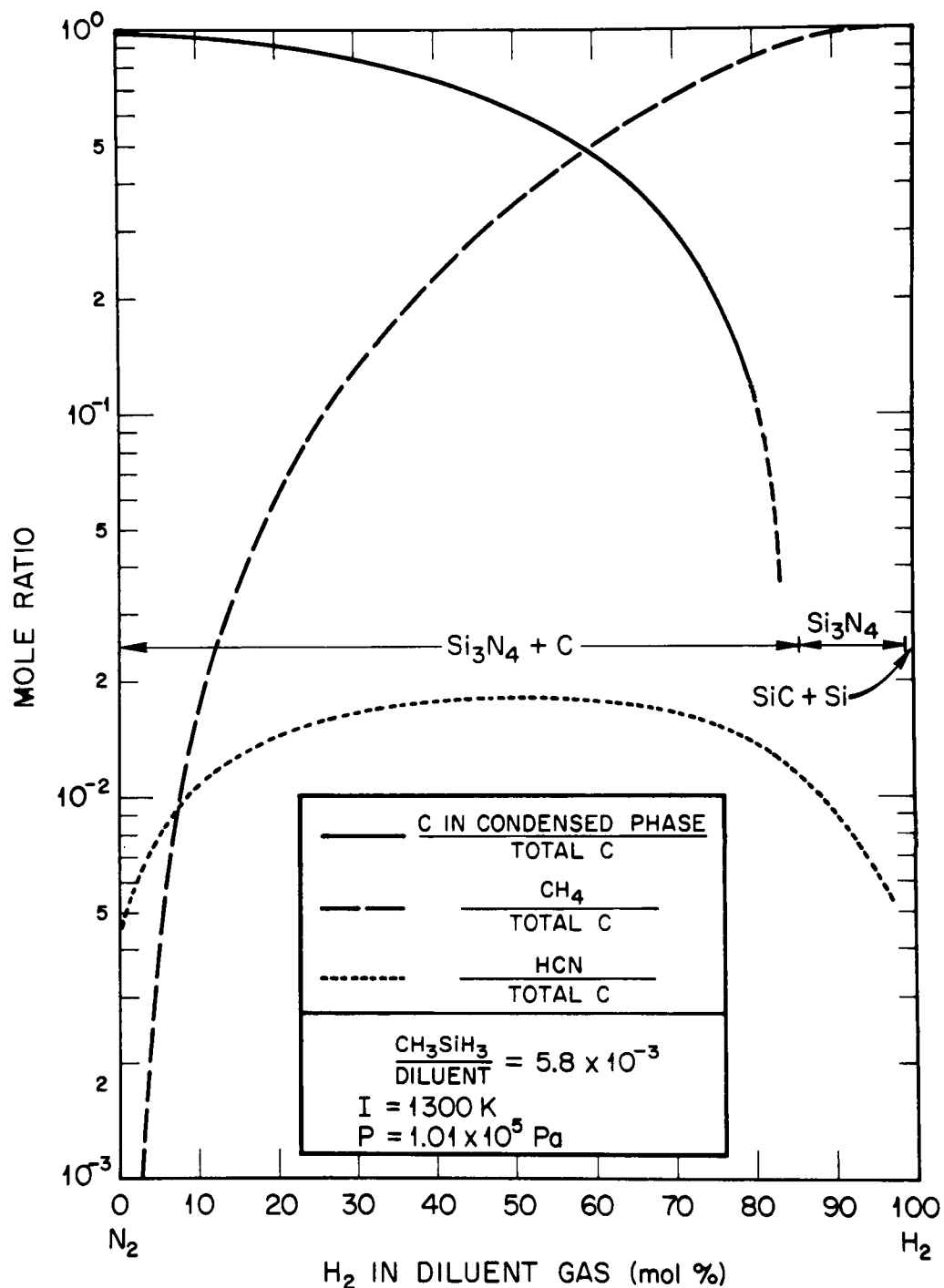


Fig. 4.10. Mole ratios of C in condensed phase/total C, CH₄/total C, and HCN/total C versus H₂ in diluent gas for the CH₃SiH₃ - C₂H₂ - (N₂ - H₂) system; CH₃SiH₃/diluent = 5.8 × 10⁻³, C₂H₂/CH₃SiH₃ = 0.0, total pressure = 1.01 × 10⁵ Pa (≈1 atm), and T = 1300 K.

silicon. Both of these efficiencies are near 100% over the entire range of conditions shown in Fig. 4.8.

Results of one set of calculations where the CH_3SiH_3 /diluent was decreased to 2.9×10^{-3} show no major effect on the phase boundaries or relative concentration in the condensed phase. The deposition efficiencies are again greater than 99% over the entire range of conditions in Fig. 4.8.

The influence of C_2H_2 or CH_4 -addition ($\text{CH}_4/\text{CH}_3\text{SiH}_4 = 3.4 \times 10^{-2}$) showed the phase boundary between $\text{Si}_3\text{N}_4 + \text{C}$ and Si_3N_4 to move toward higher hydrogen content in the diluent gas by about 10 mol %. The deposition efficiencies did not change significantly.

CVD of Silicon Carbide

Initial Experiments

A set of experiments was performed to determine the optimum experimental conditions affecting the thermal decomposition of CH_3SiH_3 and subsequent formation of SiC . These initial experiments were the first ever performed with CH_3SiH_3 in a fluidized-bed reaction vessel. The general objective was to obtain sufficient understanding of the decomposition process to more logically design a subsequent experiment. Coating parameters which were evaluated included temperature, reactant and diluent gas flow rates, amount of substrate loaded in the fluidized-bed coater, and substrate properties such as surface area per unit mass, diameter, and density. The results from this set of experiments were valuable in indicating the direction to proceed with further experiments.

The 1073 to 1685 K temperature range was chosen to evaluate (1) a low temperature coating process if needed for substrates of low thermal stability and (2) an intermediate temperature range if higher temperatures were required to achieve dense coatings.

Pyrolytic carbon coated Al_2O_3 substrate particles were chosen to simplify the analytical procedures required to properly analyze the coatings and substrates. The characteristics of the substrate particles have been presented in a previous section. The reactant and diluent gas flow rates as well as the substrate charge size (amount of material to be coated) were chosen to achieve a range of coating rates. Both high density and low density SiC coatings were to be studied. Low density coatings are sometimes needed between the substrate and a dense outer coating layer to prevent fracture of the dense coating. This sometimes occurs if large thermal expansion differences exist between the substrate and a dense coating. The experiments were separated into two main types, one based on a 100 mol % Ar diluent gas and a second based on 100 mol % H_2 diluent gas.

The experimental coating parameters and resultant coating properties are shown in Table 4.2. The nominal set of conditions for this set of experiments are as follows:

Temperature — 1073 to 1685 K

Particle charge — ≈ 7 g

Diluent gases — Ar and H_2

Mole ratio $\text{CH}_3\text{SiH}_3/\text{diluent}$ — 8×10^{-6} to 2×10^{-4}

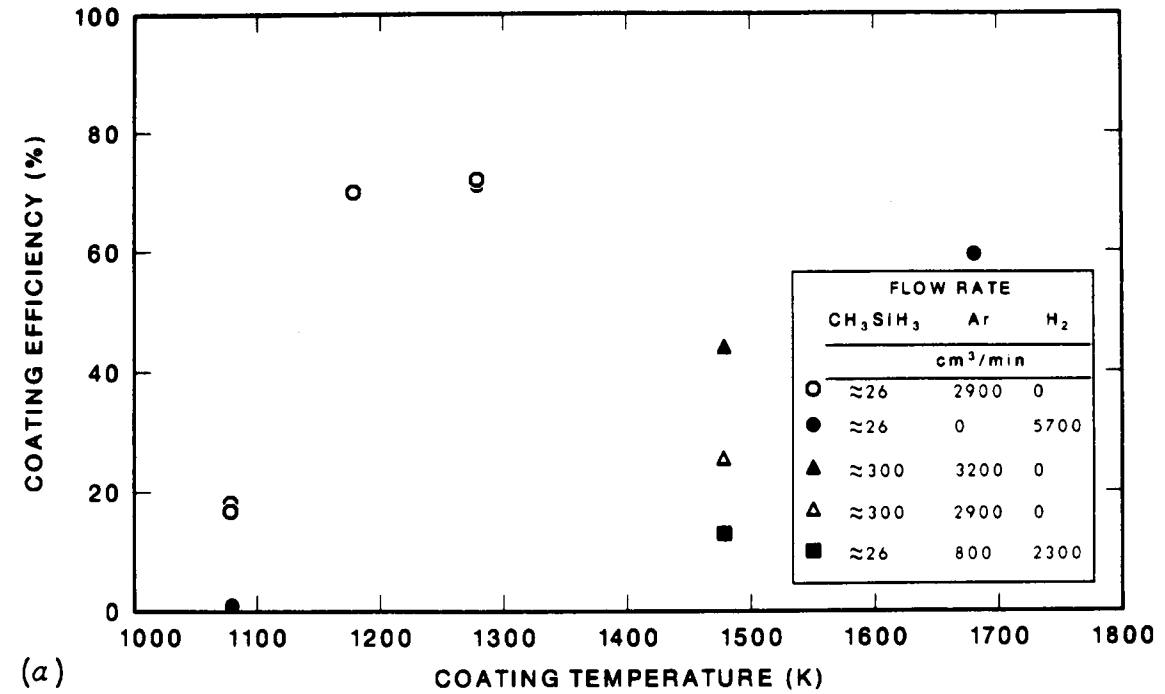
Table 4.2. Experimental coating parameters and coating property data for initial SiC coating experiments

Coating Parameters														
Run number ^a	Tempera- ture (K)	Time (min)	Particle charge (g)	Flow rate			Particle charge		Coating effi- ciency (%)	Thickness ^c (μm)	Density			Coating rate ($\mu\text{m}/\text{min}$)
				CH ₃ SiH ₃	Diluent gas		Mass gain (g)	Volume gain (cm ³)			ρ_1	Density		
					Ar	H ₂						ρ_2	ρ_3	
(cm ³ /min)														
31	1483	10	7.33	300	3200	0	2.49	9.8	46	117.9 [12.6]	g	g	g	11.8
32	1483	75	7.33	290	2900	0	1.0	3.2	26	56.0 [4.7]	g	g	g	0.75
33	1483	75	6.95	350	0	5700	1.2	2.0	25	38.3 [5.7]	1.70	1.44	g	0.51
34	1685	30	7.07	24	0	5700	.79	0.5	61	8.3 [0.6]	2.93	3.12	g	0.11
35	1280	75	6.69	29	2900	0	2.86	2.2	73	39.1 [1.5]	2.38	2.38	g	0.52
37	1483	75	7.05	30	800	2300	0.63	6.4	15	105.6 [32.9]	g	g	g	1.41
38	1280	75	7.00	30	0	5700	2.88	1.9	72	35.6 [1.0]	2.97	3.04	g	0.48
39	1073	75	7.28	22	0	5700	0.06	g	2	7.2 [0.4]	g	g	g	0.09
41	1073	42	7.08	29	2900	0	0.33	0.1	15	5.0 [0.5]	3.02	(4.45)	g	0.12
42	1073	20	7.06	25	2900	0	0.89	0.5	17	12.0 [0.6]	2.88	3.11	g	0.10
43	1180	75	7.21	29	2900	0	2.81	1.8	70	38.3 [1.9]	3.06	3.13	3.15	0.51

^aFluidized bed experiments performed with 2.54 cm diameter cone.^bPyrolytic carbon coated microspheres.^cData in brackets are 95% confidence level, number of measurements = 50.^dDetermined from mercury density measurements, and coating thickness measured from macro-radiographs.^eDetermined from mercury density measurements and mass gain.^fDetermined by gradient density measurements on fractured coatings.^gNot determined.

Since there are many variables which can affect the characteristics of coatings, it was decided to keep as many variables as possible constant at least until some reproducibility could be achieved.

The coating efficiency versus temperature data are presented in Fig. 11(a). The coating efficiency is very low, $\approx 2\%$, at a coating temperature of 1073 K and with hydrogen as the diluent gas. In that experiment very little powder was observed in the fluidization assembly during the run indicating the reactant may not have achieved a sufficiently high temperature to decompose. The coating efficiency was higher ($\approx 17\%$) for the experiment where the diluent gas was 100 mol % Ar. Coating efficiency increased dramatically as the coating temperature was increased to 1280 K. At a coating temperature of 1280 K the coating efficiency was $\approx 70\%$ irrespective of the type of diluent gas. The coating efficiency decreased to 60% as the coating temperature was increased to 1685 K (hydrogen diluent gas). Two experiments were performed at 1483 K with argon diluent gas. However, the CH_3SiH_3 flow rate was ≈ 10 times greater than that used in the other experiments. The coating efficiency for these experiments was decreased substantially to ≈ 46 and 25%. The higher coating efficiency (46%) was obtained in the experiment with the higher argon diluent flow rate of $3200 \text{ cm}^3/\text{min}$ compared to $2900 \text{ cm}^3/\text{min}$. The experiment with the lowest coating efficiency, at a coating temperature of 1483 K, was performed with a mixture of argon and hydrogen diluent gas at flow rates of 800 and $2300 \text{ cm}^3/\text{min}$ respectively. These last results indicate that reactant and diluent gas flow rates can affect the coating process in a substantial manner.



ORNL-DWG 85C-11857

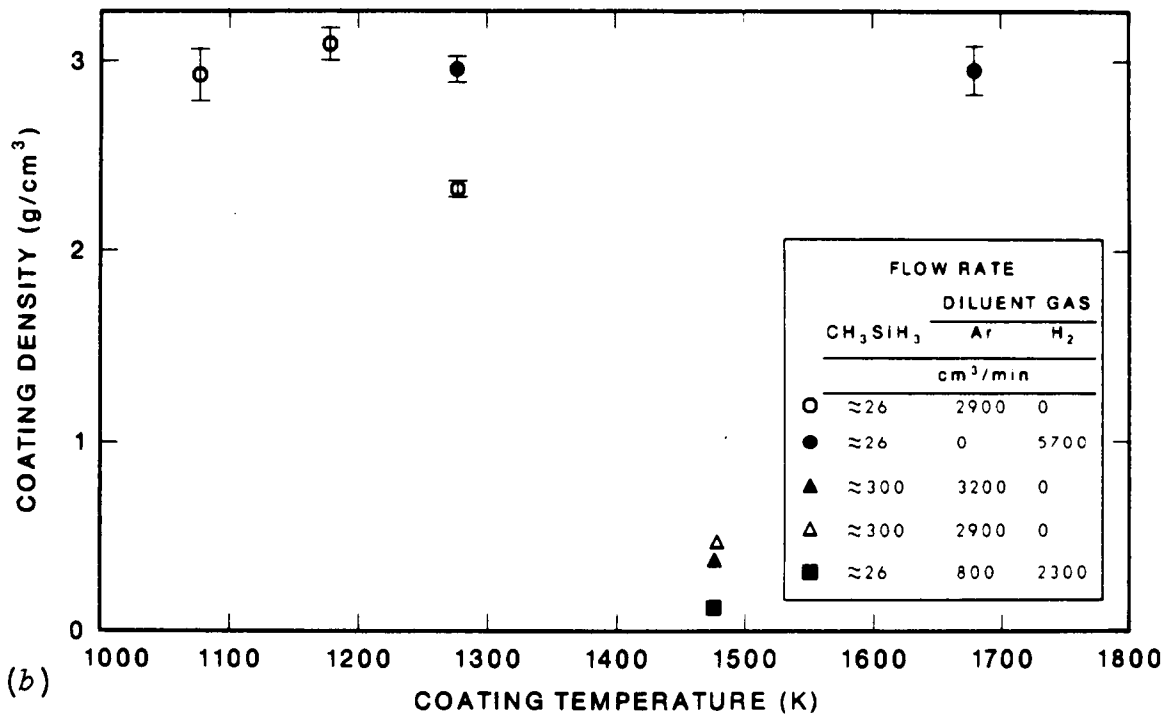


Fig. 4.11. SiC deposited onto PyC coated alumina substrate particles, 7 g charge (a) coating efficiency versus coating temperature, and (b) coating density versus coating temperature. (Values at 1483 K determined by tap density measurements.)

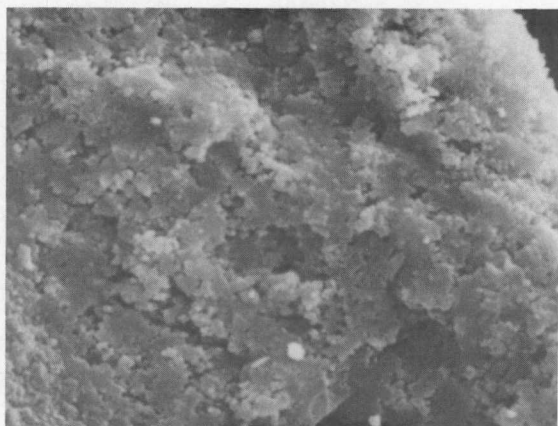
Coating densities are presented in Fig. 4.11(b). The highest coating density achieved was 98% of theoretical for SiC. It occurred in an experiment performed at 1180 K with an argon diluent gas flow rate of 2900 cm³/min. For experiments made with argon diluent gas the coating density decreased substantially as the coating temperature increased from 1180 to 1280 K. The coating density for the hydrogen diluent experiment performed at 1273 K was higher than the corresponding one using argon as the diluent.

Scanning Electron Microscopy (SEM) micrographs of SiC coating fracture surfaces are shown in Fig. 4.12 for coatings deposited using a diluent gas of 100 mol % Ar. The micrographs show the porosity increases as the deposition temperature increases from 1073 to 1280 K. The coating at 1280 K is an open structure and perhaps suitable for low density buffer coating. The coating produced at 1073 K possessed the dense microstructure. Also note the mottled appearance in the 1073 K coating which may be related to growth processes. Scanning electron micrographs of SiC fracture surfaces for SiC coatings deposited using a 100 mol % H₂ diluent gas are shown in Fig. 4.13. Porosity is observed in both the 1280 and 1685 K coatings but both appear to be relatively dense. The 1280 K coating formed in an hydrogen diluent gas appears to be more dense than the corresponding coating deposited using argon diluent gas, in agreement with the density measurements.

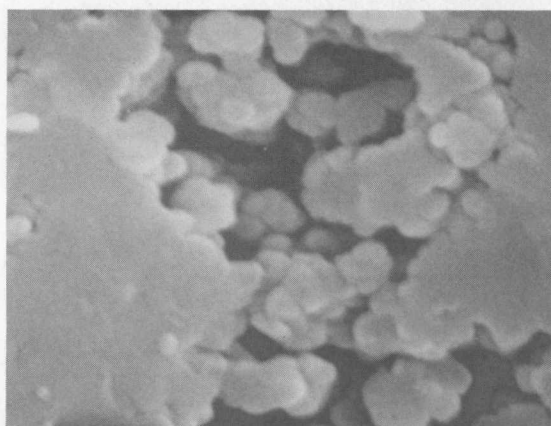
The surface structure of the coatings are shown in Fig. 4.14. The surfaces have different morphologies depending upon coating temperature and hydrogen content in the diluent gas. The surface of the 1685 K coating has a "cauliflower" type appearance which is similar

M-11196

M-11194



(a)



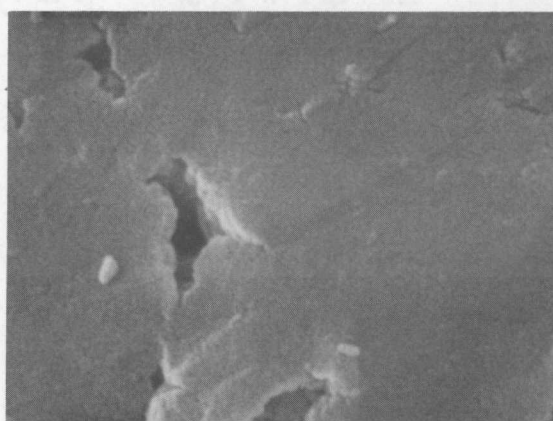
(b)

M-11257

M-11255



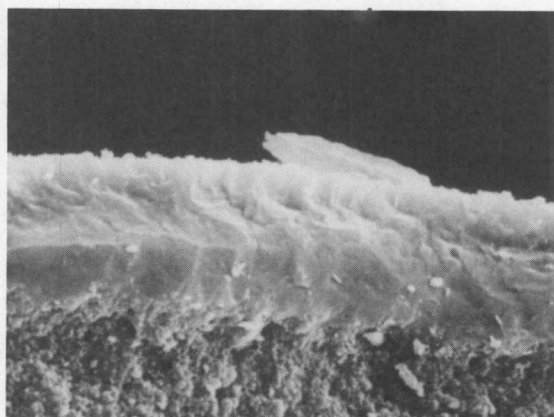
(c)



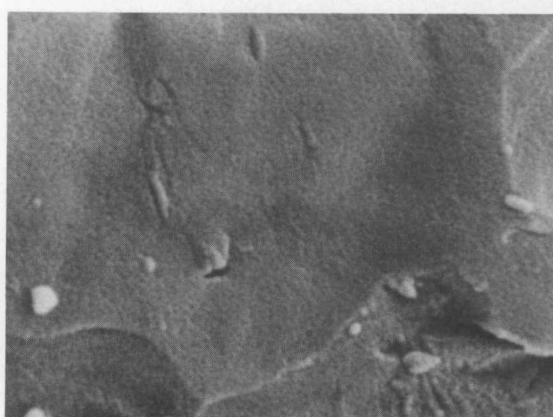
(d)

M-11249

M-11247



(e)

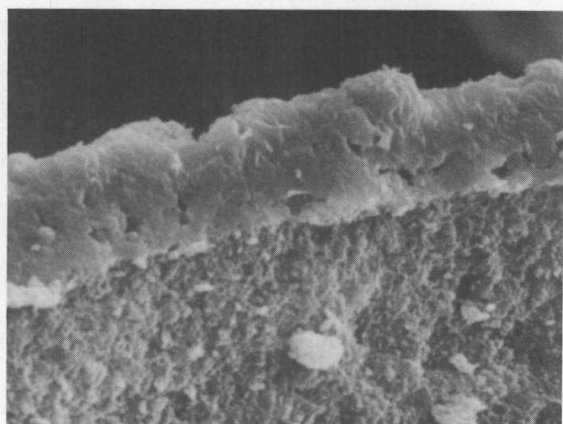
10 μm 

(f)

2 μm

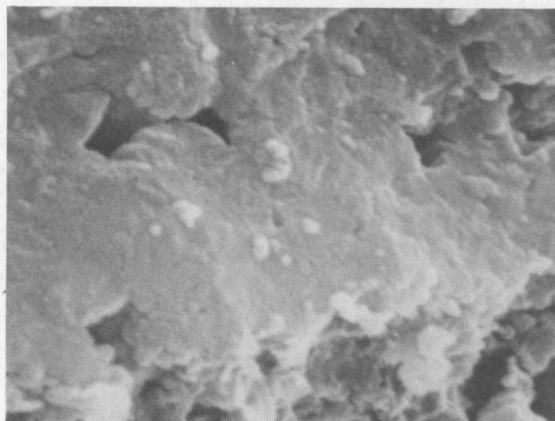
Fig. 4.12. Secondary electron micrographs of SiC fracture surfaces - 100% Ar diluent (a,b) Run 35, $T = 1280$ K, (c,d) Run 43, $T = 1180$ K, and (e,f) Run 42, $T = 1073$ K.

M-11180



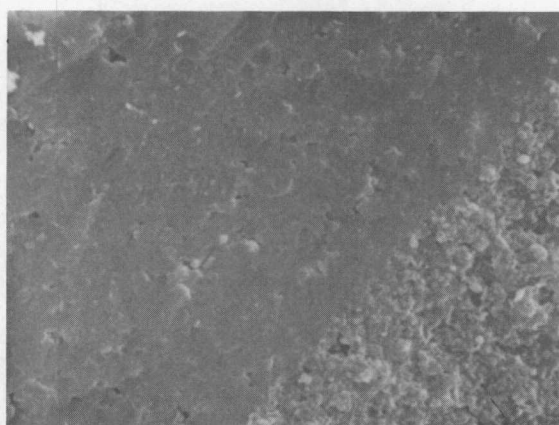
(a)

M-11178



(b)

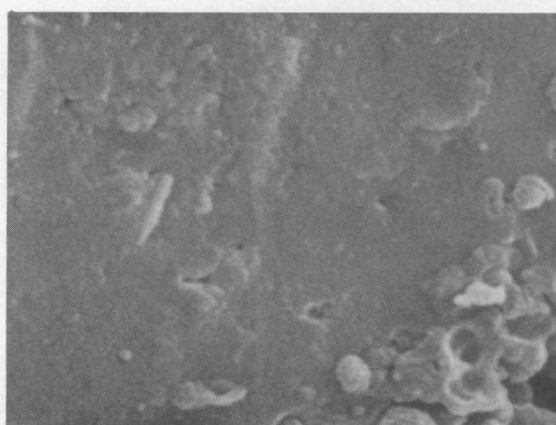
M-11209



(c)

10 μm

M-11207



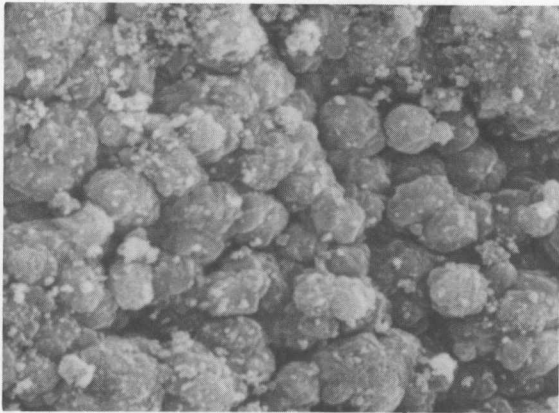
(d)

2 μm

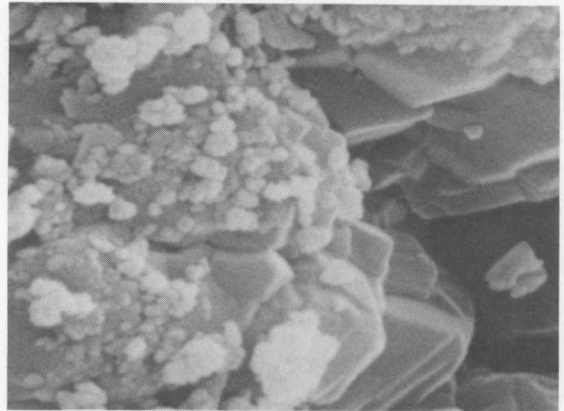
Fig. 4.13. Secondary electron micrographs of SiC fracture surfaces - 100% H_2 diluent (a,b) Run 34, $T = 1685 \text{ K}$, and (c,d) Run 38, $T = 1280 \text{ K}$.

M-11175

M-11173



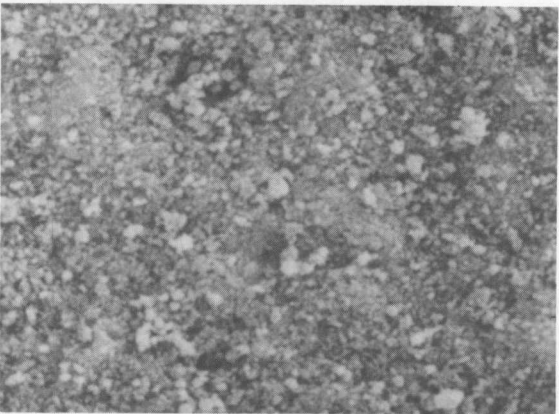
(a)



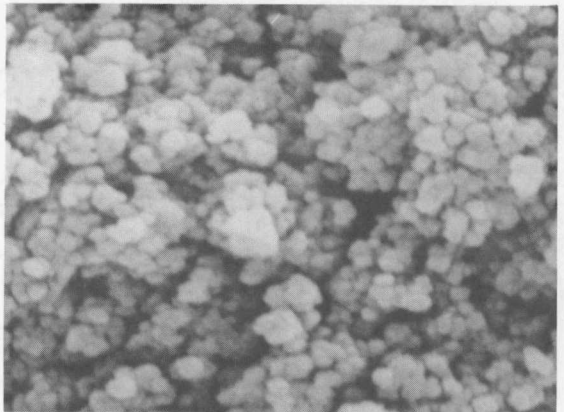
(b)

M-11191

M-11189



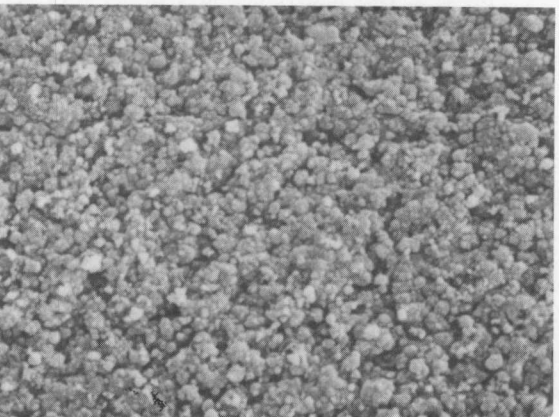
(c)



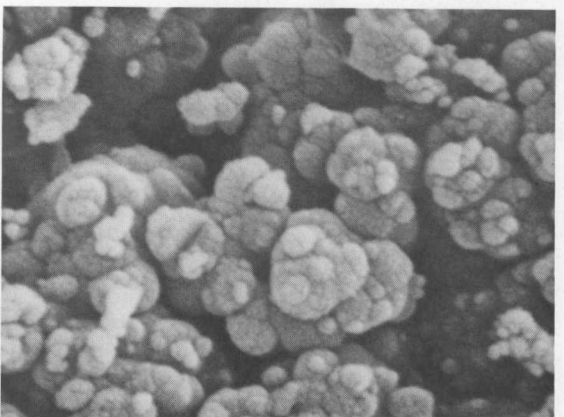
(d)

M-11244

M-11242



(e)

10 μm 

(f)

2 μm

Fig. 4.14. Secondary electron micrographs of SiC surfaces (a,b) Run 34, $T = 1685$ K, 100% H_2 diluent, (c,d) Run 35, $T = 1280$ K, 100% Ar diluent, and (e,f) Run 42, $T = 1073$ K, 100% Ar diluent.

to many of the HTGR SiC coatings deposited from CH_3SiCl_3 at approximately the same temperature. The surface of the 1280 K coating is very "powdery." This appearance indicates the CH_3SiH_3 may have nucleated and grown in the gas phase prior to depositing on the substrate. The surface of the 1073 K coating resembles the 1685 K coating except that the substructures (mottle appearance) are much smaller. The substructure which can be seen in both the 1685 and 1073 K coating indicates a particle growth and sintering reaction.

The open porosity and defective particle fraction data for the SiC coated particles are presented in Table 4.3. Coatings deposited at 1473 K were very porous and of low density. The mercury intrusion method confirmed the conclusion one obtains from examining the SEM micrographs. For coatings deposited at 1273 K the open porosity and defective particle fraction were higher for argon than for hydrogen. The open porosity was 7.8 and 1.3% for the argon and hydrogen diluent experiments, respectively. The defective fraction for those same coatings was 1.0 and $<5 \times 10^{-4}$ respectively. Low bulk density porous SiC coatings may be useful for thermal insulators and for buffer layers to accommodate thermal expansion differences between the substrate and a dense coating deposited onto the substrate. All coatings deposited at 1073 or 1180 K, irrespective of the type of diluent gas had open porosity measurements of less than 1.3%. These same coatings also had very low defective particle fractions of $<4 \times 10^{-4}$. No defective particles were actually observed; however, the 4×10^{-4} value is based on one particle being defective and is chosen as an upper limit. Since the defective particle fraction is low, more than 1.2 g of coated

Table 4.3. Open porosity and defective particle fraction of SiC coated particles

Coating run number	Open porosity ^a (%)	Number of defective particles ^b	Defective particle fraction
31	c	d	1.0
32	c	d	1.0
33	16.5	d	1.0
34	1.7	3	3.5×10^{-4}
35	7.8	d	1.0
37	c	c	c
38	1.3	0	$<5 \times 10^{-4}$
39	0.5	0	$<5 \times 10^{-4}$
41	0.5	0	$<5 \times 10^{-4}$
42	0.8	0	$<5 \times 10^{-4}$
43	1.2	0	$<5 \times 10^{-4}$

^aDetermined from mercury pycnometry (1×10^5 Pa and 102 MPa measurements).

^b ≈ 1.2 g of SiC coated particles tested (≈ 2000 particles).

^cNot determined.

^dAll particles.

particle per test are needed to obtain a more precise value of the defective fraction. The densities for coatings deposited at 1073 and 1180 K are less than 100% of theoretical. When compared to the open porosity data, these data indicate that closed porosity may also be present.

The coating rate for the coatings with densities <2.5 g/cm³ ranged from 0.5 to 11.8 μ /m. For coating experiments between 1073 and 1280 K, the coating rate increased as the temperature increased. This occurred for experiments made with either type of diluent gas. The coating rate is related to both the efficiency of the decomposition process and the density of the coating.

Coating of Pyrocarbon Coated Alumina Substrates

A second set of experiments were performed to evaluate in a more complete manner the chemical vapor deposition of SiC from CH_3SiH_3 . Pyrocarbon coated alumina microspheres were again used as substrates. Since one objective of this research was to evaluate the CVD of SiC at as low a temperature as reasonable, it was decided to lower the coating rate in an attempt to achieve an increase in the SiC coating density. All experiments, except for one, in this set were performed with ≈ 20 g of substrate particles coated per experiment. The increase in substrate charge required an increase in the diluent gas flow rate to properly fluidize the particle bed. Increasing the diluent gas flow rate increased the possibility that CH_3SiH_3 would decompose within the fluidized-bed region. This would improve coating efficiency since less CH_3SiH_3 would react and coat the entrance line of the reaction cone. The general conditions for this set of experiments were

Coating time — 180 min

Coating temperature — 873 to 1280 K

H_2 content in (Ar — H_2) diluent gas — 0 (100% Ar), 8.6, 77,
and 100% H_2

Total System Pressure — 1.01×10^5 Pa (≈ 1 atm)

CH_3SiH_3 flow rate — ≈ 27 cm^3/min for most coating experiments;
230 or 780 cm^3/min for low density buffer
coatings.

From the results of the previous section it is clear that high density coatings can be achieved at temperatures lower than 1280 K. Thus experiments were planned which emphasized this lower temperature

regime. A few experiments were also included to evaluate low density SiC buffer coatings since these may also be useful if a friable buffer layer is required to prevent fracturing of the dense SiC coating. The diluent gases studied were argon, hydrogen, and Ar — H₂ mixtures. The CVD of CH₃SiH₃ was thus evaluated as a function of hydrogen content in the diluent gas. The requirements for coating nuclear waste ceramics could prevent use of gaseous systems with hydrogen concentrations greater than the explosive limit, however this evaluation was also to be a basic one in that the CVD process was being evaluated in a systematic manner and the influence of hydrogen is an important system variable.

The experimental variables of coating temperature, amount of substrate to be coated, reactant and diluent gas flow rates are shown in Table 4.4. Also shown are the coating efficiency, coating thickness, density and coating rate results.

The coating efficiency data are presented in Fig. 4.15. The coating efficiency generally increases with increasing temperature. The efficiency for the 873 K argon diluent experiment was ~1%. For this case no reaction was seen to occur when observing the fluidized-bed region through the top sight port of the coating system. At a temperature of 973 K the coating efficiency increased to 18% and a coating was deposited onto the substrate. Even in this case there was very little reaction product in the form of powder. The coating efficiency increased to 73% as the coating temperature was increased to 1073 K. This is a substantial increase from the results presented in the previous section. The coating efficiency remained nearly constant

Table 4.4. Experimental coating parameters and coating property data for SiC coating of pyrocarbon coated alumina substrates

Coating Parameters														
Run number ^a	Temperature (K)	Time (min)	Particle charge (g)	Flow rate			Particle charge		Coating efficiency (%)	Thickness ^c (μm)	Density			Coating rate (μm/min)
				CH ₃ SiH ₃	Diluent gas		Mass gain (g)	Volume gain (cm ³)			ρ ₁	ρ ₂	ρ ₃	
					Ar	H ₂								
(cm ³ /min)														
45	1073	180	21.34	24	4750	0	5.55	2.7	73	30.5 [0.4]	2.85	2.93	g	0.17
52	873	180	20.86	24	4750	0	0.07	g	1	0	g	g	g	0.0
60	973	180	21.35	24	4750	0	1.40	0.3	18	12.8 [0.5]	2.67	2.89	g	0.07
75	1073	180	21.21	21	0	9800	1.10	0.2	16	13.1 [0.8]	2.69	3.22	g	0.07
76	1073	180	21.81	29	1400	4300	1.79	0.8	19	14.8 [0.6]	2.73	2.95	g	0.08
77	1073	30	21.73 ^h	230	4750	0	6.41	3.9	53	35.9 [0.5]	2.55	2.56	g	1.2
82	973	180	40.0	27	4750	0	2.59	0.8	30	13.2 [0.7]	3.19	g	g	0.07
84	1180	180	18.96 ^h	21	4750	0	5.18	2.4	75	25.8 [0.8]	2.93	2.96	g	0.14
85	1180	180	19.56 ^h	29	0	9800	6.84	3.7	72	34.3 [0.6]	2.91	3.00	g	0.19
88	1180	180	19.45 ^h	27	1700	5700	7.16	3.7	82	34.6 [0.6]	2.98	3.05	g	0.19
89	1180	180	19.51 ^h	27	5300	500	5.22	2.6	60	25.6 [0.8]	3.01	3.09	g	0.14
90	1073	180	19.41 ^h	27	5300	500	4.58	2.1	53	26.4 [0.8]	2.77	3.01	g	0.14
91	1180	5	19.54 ^h	780	4750	0	4.01	3.8	58	27.1 [1.3]	2.52	2.81	g	5.4
92	1280	180	19.62 ^h	27	4750	0	6.51	4.6	75	38.5 [1.3]	2.26	2.27	g	0.21
99	1280	180	19.57 ^h	27	0	9800	5.69	3.2	65	28.4 [0.7]	2.81	2.87	g	0.16

^aFluidized bed experiments performed with 2.54 cm diameter cone.^bPyrolytic carbon coated alumina microspheres.^cData in brackets are 95% confidence level, number of measurements = 50.^dDetermined from mercury density measurements, and coating thickness measured from macroradiographs.^eDetermined from mercury density measurements and mass gain.^fDetermined by gradient density measurements on fractured coatings.^gNot determined.^hAdditional 0.5 g of uncoated Al₂O₃ microspheres.

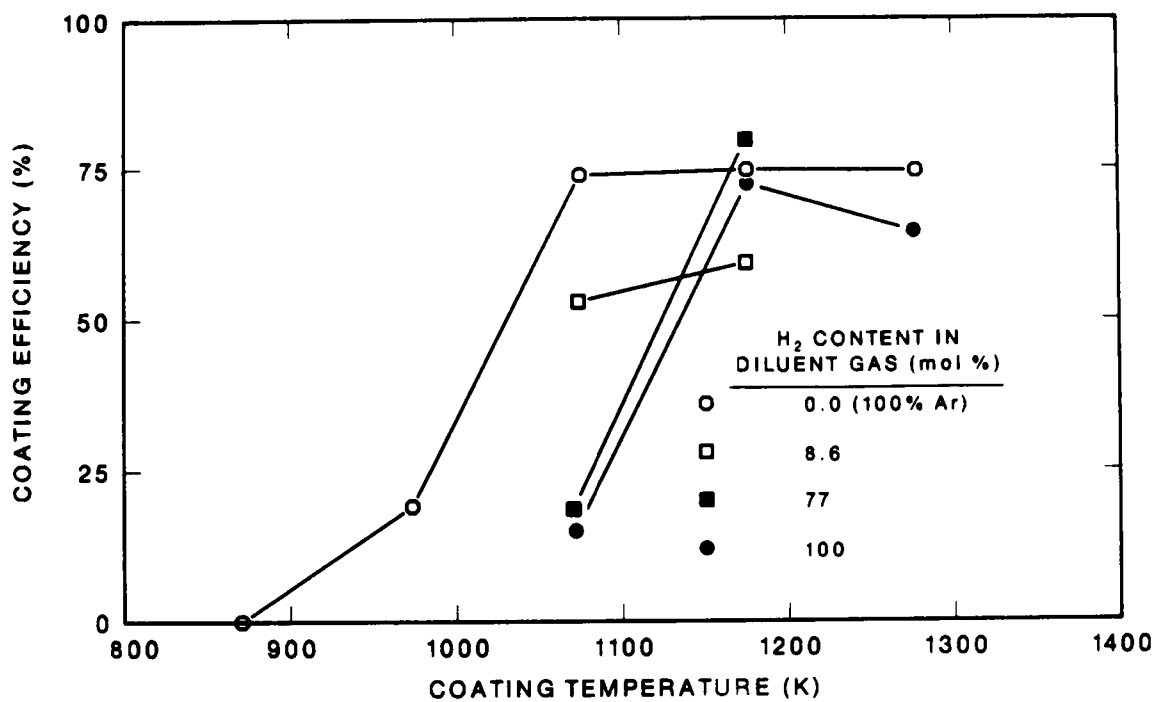


Fig. 4.15. Coating efficiency versus coating temperature (SiC deposited onto PyC coated alumina substrate particles, 20 g charge).

for experiments made at 1180 and 1280 K. The coating efficiency increased as the amount of substrate particles in the coater was increased. The coating efficiency for the 973 K with argon diluent and 20 g of substrate particles experiment was 18%, but it increased to 30% when the amount of substrate was increased to 40 g.

The coating efficiency for the 1073 K experiment with a diluent gas of 100% hydrogen was only $\approx 16\%$. This is significantly less than the 73% value achieved with a diluent of 100% argon. At higher coating temperature the coating efficiency increased to $\approx 75\%$ irrespective of the hydrogen content of the diluent gas. The results show that relatively high coating efficiencies can be obtained at temperatures as low as 1073 K during the chemical vapor deposition of SiC from Methylsilane in a fluidized-bed coater.

The SiC coating densities reported in Table 4.4 indicate a number of trends in the thermal decomposition process. The density of coatings deposited at 1180 K are generally $\approx 10\%$ higher than those of coatings deposited at 1073 K. This result seems to hold irrespective of the hydrogen content in the diluent gas. In addition for experiments when the diluent gas is 100% argon, the coating density decreases as the coating temperature increases from 1180 to 1280 K. However in 100% hydrogen diluent gas the SiC coating density for material synthesized at 1280 K remains nearly the same to that of the 1180 K coating. The density measurements for SiC coatings deposited at 973 K are not considered reliable since either the mass gain or coating thickness measurements lead to large relative errors in the resultant density calculation.

The open porosity and defective particle fraction results are presented in Table 4.5. These data indicate there is a range of conditions where coatings with relatively low open porosity $<0.5\%$ can be formed. No defective particles were observed in any of the coatings synthesized at 1180 K. For dense coatings deposited at 1073 K, only the one synthesized in pure argon had one defective particle. However coatings deposited at 1280 K possessed relatively high open porosity irrespective of diluent gas type, and both coatings resulted in high defective fractions. Defective particle fractions correlated well with the open porosity measurements. For coatings with very low open porosity, $\approx 0.5\%$, no defective particles were observed. Apparently, either the mercury cannot penetrate the pores, or the porosity is not completely interconnected through the coating to the substrate.

Scanning electron micrographs were again used to reveal microstructural features of the SiC coatings. Both SiC coating fracture surfaces and outer surfaces of the SiC coated microspheres were analyzed. The fracture surface results for the argon diluent case are shown in Fig. 4.16. The coating deposited at 1280 K is seen to be very porous. However, the porosity seems to be nearly completely eliminated in coatings deposited at or below 1180 K. Porosity was not observed in coatings deposited at 973 K. Coatings deposited with an hydrogen content in the diluent gas of ≈ 8 and 77% show similar behavior. Coatings deposited at 1073 and 1180 K in 100% hydrogen, (Fig. 4.17) show little or no porosity. The porosity observed in the coating deposited at 1280 K in 100% hydrogen is much less than in its counterpart synthesized in 100% argon.

Table 4.5. Open porosity and defective particle fraction of SiC coated particles

Coating run number	Temperature (K)	Open porosity ^a (%)	Number of defective particles ^b	Defective particle fraction
45	1073	0.6	1	5×10^{-4}
52	873	1.0	c	c
60	973	0.5	0	$<5 \times 10^{-4}$
75	1073	0.5	0	$<5 \times 10^{-4}$
76	1073	0.4	0	$<5 \times 10^{-4}$
77	1073	1.5	45	2.2×10^{-2}
82	973	1.0	2	1×10^{-3}
84	1180	1.2	0	$<5 \times 10^{-4}$
85	1180	0.1	0	$<5 \times 10^{-4}$
88	1180	0.5	0	$<5 \times 10^{-4}$
89	1180	1.2	0	$<5 \times 10^{-4}$
90	1073	0.8	41	2×10^{-2}
91	1180	8.4	d	1.0
92	1280	8.7	d	1.0
99	1280	2.4	d	1.0

^aDetermined from mercury pycnometry (1×10^5 Pa and 102 MPa measurements).

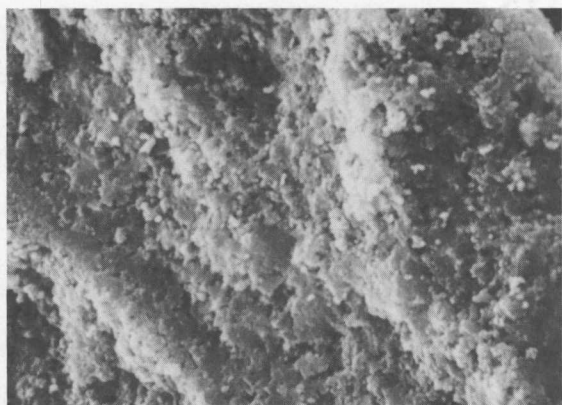
^b ≈ 1.2 g of SiC coated particles tested (≈ 2000 particles).

^cNot determined.

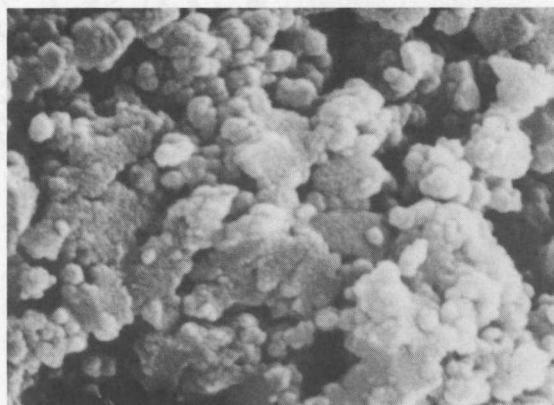
^dAll particles.

M-11422

M-11420



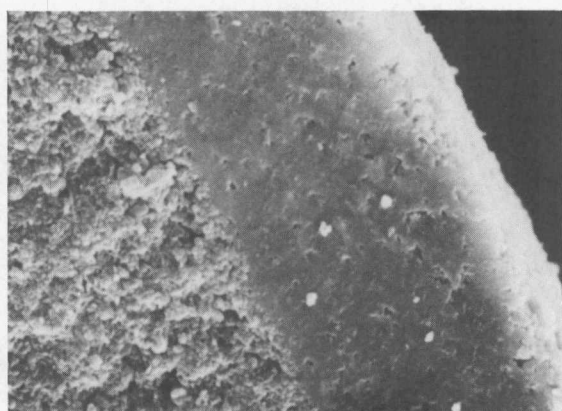
(a)



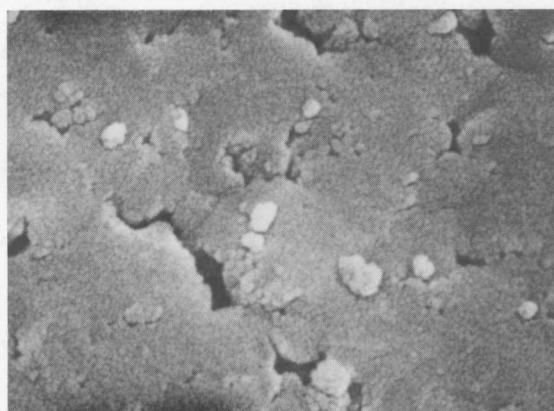
(b)

M-11336

M-13121



(c)



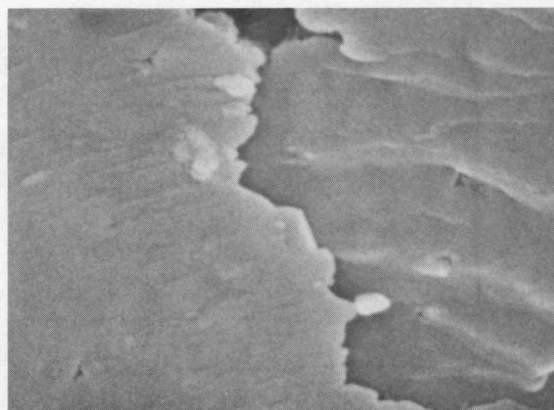
(d)

M-11188

M-11186



(e)



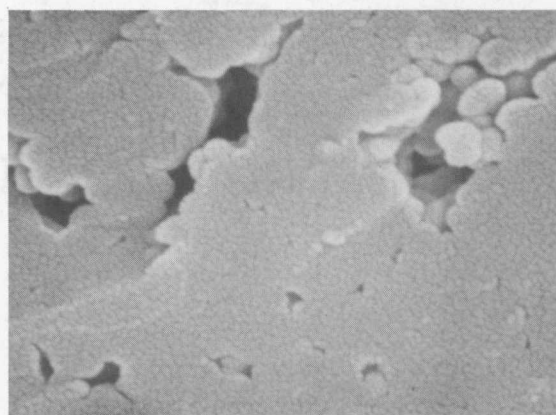
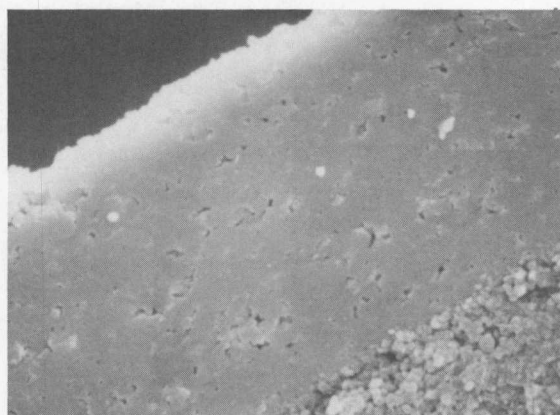
(f)

10 μm 2 μm

Fig. 4.16. Secondary electron micrographs of SiC fracture surfaces — 100% Ar diluent (a,b) Run 92, $T = 1280$ K, (c) Run 84, $T = 1180$ K, (d) Run 84, $T = 1180$ K, annealed 1180 K, and (e,f) Run 45, $T = 1073$ K.

M-11430

M-11428

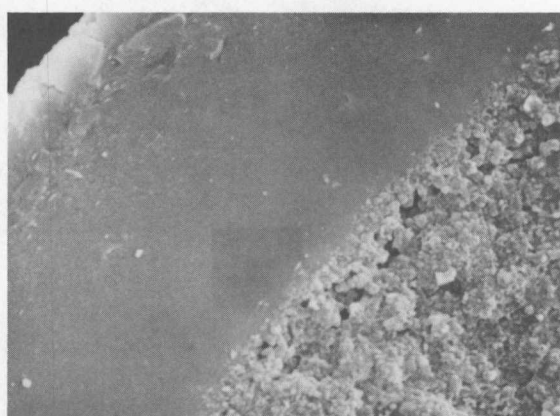


(a)

(b)

M-11344

M-11342

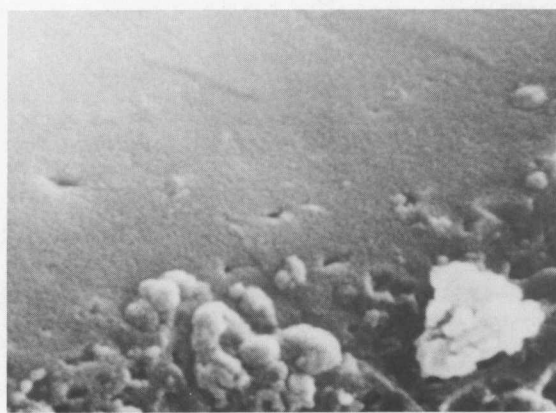
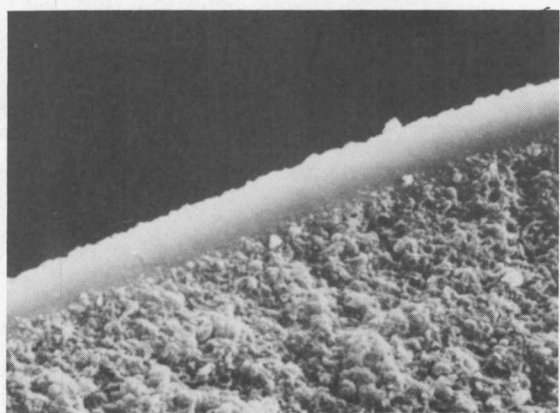


(c)

(d)

M-11304

M-11302



(e)

(f)

10 μm 2 μm

Fig. 4.17. Secondary electron micrographs of SiC fracture surfaces — 100% H_2 diluent (a,b) Run 99, $T = 1280$ K, (c,d) Run 85, $T = 1180$ K, and (e,f) Run 75, $T = 1073$ K.

The outer surfaces of the SiC microspheres also reveal microstructures which vary with deposition temperature and hydrogen content in the diluent gas. Shown in Fig. 4.18 are the outer surfaces of coatings deposited in 100% argon at 973 and 1180 K, and coatings deposited in 100% hydrogen at 1180 and 1280 K. The surface of the coating deposited at 973 K in argon is relatively smooth, however that of the 1180 K coating deposited in argon is "powdery" and consists of particles of ≈ 200 nm diameter. The surface of the specimens deposited in 100% hydrogen show similar characteristics with the coating deposited at the higher temperature possessing the powdery surface structure. These results indicate that SiC nucleates and grows in the gas phase rather than on the surface of the substrate.

The effects of annealing at 1523 K for 3 h coatings deposited at 973 and 1180 K in argon diluent are shown in Fig. 4.19 and 4.20. The outer surface of both particles are shown in Fig. 4.19(a) and (b). Annealing of the 973 coating resulted in surface cracks. However surface cracks were not observed in the annealed 1180 K coating. Scanning electron micrographs of the fracture surface of the 973 K coating which was annealed to 1523 K are shown in Fig. 4.20. Note the microcracks in the coating. The microcracks form at the surface and culminate within the coating layer. This indicates that the microcracking did not originate from thermal expansion differences between the coating and the pyrocarbon substrate layer. These results can be attributed to crystallization of the coating produced at 973 K. X-ray diffraction showed that the coating was amorphous in the deposited condition, whereas crystalline SiC was observed after the

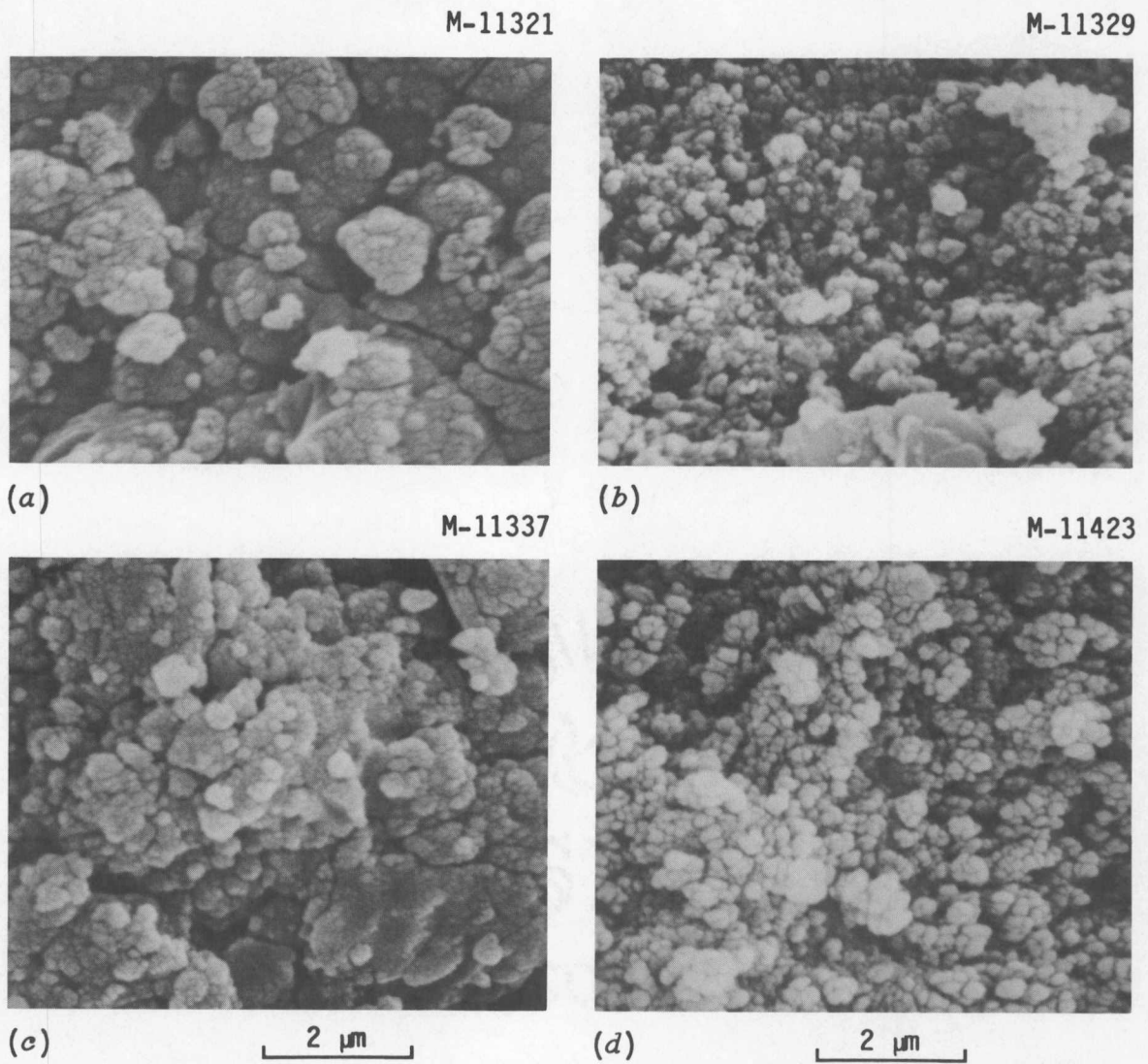


Fig. 4.18. Secondary electron micrographs of SiC surfaces (a) Run 82, $T = 973$ K, 100% Ar diluent, (b) Run 84, $T = 1180$ K, 100% Ar diluent, (c) Run 85, $T = 1180$ K, 100% H_2 diluent, and (d) Run 99, $T = 1280$ K, 100% H_2 diluent.

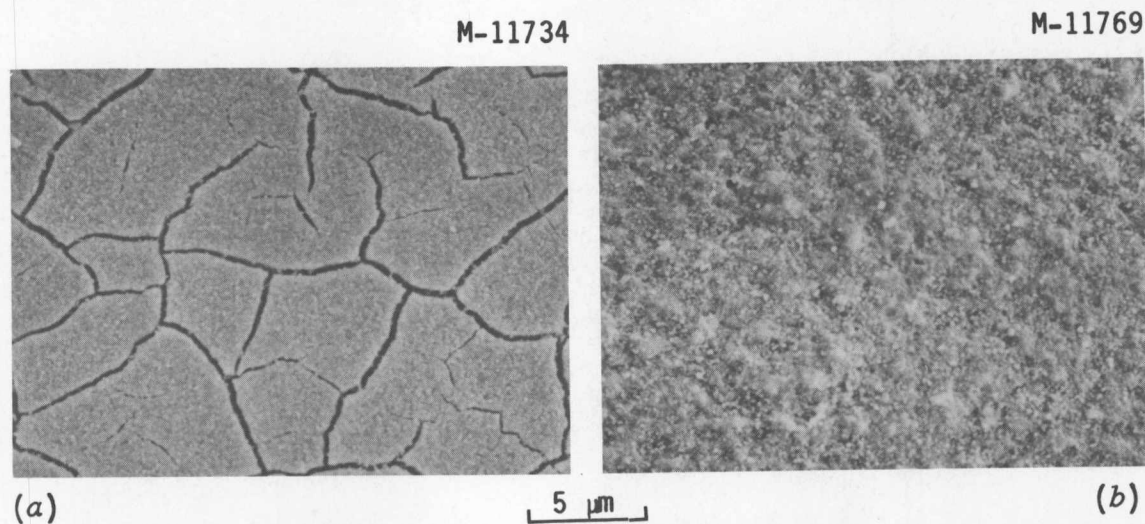


Fig. 4.19. Secondary electron micrographs of SiC surfaces
(a) Run 82, $T = 973$ K, annealed 1523 K, and (b) Run 84, $T = 1180$ K,
annealed 1523 K.

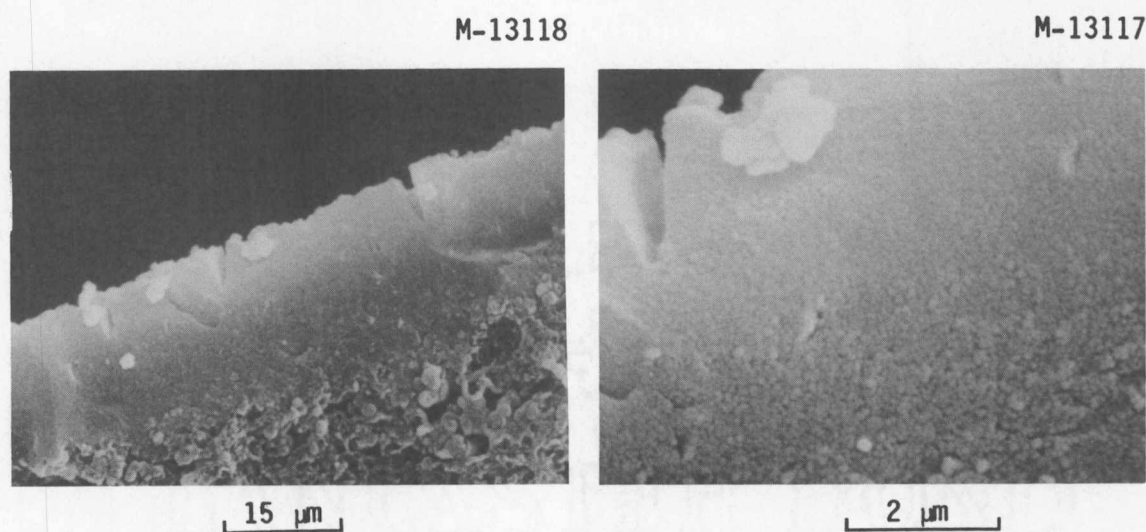


Fig. 4.20. Secondary electron micrographs of SiC coating fracture
surface; Run 82, $T = 973$ K, annealed 1523 K.

1523 K anneal in an argon atmosphere. The coating produced at 1180 was crystalline and, although there was an increase in its crystallite size after the 1523 K anneal, no microcracking was observed.

The as-produced SiC coated particles were analyzed by x-ray diffraction to determine the phases present and the SiC crystallite size. The data from these experiments are presented in Table B.1, (p. 151). The crystallite size versus coating temperature for specimens deposited at the four diluent gas compositions are presented in Fig. 4.21(a). All specimens produced at 1073 K or below, irrespective of hydrogen content in the diluent gas, were amorphous. The data indicate the amorphous to crystalline transformation occurs between 1073 and 1180 K. All specimens synthesized at 1180 K were crystalline. The crystallite size decreased as the hydrogen content in the diluent gas increased [Fig. 4.21(b)]. The SiC crystallite size for coatings synthesized at 1180 K in argon was ≈ 9.5 nm versus ≈ 3 nm for those produced in an hydrogen diluent atmosphere. In general these results are in agreement with transmission electron microscopy results. The x-ray diffraction peaks are rather broad for these materials. The major phase in the crystalline coatings is β -SiC but α -SiC is also present.

The coated particles were annealed to evaluate the SiC amorphous-to-crystalline transformation and crystal growth versus temperature. These results are also presented in Appendix B. Some of the x-ray diffraction data for the coating deposited at 1180 K in an argon diluent are shown in Fig. 4.22. The peaks can be attributed to SiC and Al_2O_3 . The Al_2O_3 peaks result from x-rays penetrating the coating and diffracting from the alpha alumina substrate. The peak near 53.5

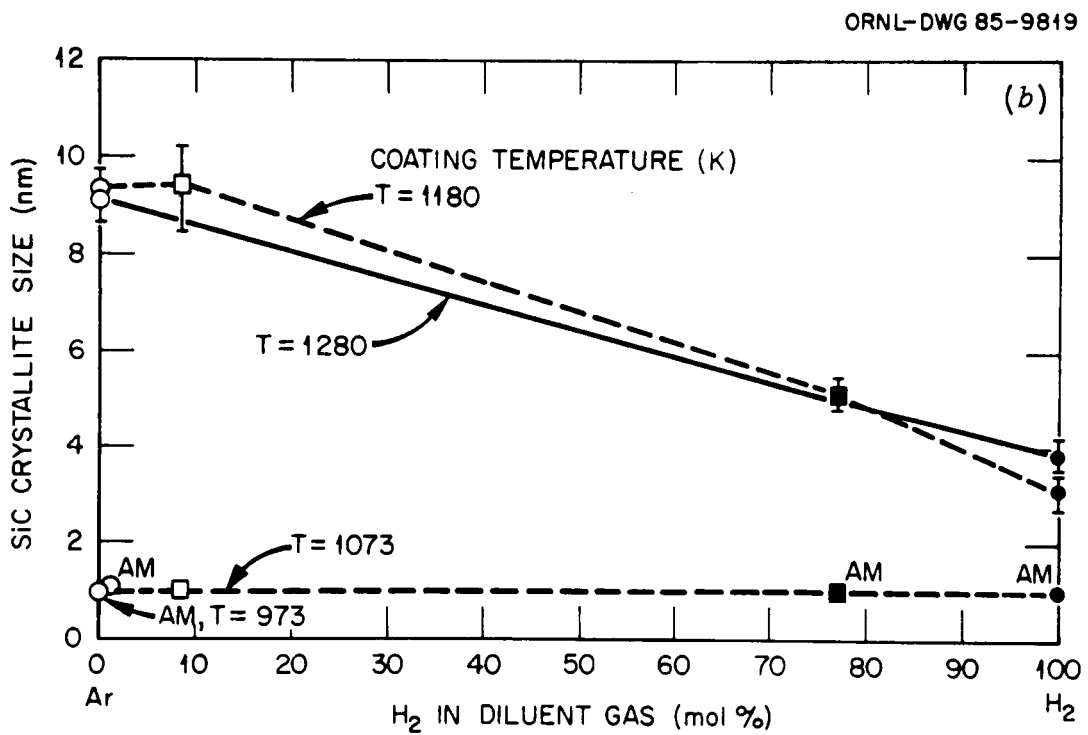
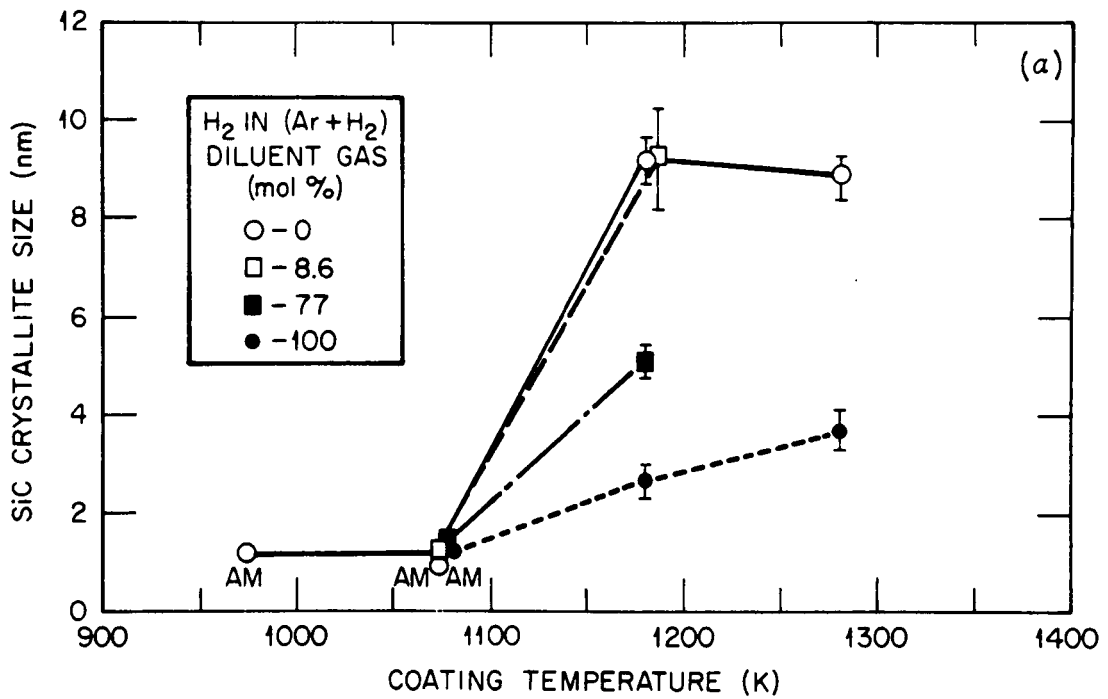


Fig. 4.21. Crystallite size of as-produced SiC coatings versus (a) coating temperature, and (b) H₂ content in the diluent gas.

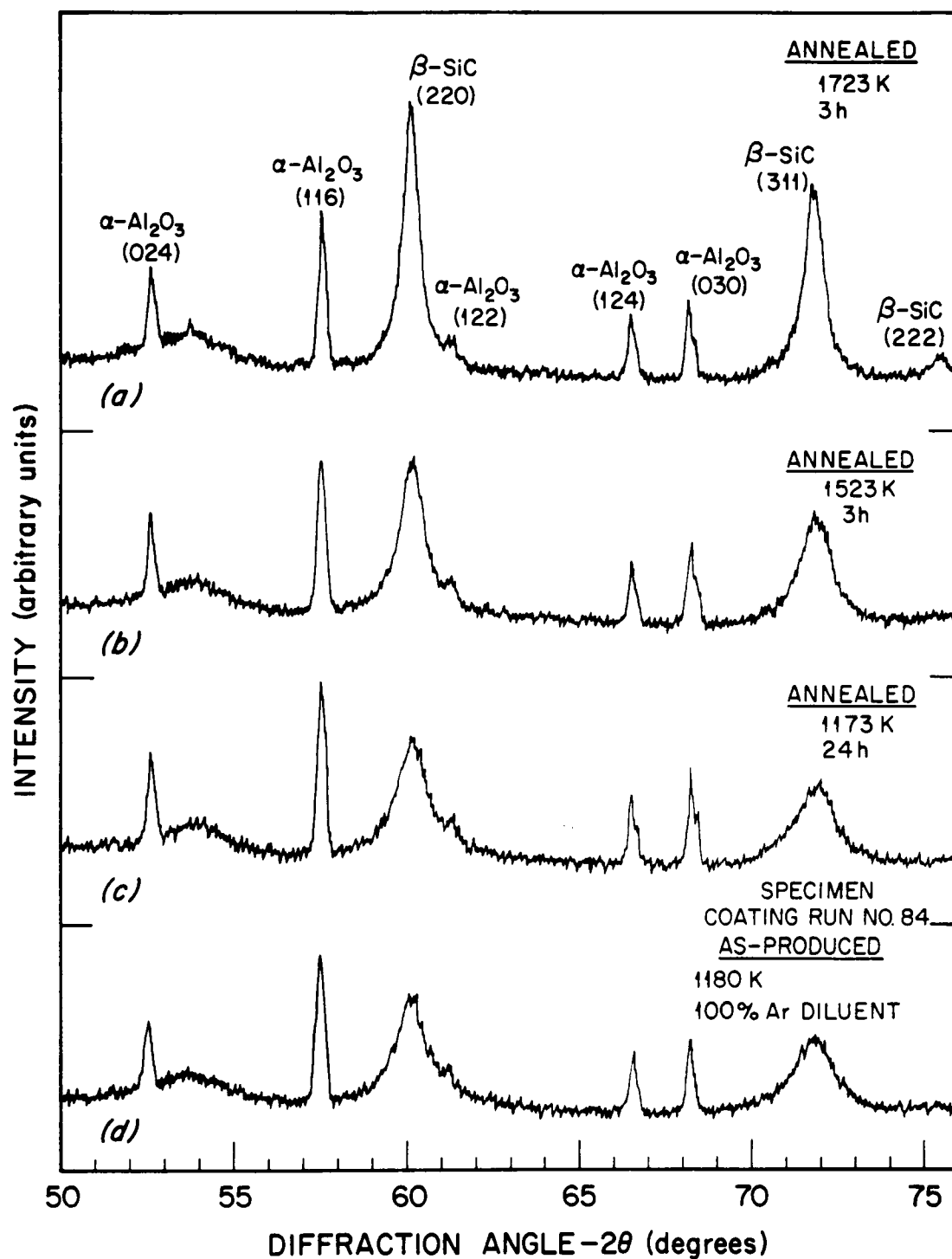


Fig. 4.22. X-ray diffraction spectra for SiC coating deposited at a temperature of 1180 K in 100% Ar diluent (a) annealed 1723 K, 3 h, (b) annealed 1523 K, 3 h, (c) annealed 1173 K, 24 h, and (d) as-produced 1180 K. Al_2O_3 peaks occur from substrate material.

degrees 2θ results from the mylar film used to cover the particles. No other crystalline phases are observed. The average crystallite size for the as-produced coating is ≈ 9 nm. The crystallite size for the specimen annealed to 1173 K for 24 h was not statistically different from the as-produced results. The crystallite size for the specimen annealed to 1523 K for 3 h did increase to ≈ 11 nm and the crystallite size for the specimen annealed to 1723 K for 3 h was ≈ 18 nm.

Results for the SiC coating deposited at the same temperature, 1180 K, but in an hydrogen diluent gas are presented in Fig. 4.23. The major peaks present in the spectra are SiC and Al_2O_3 . Crystalline silicon is observed in the specimens annealed at 1523 and 1723 K. This is a significant result and a major difference between coatings deposited in argon versus those prepared in hydrogen. This coating may contain excess silicon. The crystallite size of the as-produced specimen was ≈ 3 nm and that of the specimen annealed to 1173 K for 24 h is ≈ 4 nm. Significant growth occurred in specimens annealed to higher temperatures. The crystallite sizes for specimens annealed for 3 h at 1523 and 1723 K were 10 and 22 nm respectively.

Silicon was detected in all the annealed specimens which were originally synthesized in diluent atmospheres rich in hydrogen (80 and 100 mol % H_2) indicating that these coatings contain excess silicon. It should also be noted that the crystallite size of nearly all specimens is approximately the same after an anneal to 1523 K for 3 h. However, the SiC crystallite size of the coatings deposited in hydrogen diluent and annealed to 1723 K for 3 h is, in nearly all cases, larger than those produced in argon. This may be due to the

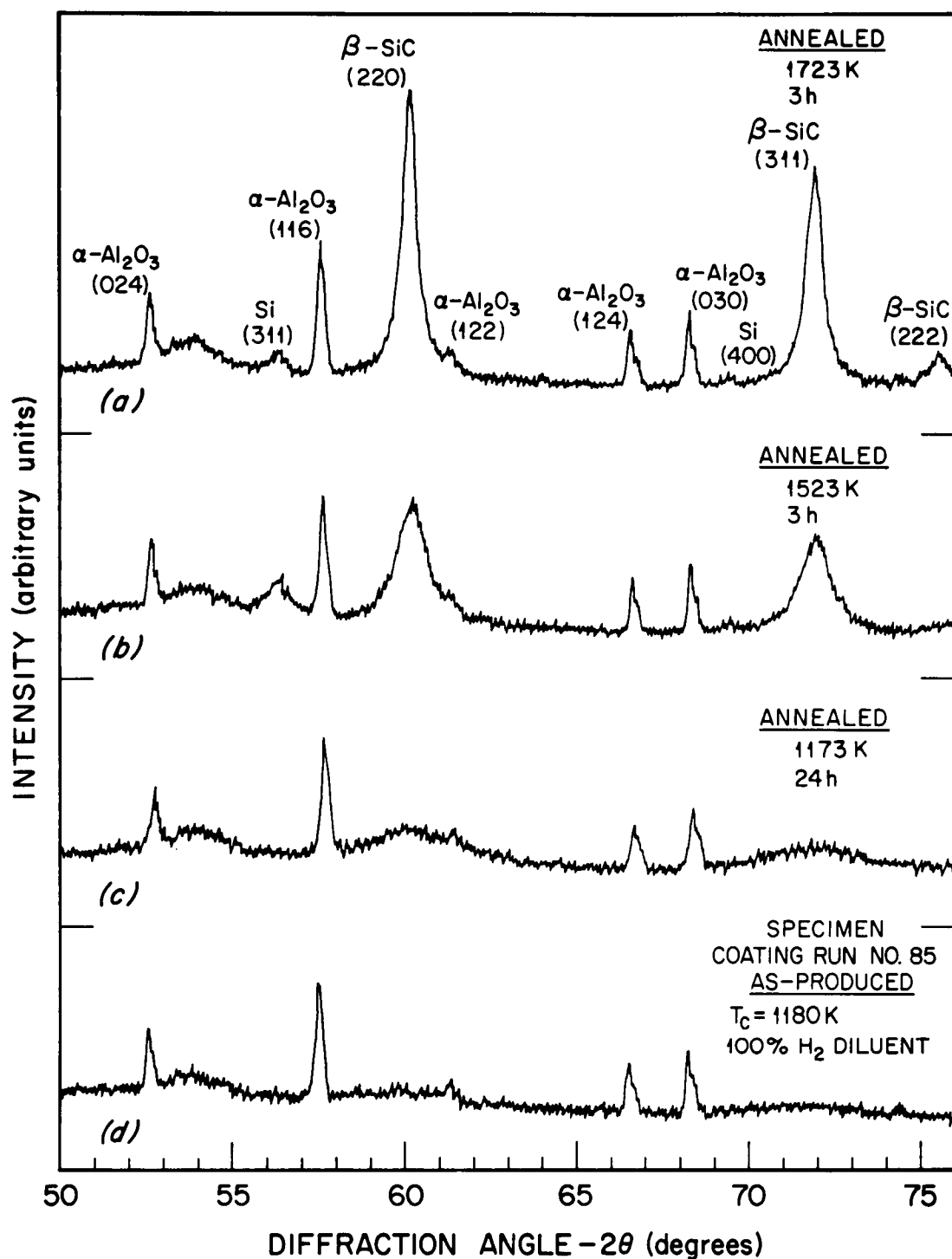


Fig. 4.23. X-ray diffraction spectra for SiC coating deposited at a temperature of 1180 K in H_2 diluent (a) annealed 1723 K, 3 h, (b) annealed 1523 K, 3 h, (c) annealed 1173 K, 24 h, and (d) as-produced 1180 K. Excess Si is present in coating. Al_2O_3 peaks occur from substrate material.

difference in composition (silicon content) of the coatings. Liquid silicon may be present at annealing temperatures greater than ≈ 1673 K. The silicon liquid may aid in densification and crystal growth.

Effect of C_2H_2 Addition

A series of coating experiments was performed to evaluate the effect of a carbon containing gaseous additive on the decomposition of CH_3SiH_3 . The results of the theoretical thermodynamic analysis indicate that the addition of C_2H_2 can influence the phases present in the coatings. The phases or their relative concentration in a two phase coating may thus be controlled by a judicious choice of coating temperature, and additive/reactant, reactant/diluent mole ratios.

Two coating experiments were performed with a controlled amount of C_2H_2 added to the system (Run 353 and Run 349). The coating conditions for these two experiments matched those of two previous experiments (Run 84 and Run 88) except for the C_2H_2 addition. The coating conditions for these four coating experiments are listed in Table 4.6.

Both as-prepared and heat treated SiC-coated particles were analyzed by x-ray diffraction and Raman spectroscopy. Data presented in Fig. 4.24 are Raman spectroscopy results for Run 84 (100% argon diluent). Note the presence of a broad peak at $\approx 487\text{ cm}^{-1}$ which is normally attributed to amorphous silicon. The two SiC peaks at 796 and 972 cm^{-1} are also very broad indicating the presence of one or more polytypes or of a very small crystallite size. There are also weak broad peaks near 1350 and 1600 cm^{-1} indicative of carbon. The Raman spectrum for the specimen annealed at 1523 K for 3 h shows narrow

Table 4.6. Coating conditions for experiments evaluating the effect of C_2H_2 on the thermal decomposition of CH_3SiH_3

Run number ^a	Temperature (K)	Time (min)	Particle charge (g)	Flow rate			
						Diluent gas	
						Ar	H ₂
				C ₂ H ₂	CH ₃ SiH ₃	(cm ³ /min)	
84	1180	180	18.96 ^b	0	21	4750	0
353 ^c	1180	180	20.0	1.1	26	4750	0
88	1180	180	19.45 ^b	0	27	1700	5700
349 ^c	1180	180	20.0	1.1	27	1700	5700

^aFluidized bed experiments performed with 2.54 cm diameter cone.

^bAn additional 0.5 g of uncoated alumina microspheres was also present during the run to evaluate SiC deposits without interference from PyC substrate coating.

^cProduct gas specimen taken and exhaust powder also collected.

SiC peaks at (796 and 972 cm^{-1}) which is an indication of improved SiC crystallinity. A broad background is also present near the SiC peaks which may be related to the presence of an α -SiC component in the coating material. The corresponding data for the coating experiment with a C_2H_2 additive ($C_2H_2/CH_3SiH_3 = 4.2 \times 10^{-2}$, Run 353) are shown in Fig. 4.25. Comparison of Fig. 4.24 with Fig. 4.25 shows that excess carbon is deposited as C_2H_2 is added to the $CH_3SiH_3 - Ar$ system. These results are in agreement with the thermodynamic equilibrium calculations. Note also that the spectrum for the as-synthesized coating is similar to that of the specimen annealed at 1523 K. The peaks representative of SiC at 796 and 972 cm^{-1} are very broad although still present. The broad peak near ≈ 487 cm^{-1} , representative of amorphous silicon, is still present.

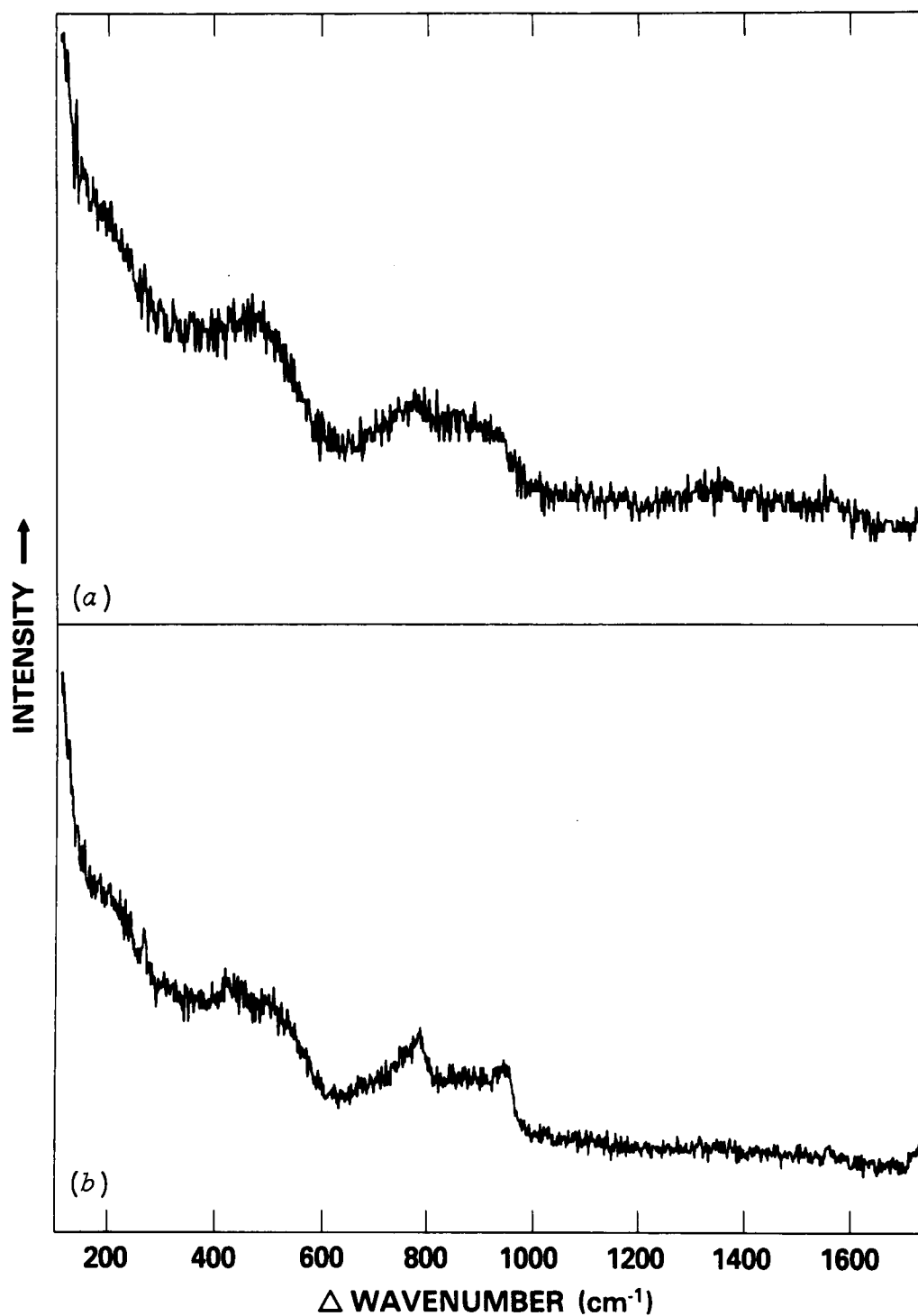


Fig. 4.24. Raman spectra for SiC coating (Run 84), $T = 1180$ K, diluent gas 100% Ar, $\text{CH}_3\text{SiH}_3/\text{diluent} = 4.4 \times 10^{-3}$ (a) as-produced, and (b) annealed 1523 K, 3 h.

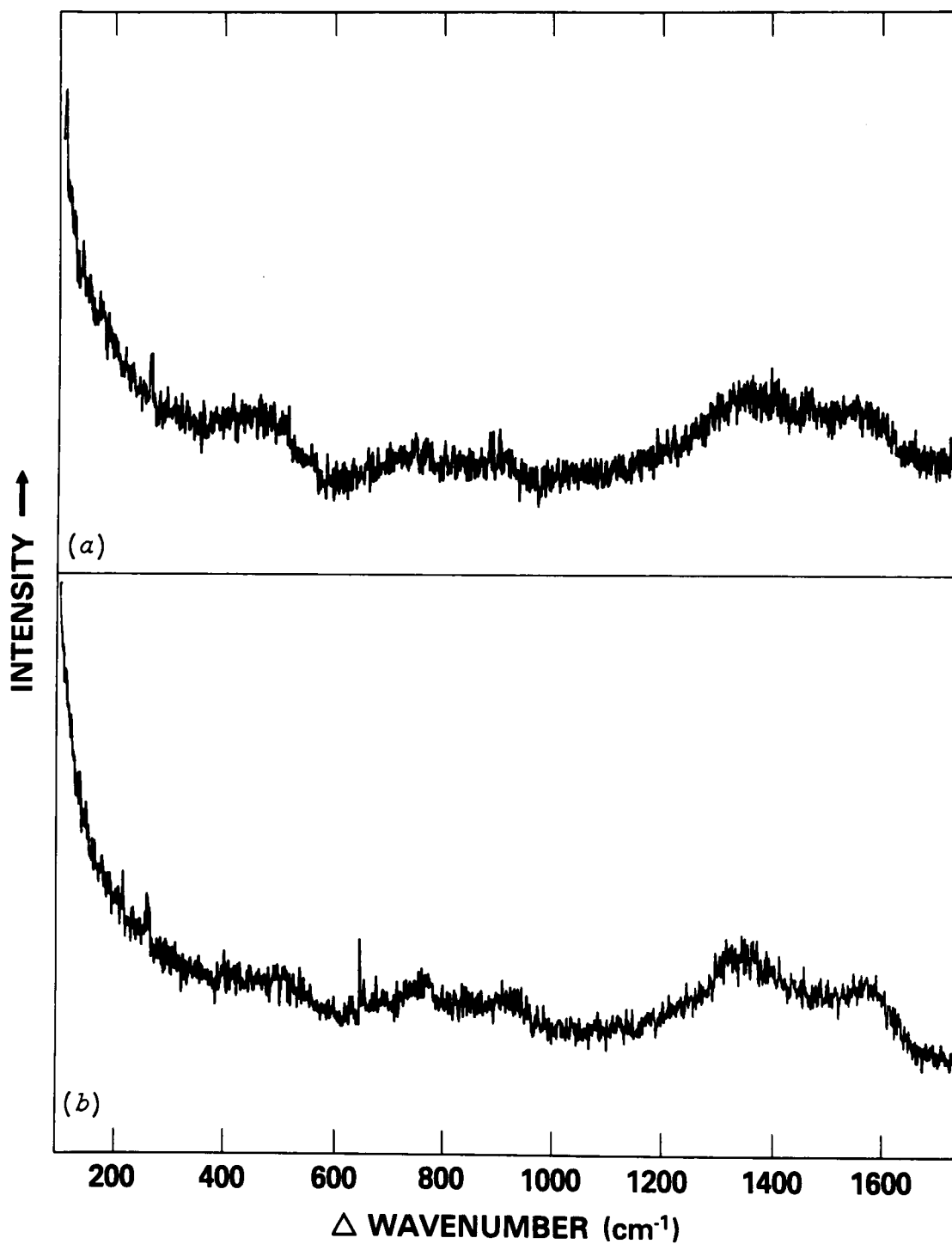


Fig. 4.25. Raman spectra for SiC coating (Run 353), $T = 1180$ K, diluent gas 100% Ar, $C_2H_2/CH_3SiH_3 = 4.2 \times 10^{-2}$, $CH_3SiH_3/\text{diluent} = 5.5 \times 10^{-3}$ (a) as-produced, and (b) annealed 1523 K, 3 h.

The experiments which were performed with a mixed ($\text{Ar} + \text{H}_2$) diluent gas will be considered next. The hydrogen content in the diluent gas for these experiments was 77 mol %. The Raman spectra for coating Run 88 are shown in Fig. 4.26. The spectrum for the as-produced coating possesses a broad peak near 500 cm^{-1} , and very broad peaks near 796 and 972 cm^{-1} . The spectrum for the specimen annealed at 1523 K (Run 88) shows a well defined peak at 506 cm^{-1} which is indicative of crystalline silicon. The peaks representative of SiC are quite broad although much more pronounced than for the as-produced specimen. The peaks representative of carbon are not present in the spectra. The presence of crystalline silicon was also confirmed by x-ray diffraction results. The spectra for the coating made with the C_2H_2 additive (Run 349) are shown in Fig. 4.27. The as-produced spectrum again possesses broad peaks near 500 , 796 , and 976 cm^{-1} . There is an indication in the as-produced spectrum of a peak representative of crystalline silicon, however its intensity is quite low and may be due to fluctuations in the noise level. The spectrum for the specimen annealed at 1523 K shows slightly sharper SiC peaks at 796 and 972 cm^{-1} . The broad peak near 500 cm^{-1} is still present and there is an indication that crystalline Si may be present (502 cm^{-1}) although the silicon content appears to be only $\approx 5\%$ of the 1523 K annealed coating Run 88. Comparison of Fig. 4.26 and Fig. 4.27 shows that as C_2H_2 is added to the CH_3SiH_3 system, with a hydrogen content in the diluent gas of 77 mol %, the silicon content decreases and approaches that of stoichiometric SiC . These results are in agreement

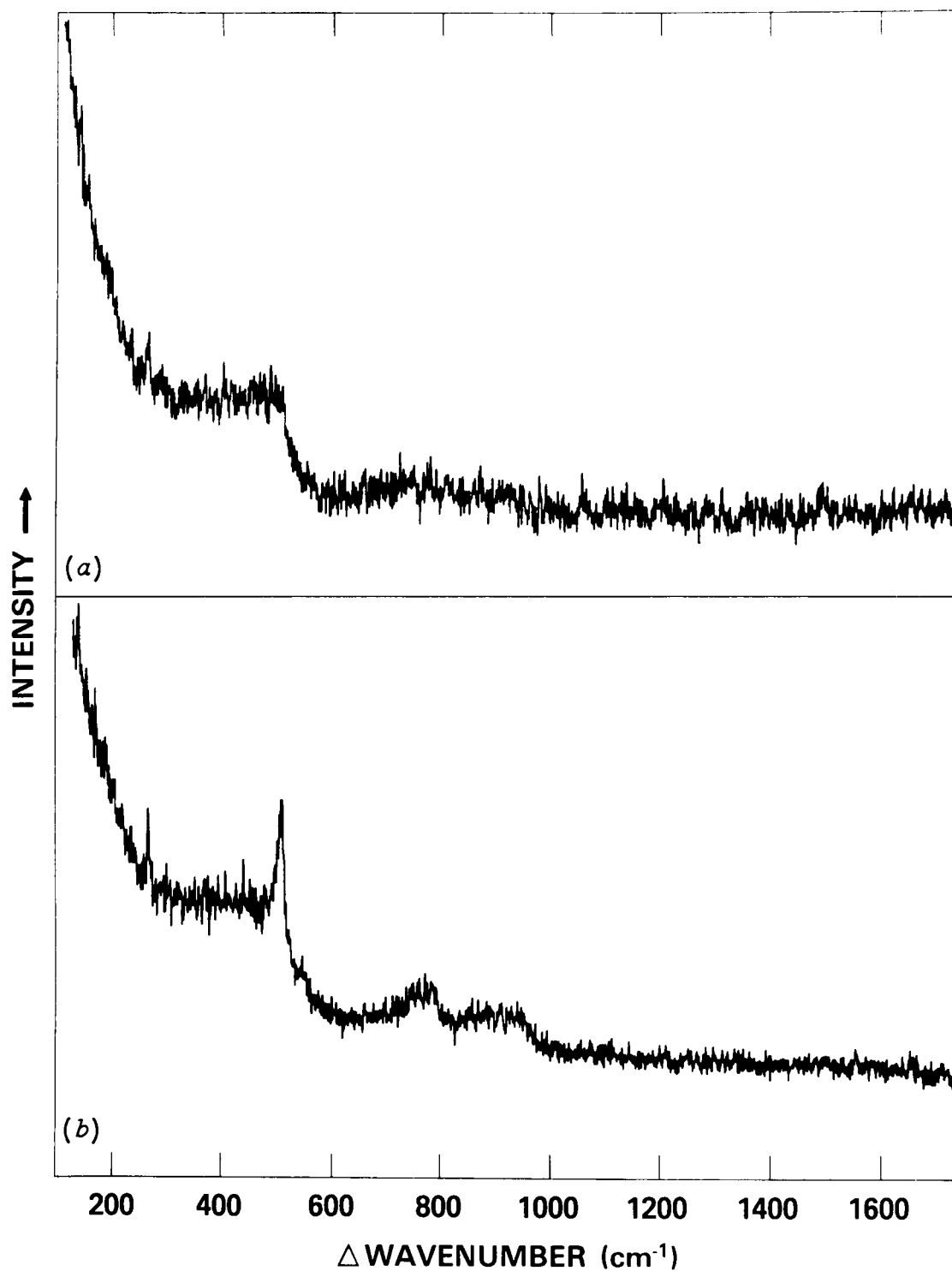


Fig. 4.26. Raman spectra for SiC coating (Run 88), $T = 1180$ K, H_2 content in (Ar - H_2) diluent gas = 77 mol %, CH_3SiH_3 /diluent = 3.6×10^{-3} (a) as-produced, and (b) annealed 1523 K, 3 h.

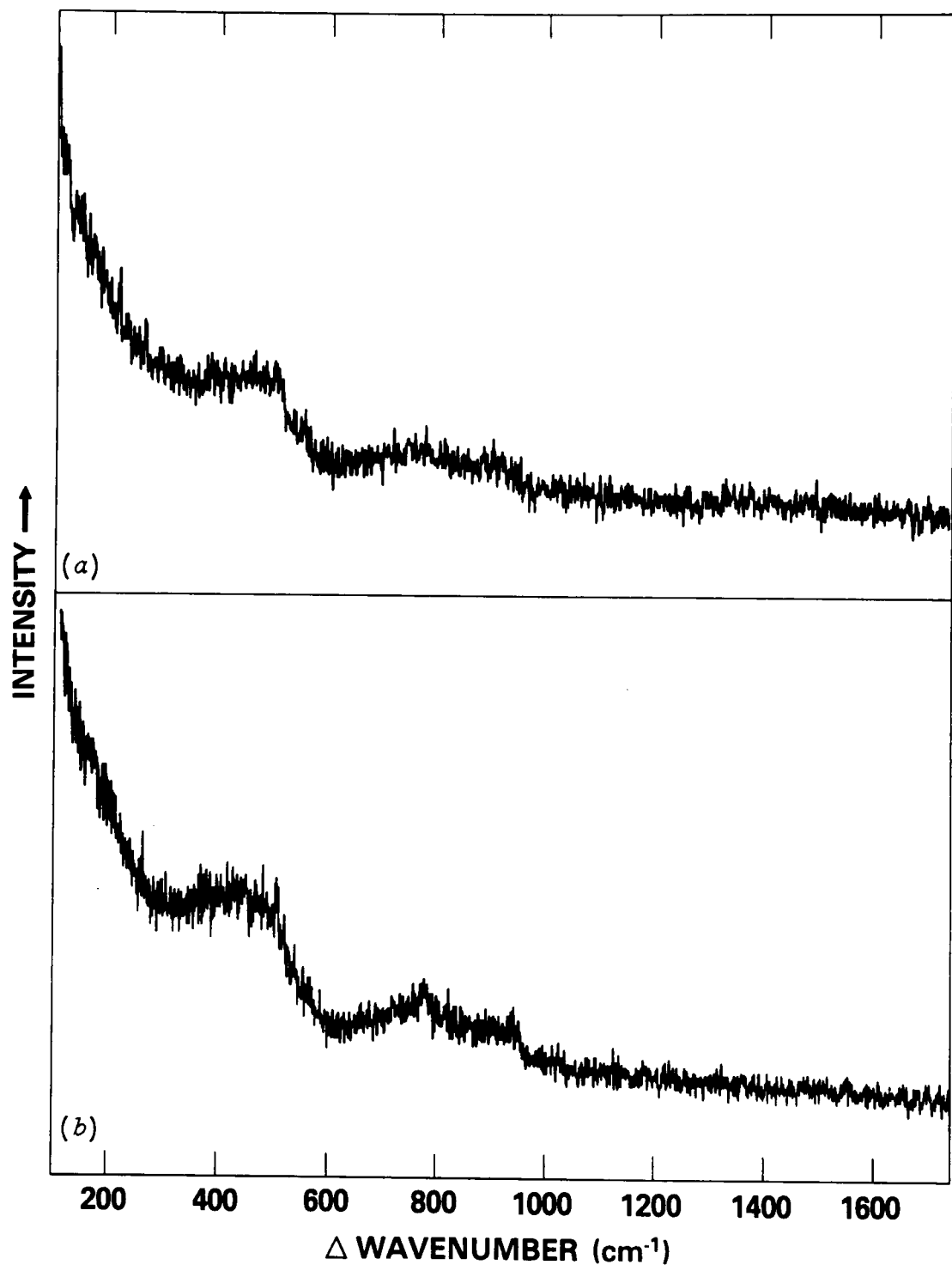


Fig. 4.27. Raman spectra for SiC coating (Run 349), $T = 1180$ K, H_2 content in (Ar - H_2) diluent gas = 77 mol %, $C_2H_2/CH_3SiH_3 = 4 \times 10^{-2}$, $CH_3SiH_3/diluent = 3.6 \times 10^{-3}$ (a) as-produced, and (b) annealed 1523 K, 3 h.

with x-ray diffraction data and the thermodynamic equilibrium calculations.

These data show that the phases and their relative content may be controlled by varying coating conditions such as temperature, reactant and diluent gas flow rates, hydrogen content in the diluent, and additions of a carbon bearing species.

The elemental composition of SiC coatings was determined to complete the evaluation of the relationships between the thermodynamic and experimental results. Raman spectroscopy and x-ray diffraction results are useful in estimating the nature of the bonding, phases present, and crystallinity of the SiC coatings. However, the elemental silicon to carbon ratio is an important system parameter which must also be determined. Qualitative and quantitative silicon content measurements of the four coatings just described were performed with an electron microprobe. The carbon contamination which can occur during an analysis was eliminated by cooling the anti-contamination device to liquid nitrogen temperature.

The specimens analyzed included those listed in Table 4.6, (p. 100) and a single crystal SiC. No elements with $Z > 11$, other than silicon, were detected with energy dispersive spectroscopy. The quantitative analyses were performed with wavelength dispersive spectrometers and the results are presented in Table 4.7. Measurements were quantified with respect to both (1) silicon and carbon (graphite), and (2) single crystal SiC standards. Although the values of the compositions determined by the two methods differ slightly, the general trend and relationships between specimens are the same. Consider first

Table 4.7. Quantitative electron microprobe analyses of SiC coatings and single crystal SiC

Coating run number	H ₂ content in diluent gas (mol %)	C ₂ H ₂ /CH ₃ SiH ₃	Si content ^a (wt %)	Si content ^b (wt %)
84	0.0 (100% Ar)	0.0	67.6 [0.3] 66.7 [0.8] 67.0 [0.8]	69.5 [0.3]
353	0.0 (100% Ar)	4.2 × 10 ⁻²	62.9 [0.8] 62.6 [1.1]	64.8 [0.9]
88	77	0.0	70.7 [0.6] 70.8 [0.2]	71.9 [0.3]
349	77	4.0 × 10 ⁻²	68.4 [0.3] 67.7 [0.9]	70.1 [0.3]
Single crystal SiC			67.7 [0.4] 67.8 [0.4]	69.6 [0.6] 69.2 [0.2]
Theoretical Si content in SiC			70.0	70.0

^aReference standards — elemental Si, and C (graphite).

^bReference standard — single crystal SiC.

Note: Si content is the average of at least 5 measurements; each measurement taken at a different location on the specimen; data in brackets are standard deviations.

the results for the coatings deposited in 100% argon diluent gas (Run 84 and 353). The silicon content results for the experiment with no C₂H₂ additive (Run 84) is essentially the same as that of the single crystal SiC. However, when C₂H₂ is added to the system (Run 353) the silicon concentration in the coating decreases. This implies that excess carbon is being deposited and is in agreement with Raman and x-ray diffraction results. Consider next the results for the coatings deposited in 77% hydrogen diluent (Runs 88 and 349). The

silicon content of the coating without C_2H_2 addition is higher than that of the single crystal SiC by ≈ 2 or 3%. This result shows that the coating contains excess silicon. The silicon content of the experiment (Run 349) with C_2H_2 added to the hydrogen diluent is nearly equal to that of single crystal SiC. These results are consistent with the Raman and x-ray diffraction data. These results also agree with thermodynamic equilibrium calculations presented earlier in this section.

Coating of Nuclear Waste Ceramics

Zeolite Substrates

The substrate material evaluated for the solidification of cesium is zeolite which is a sodium-alumina-silicate oxide. The substrate used is zeolite IE-95, a synthetic chabazite ($Ca_2Al_2Si_4O_{12} \cdot 6 H_2O$), well known for its affinity toward cesium. The cesium is accepted by an ion-exchange mechanism. It is currently used to store large amounts of cesium in defense-related processes. After the zeolite was loaded with cesium to a level of ≈ 5 wt % it was heat treated to eliminate water of hydration and stabilize the structure.^{55,60} Thermogravimetric, differential thermal analysis, and mass spectrometric analyses were performed to determine the optimum heat treating schedule and thermal stability of the material. The microstructure of the zeolite at various stages of development was analyzed. Cs-loaded zeolite was annealed to 923 K in air for 4 h to stabilize the material prior to being coated with either pyrolytic carbon or silicon carbide.^{46,60,83} Aqueous leach testing of the

heat treated and pyrocarbon coated Cs-loaded zeolite was performed. Leach results of uncoated 923 K heat treated material were comparable to borosilicate glass, and the leach rates for the pyrocarbon coated specimens were below detection limits.

The thermal stability of Cs-loaded zeolite in both air as well as Ar — 4% H₂ was evaluated. The zeolite was tested in an Ar — 4% H₂ atmosphere since the substrate would later be coated in a carbon furnace with the composition of the gaseous product atmosphere approximating that of an Ar — 4% H₂ atmosphere. Thermal gravimetric and mass spectrometric data for IE-95 zeolite loaded with ~5 wt % Cs are shown in Fig. 4.28(a). Heat treating the zeolite in a thermogravimetric analyzer allows one to monitor the mass loss of the specimen as a function of temperature. The data shown in Fig. 4.28(a) compares the mass loss versus temperature behavior of the Cs-loaded zeolite in two different atmospheres, air and Ar — 4 % H₂. The data have similar shapes up to ~1100 K indicating the materials undergo similar reactions in the 300 to 1100 K range. The largest fractional mass loss occurs from 300 to ~550 K and a second mass loss regime occurs at ~920 K. However above ~1000 K the mass loss behavior in the two different atmospheres is slightly different. In the 1000 to 1300 K temperature range the material heated in air undergoes almost no mass loss indicating the material has stabilized. The data from the experiment performed in Ar — 4% H₂ show a slight but continual mass loss indicating a reduction of the specimen at these experimental conditions. The mass spectrometric data presented in Fig. 4.28(b) were obtained to determine the volatile species evolved during

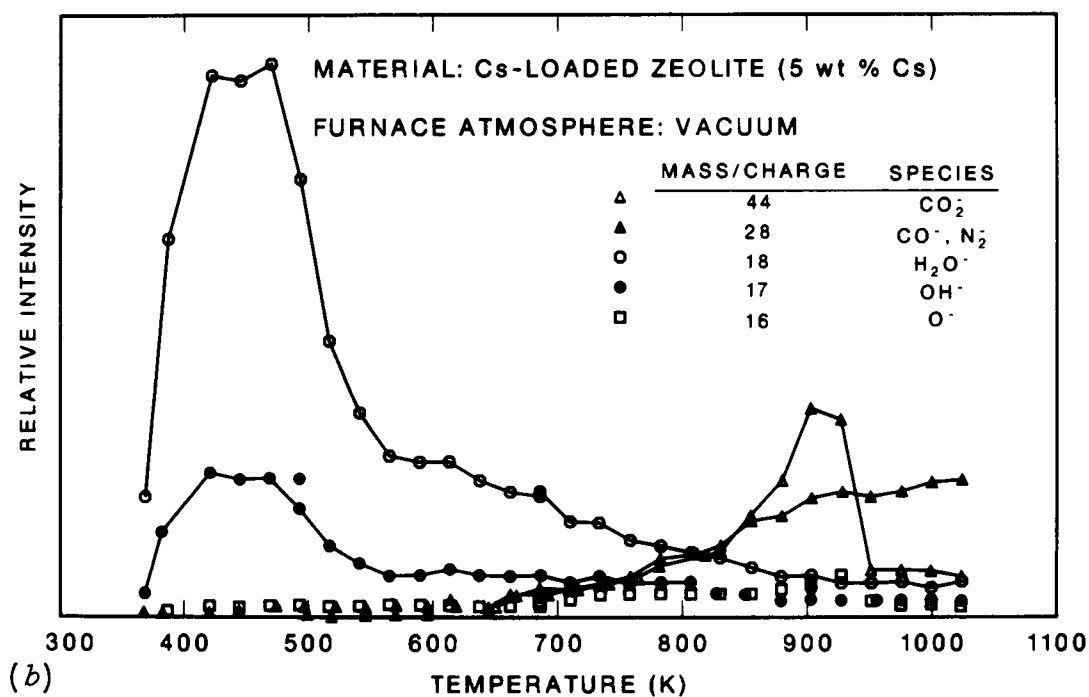
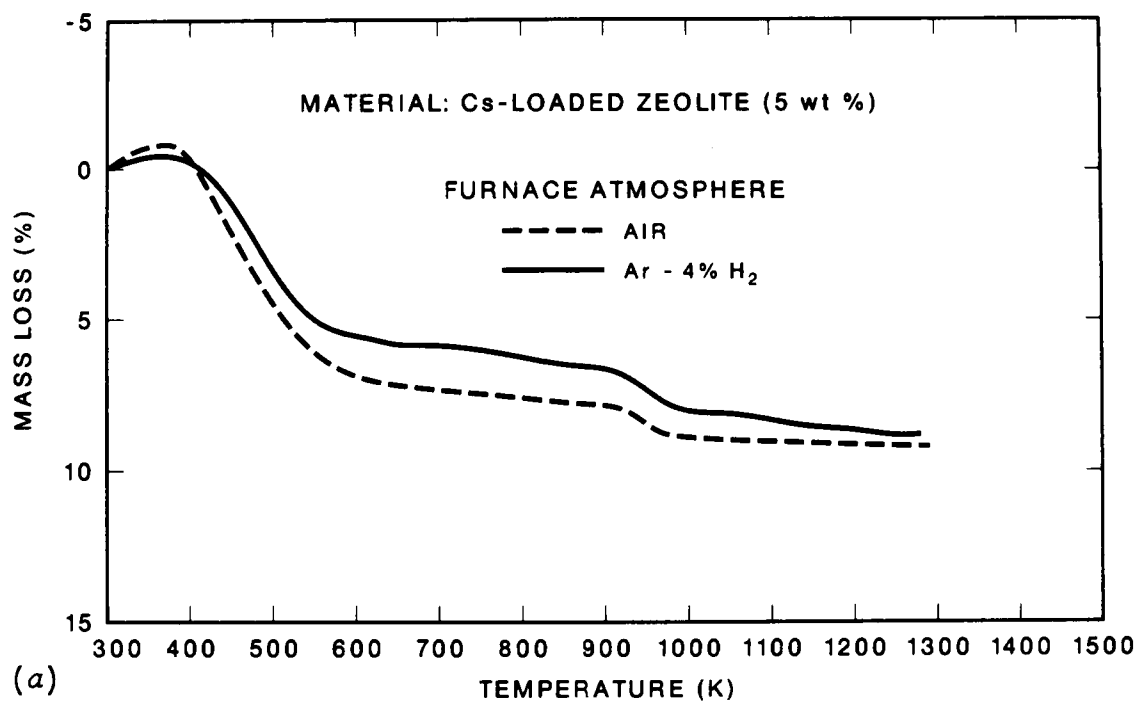


Fig. 4.28. Thermal analyses of Cs-loaded zeolite (≈ 5 wt % Cs)
 (a) thermal gravimetric data to 1300 K in air and Ar - 4% H₂, and
 (b) mass spectrometric data to 1023 K.

calcination of the Cs-loaded zeolite. The species identified in the 300 to 500 K temperature range were H_2O and OH . Thus the first mass-loss regime shown in Fig. 4.28(a) is due to the removal of water from the specimen. The species evolved in the 850 to 950 K temperature range [see Fig. 4.28(b)] were identified as CO_2 , O , and either CO or N_2 . The second mass-loss regime seems to be correlated to the release of these species, but the temperature where the CO_2 is evolved is ≈ 100 K lower than the corresponding mass-loss data. This temperature shift may result from the mass spectrometric analyses being performed in vacuum. The data indicate that the Cs-loaded zeolite would need to be heat treated to at least 900 K to remove the volatile constituent prior to being coated. Little or no change in surface characteristics of the zeolite was observed from analysis of optical micrographs of the Cs-loaded zeolite heat treated at 873 or 1073 K for 4 h in air. X-ray diffraction data showed that the material heat treated at 873 K still maintained the chabazite structure and the material heat treated at 1073 K was nearly amorphous with a second unidentified phase. Heat treating the zeolite at 1273 K in an Ar — 4% H_2 atmosphere resulted in partial melting of the granules.

Specimens of Cs-loaded zeolite were thus heat treated at 900 K in air for 4 h prior to being coated. The heat treatment resulted in a stabilized material suitable for coating with either pyrocarbon or silicon carbide. Pyrocarbon coatings were deposited at 1273 K with C_2H_2 and argon.⁶⁰ The pyrocarbon was found to be compatible with the zeolite in terms of thermal expansion, and therefore a low density buffer coating was not required. Heat-treated Cs-loaded zeolite was

also coated with silicon carbide deposited at 1180 K (see Fig. 4.29) from the CVD of CH_3SiH_3 in an argon diluent gas. A low density SiC buffer was required prior to depositing the high density SiC. The SiC coating conditions were similar to those of Run 91 for the low density buffer SiC coating and Run 84 for the high density SiC coating.

Aqueous leach test results, performed according to the MCC-1 procedure, of the heat treated and pyrocarbon coated Cs-loaded zeolite,⁸³ are presented in Table 4.8. The values obtained for the uncoated heat-treated zeolite are comparable to other alternative waste forms. The data for the coated zeolite, however, is at least three orders of magnitude lower than other nuclear waste forms.

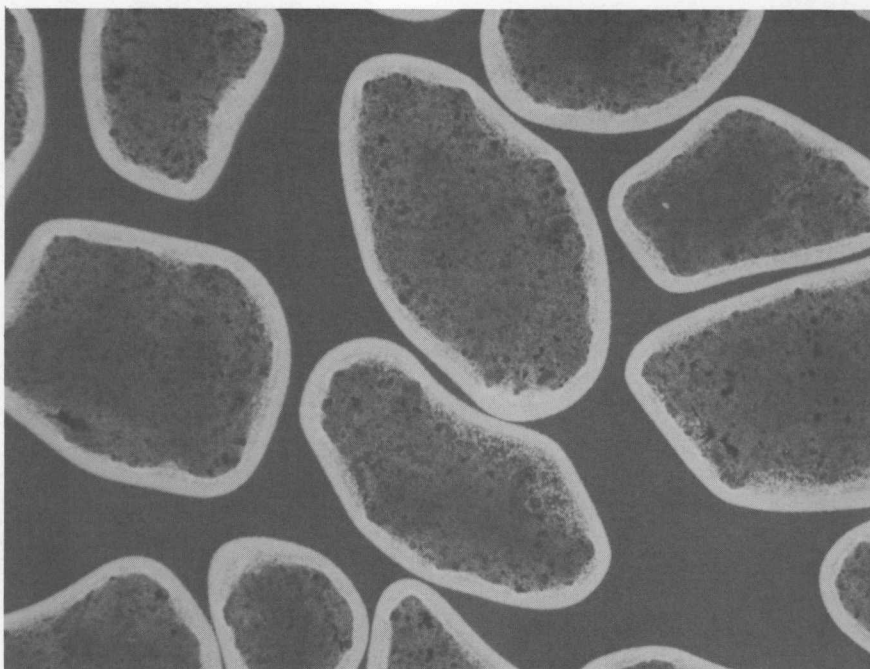
Table 4.8. Leach rate results for uncoated and pyrocarbon coated Cs-loaded zeolite

Leach tests of Cs-loaded zeolite ^a			
Element	Leach rate [$\text{g}/(\text{m}^2 \cdot \text{d})$]		
	Detection limit (for 28 d test)	Uncoated zeolite	Pyrocarbon coated zeolite
Cs	6×10^{-6}	1×10^{-2}	b
Al	6×10^{-6}	2×10^{-2}	b
Si	6×10^{-5}	3×10^{-2}	b

^aMCC-1 leach test; 363 K, deionized water, 28 day test.

^bAt or below detection limit.

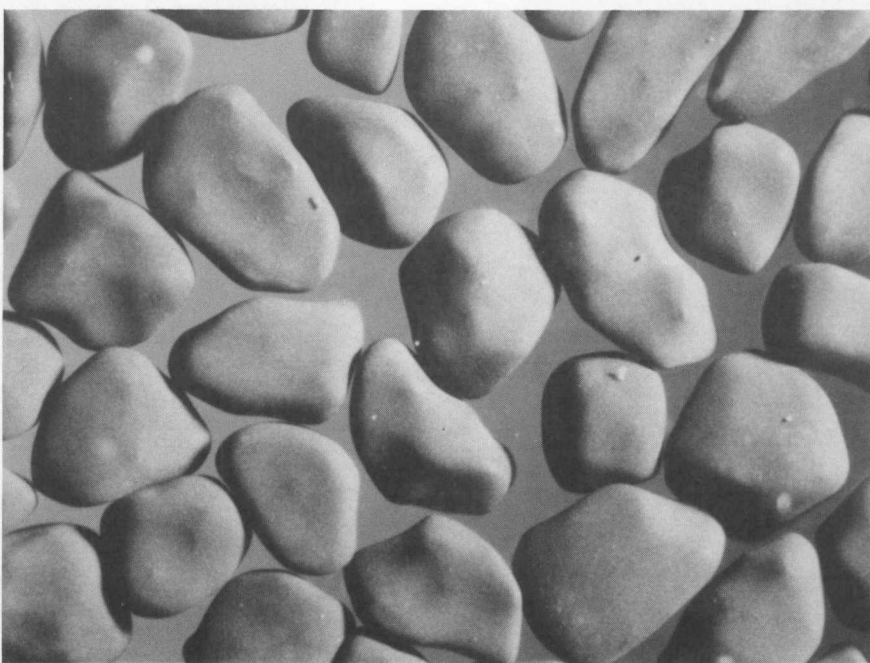
Y-201914



(a)

400 μm

Y-201837



(b)

400 μm

Fig. 4.29. Optical micrographs of silicon carbide coated zeolite (a) polished section and (b) macrograph of surface.

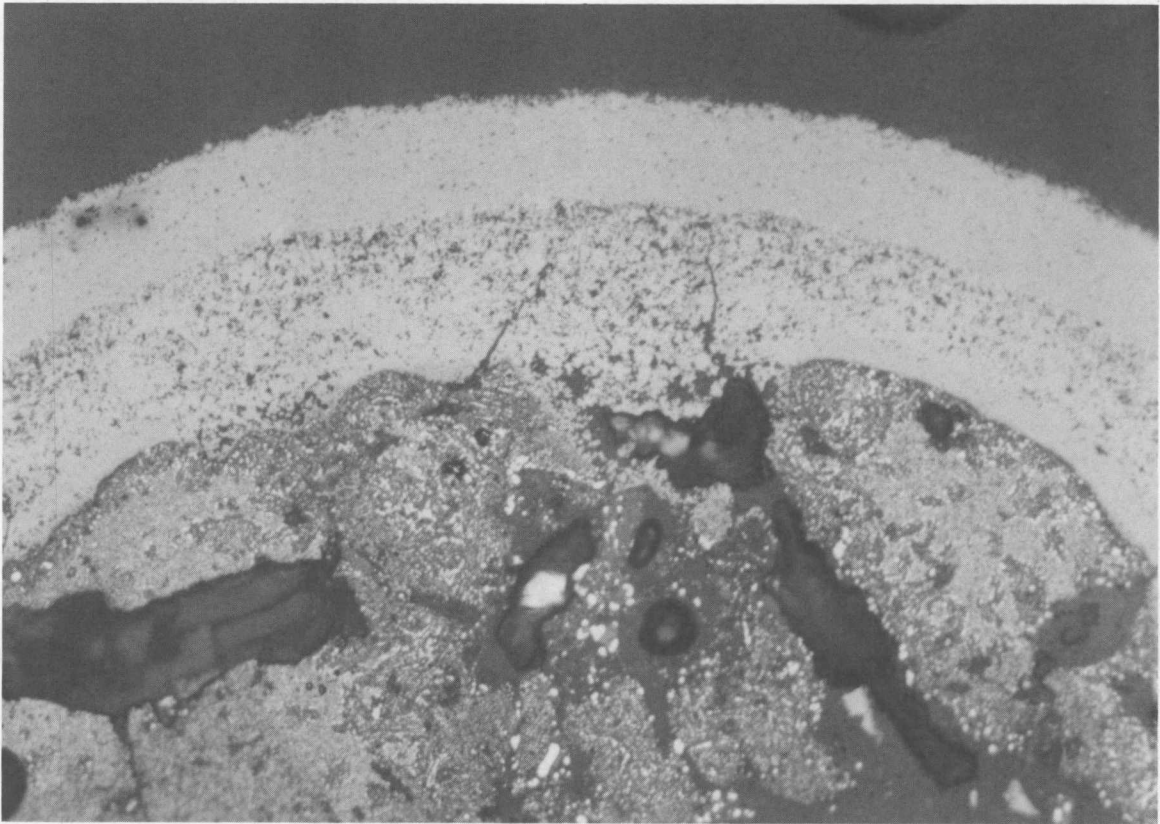
Substrates of High Waste Loading

Coating studies of gel-derived substrate microspheres with high waste loading (>70 wt %) were also conducted. These types of substrates may be advantageous since a smaller volume of material would need be stored in repositories. In addition, these substrates may be simpler to form from the gelation process than substrates of lower waste loading.⁵⁵ However the microspheres may or may not have the required thermal and physical stability desired in a coating process. Reactions can also occur between the coating and the substrate particle.⁶⁰ The coating of two types of substrate particles will be described. The composition of the 70/30 and 90/10 substrates are presented in Table A.1, (p. 149) and both deal with the solidification of simulated high-level-defense nuclear waste from the Savannah River Plant (SRP).

In the first case, the coating of 70/30 (70 wt % Savannah River Plant waste, 30 wt % additives) substrate microspheres of $\approx 800 \mu$ diameter with SiC and then overcoated with pyrocarbon will be described. As was shown in Fig. 2.3, p. 16, substrates of high waste loading were not compatible with the pyrocarbon coating process.⁶⁰ Possible explanations for the reactions are (1) the substrate may not be sufficiently stable at 1280 K, (2) the high hydrogen content in the product gas during C_2H_2 decomposition may reduce some of the phases, or (3) carbon may also reduce various phases in the substrate. However, the chemical vapor deposition of SiC from CH_3SiH_3 can be performed at 1180 K in argon. Thus the particles were first coated with a low density buffer coating, similar to coating Run 91, to

minimize stresses due to thermal expansion differences between the coating and the substrate. A dense outer SiC coating, similar to coating Run 84, was then applied over the SiC buffer layer. Some of these particles were tested in a thermogravimetric analyzer in air to a temperature of 1373 K to evaluate their thermal stability. The substrate particles did not react with the SiC buffer layer as shown in Fig. 4.30. This shows that the substrate particles are compatible with the SiC coatings and the CVD process. Substrate particles coated with SiC at 1180 K were later successfully overcoated with pyrocarbon (C_2H_2 , Ar, 1280 K) and leach tested.

Gel-derived 90/10 (90 wt % Savannah River Plant waste, 10 wt % ZrO_2) microspheres were prepared. The particles were sintered in an Ar — 4% H_2 atmosphere at 1273 K for 1 h to a density of 5.1 g/cm³. The SiC coating conditions were again similar to Run 91 for the low density buffer coating and to Run 84 for the high density SiC coating. However, some changes were made in the coating process. These types of particles were coated using CH_3SiH_3 reactant and nitrogen diluent gas. The flow rates were controlled so that the hydrogen concentration in the product gas was always less than the 4% H_2 limit. A low density buffer layer was deposited at 1280 K and the dense outer layer at 1180 K. Shown in Fig. 4.31 are micrographs of 90/10 microspheres (a) sintered, and (b), (c), (d) SiC coated. The SiC coated 90/10 substrate particles were later overcoated with pyrocarbon (propylene as the reactant gas) at a deposition temperature of 1480 K (see Fig. 4.32). X-ray diffraction analyses of SiC coated 90/10

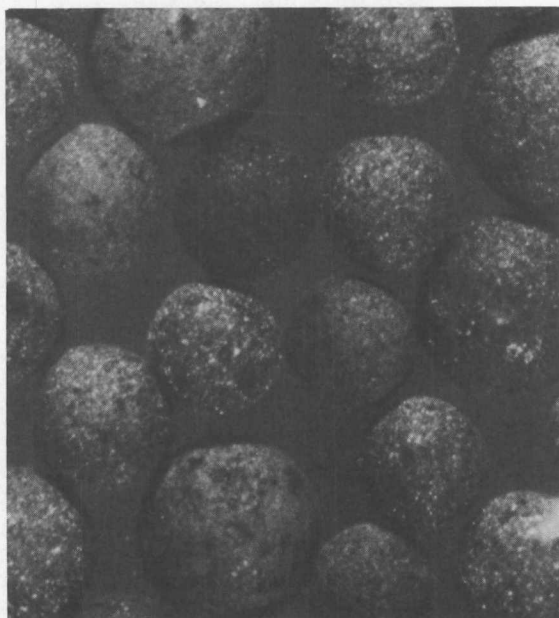


50 μm

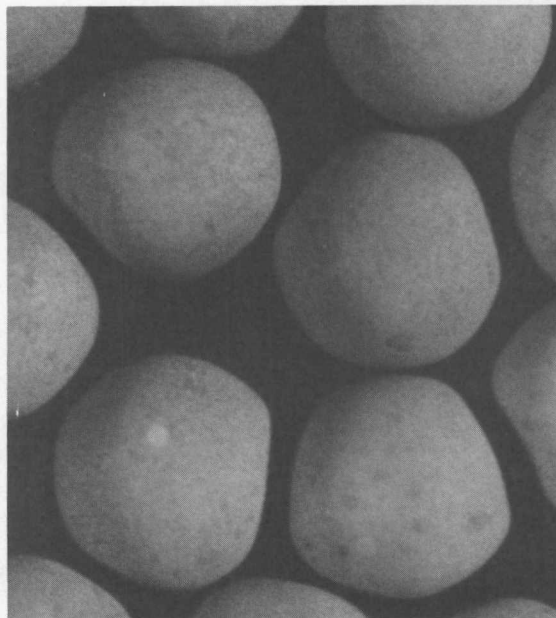
Fig. 4.30. Gel-derived substrate particle of 70/30 (70 wt % simulated Savannah River Plant waste, 30 wt % additives) coated with low density buffer layer of SiC and dense outer layer of SiC; the polished section shown is of a coated particle after being heat-treated in Ar — 4% H₂ to 1373 K to evaluate substrate-coating compatibility.

ORNL-DWG 81-10207

ORNL-DWG 81-10212

(a) 1000 μm

Y-201876

(b) 1000 μm

Y-201880

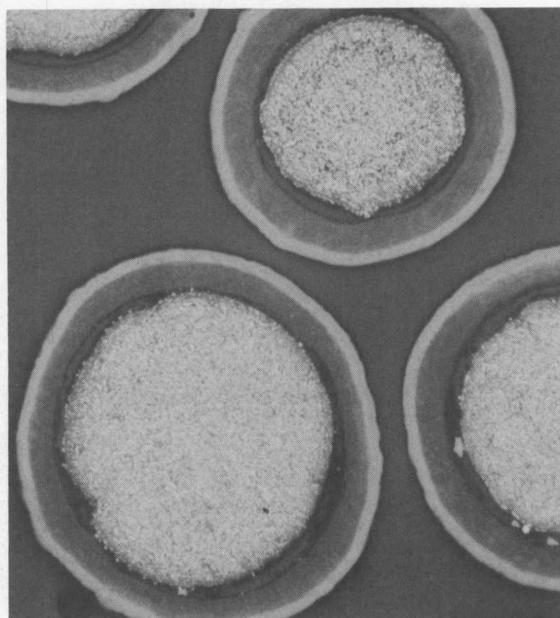
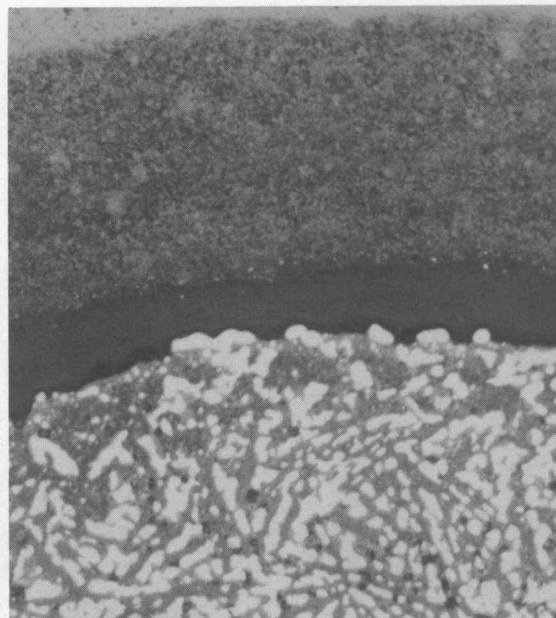
(c) 400 μm (d) 50 μm

Fig. 4.31. Micrographs of 90/10 (90 wt % simulated Savannah River Plant waste, 10 wt % ZrO_2) microspheres (a) sintered, (b), (c), and (d) SiC coated microspheres.

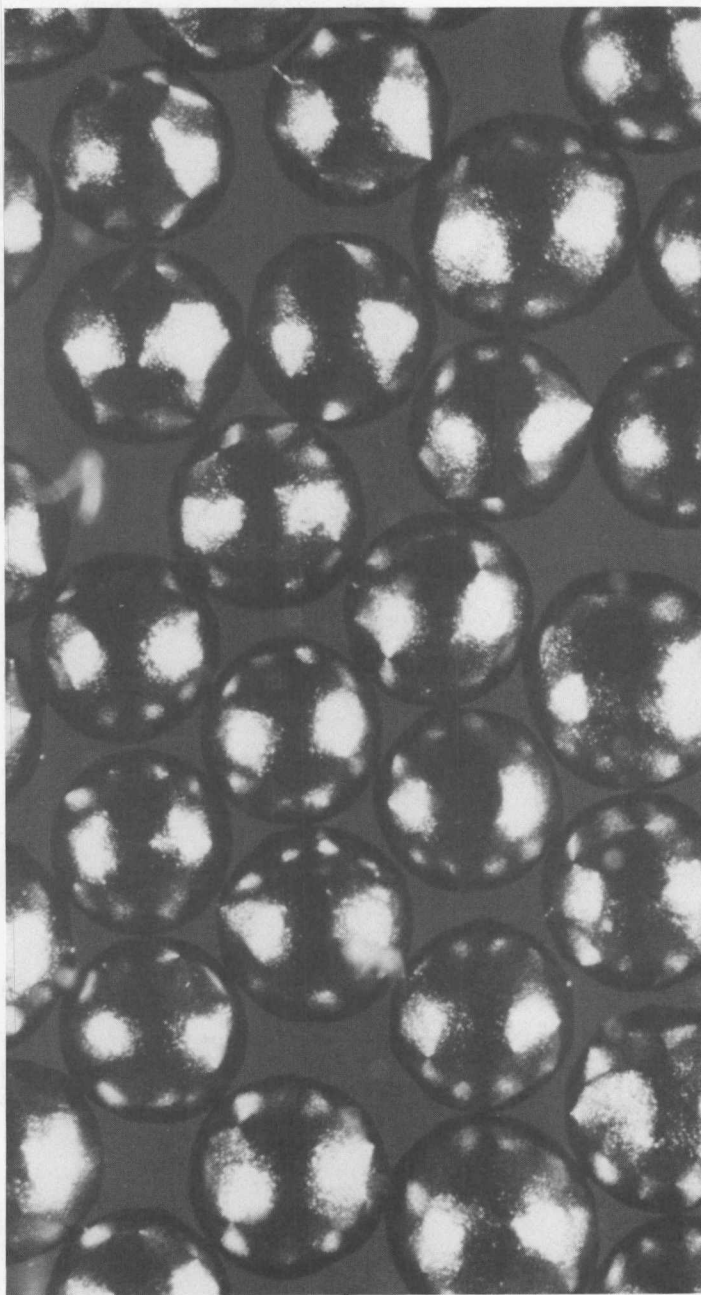


Fig. 4.32. SiC and pyrocarbon coatings were applied to gel-derived substrates of 90/10 (90 wt % simulated Savannah River Plant waste, 10 wt % ZrO₂); nonflammable mixtures; SiC coating from CH₃SiH₃ - N₂; and pyrocarbon coating from propylene and N₂.

substrates (nitrogen diluent) indicate the coating to be β -SiC with a small fraction of α -SiC.

Leach testing of uncoated 70/30, pyrocarbon overcoated SiC coated 70/30, and uncoated sintered 90/10 materials was performed and are reported in Table 4.9.^{60,61} Leach rates for the uncoated substrates are equivalent to results of the SYNROC-D gel-derived particles.⁶⁰ Leach rates of the coated 70/30 particles were below the detection limits and lower than any other nuclear waste form.

Table 4.9. Leach test results for uncoated and pyrocarbon coated sol-gel derived particles^a

Element	Leach rate [g/(m ² • d)]			
	Detection ^b limit (5 d)	Uncoated 70-30 (3 d)	Coated 70-30 (3 d)	Uncoated 90-10 (28 d)
Fe	3×10^{-5}	7×10^{-3}	c	3×10^{-3}
Al	1×10^{-4}	6×10^{-3}	c	d
Mn	2×10^{-5}	2×10^{-3}	c	2×10^{-2}
U	1×10^{-5}	3×10^{-3}	c	5×10^{-4}
Ca	2×10^{-4}	5×10^{-2}	c	3×10^{-3}
Ni	4×10^{-5}	2×10^{-3}	c	d
Si	1×10^{-4}	d	c	3×10^{-1}
Na	6×10^{-4}	3×10^{-3}	c	d
Zr	2×10^{-5}	2×10^{-4}	c	d
Ti	5×10^{-6}	9×10^{-4}	c	d
Ba	2×10^{-4}	e	e	e
Mo	1×10^{-3}	d	c	d
Ce	4×10^{-4}	4×10^{-3}	c	d
Nd	1×10^{-3}	d	c	d
Sr	1×10^{-5}	8×10^{-2}	c	9×10^{-3}
Cs	4×10^{-5}	e	e	e

^aLeach rate — $M_i / (f_i SA \Delta t)$; M_i = mass of element in solution (g); f_i = fraction of element in kernel; SA = surface area of sample (m²); Δt = time period of leach (d). Leach test MCC-1; deionized H₂O; 363 K. Detection limit determined by averaging blanks submitted during test ($V_{sol} = 20 \text{ cm}^3$, $\Delta t = 5 \text{ d}$, $SA = 75 \times 10^{-4} \text{ m}^2$).

^bDetection limit for 28 d samples is a factor of 5 lower than limit listed.

^cBelow detection limit.

^dNot measured.

^eElement not present in waste form.

CHAPTER V

DISCUSSION

The chemical vapor deposition of silicon carbide from methylsilane was evaluated. Methylsilane is a reactant which contains equimolar amounts of Si and C, does not contain chlorine, and can be decomposed to form either amorphous or crystalline silicon carbide. Experimental variables for the fluidized-bed coating study were reactant gas flow rate, diluent gas type (either argon or nitrogen) and flow rate, hydrogen content in the diluent gas, additive gas, flow rate of additive gas (C_2H_2), coating temperature, and substrate particle type. Thermodynamic equilibrium calculations were performed by a method which determined a system's composition by minimizing the free energy. Emphasis was placed on results concerning not only the gaseous phase but also the condensed phase compositions. The initial elemental contents of the system were chosen to closely match the experimental conditions necessary for proper fluidization of substrate particles in the CVD system. Results of the thermodynamic calculations are in agreement with experimental data. Alternative nuclear waste ceramics were coated with silicon carbide in a fluidized-bed coating system. The thermal stability of the substrate particles was found to be an important factor in being able to apply highly leach-resistant coatings of either pyrocarbon or silicon carbide. Coating process variables such as the use of non-halogenated reactants, low deposition temperatures, and low hydrogen contents in the diluent gas were also significant in maintaining substrate-coating process compatibility.

Both Cs-loaded zeolite and gel-derived ceramic substrates of high waste content were coated. Leach testing of the coated particles showed them to be the most leach resistant waste form.

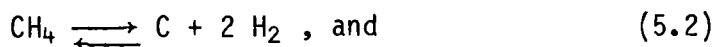
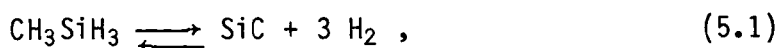
Chemical Vapor Deposition of Silicon Carbide from Methylsilane

Equilibrium thermodynamic calculations were performed to evaluate both the gaseous and condensed phases which form from the CVD of SiC from CH_3SiH_3 . The calculations are summarized as partial pressure versus temperature plots for the gaseous products and CVD phase diagrams for the condensed phase. Many gaseous and condensed phase species were included in the calculations. However, kinetic factors can also influence the experimental results. The CVD of SiC was performed in a fluidized-bed system. This is a very dynamic process. Thermodynamic equilibrium conditions may not be achieved although the process may achieve a steady-state. The reactant may not have sufficient time to reach equilibrium. The gas flow rates required to fluidize the substrate particles result in the bed-volume being exchanged approximately every 0.3 s. The relatively short residence time of the reactant in the fluidized-bed region may limit the extent of any intermediate reactions necessary for the complete decomposition of CH_3SiH_3 . In addition, the coating system has a carbon fluidization assembly. The carbon may react with reactant or diluent gases thereby changing the gas-phase composition.

The substrate may also react not only with the gaseous reactants and products, but also with the carbon fluidization assembly. Although there are certainly many factors which can influence the morphology,

and composition of the coating, thermodynamic equilibrium calculations are a first and important step in understanding the process.

One of the systems evaluated was $\text{CH}_3\text{SiH}_3 - (\text{Ar} - \text{H}_2)$. Although many gaseous and condensed phase species were included in the calculations, the results show that argon and hydrogen are the major species in the gaseous product. The calculations were performed at constant pressure and in the 900 to 1600 K temperature range. The partial pressure of all other species, for the conditions evaluated, are much lower than for argon or hydrogen. However of the minor species, CH_4 and SiH_4 were found to be the most significant. The carbon and silicon bearing gases with the highest partial pressure are CH_4 and SiH_4 respectively as shown by results presented in Fig. 4.2 (p. 57) and 4.3 (p. 58). This result is in agreement with the literature³⁹⁻⁴¹ and implies that the system may be simplified by considering the following reactions



The results of Fig. 4.2 (p. 57) and 4.3 (p. 58) show that the partial pressure of CH_4 , SiH_4 and most other gaseous species increases as the hydrogen content in the diluent gas increases. These results can be compared directly with the equations just presented. As the hydrogen

content in the diluent atmosphere is increased, the increase in hydrogen partial pressure increases the possibility of reverse reactions resulting in higher CH_4 and SiH_4 partial pressures. The decomposition of CH_3SiH_3 can be influenced by temperature and hydrogen content in the diluent gas for a given CH_3SiH_3 content and total system pressure. These results are also in agreement to those of Kingon⁷⁹ who performed a thermodynamic evaluation of the CH_3SiCl_3 , and SiH_4 -hydrocarbon system.

The results for the condensed phase are presented as CVD phase diagrams. These diagrams should not be confused with typical phase diagrams. The CVD phase diagrams show only the range of process conditions where either single phase or codeposits form. Results for the $\text{CH}_3\text{SiH}_3 - (\text{Ar} - \text{H}_2)$ system are presented in Fig. 4.1 (p. 55). Conditions exist where either single phase SiC or codeposits of $\text{SiC} + \text{Si}$ are computed to form. In a pure argon diluent $\text{SiC} + \text{Si}$ may codeposit up to ≈ 1450 K, and single phase SiC above this temperature. Codeposits of $\text{SiC} + \text{Si}$ are computed to form for nearly all other conditions within the initial conditions of the calculation. The relative content of silicon in the condensed phase increases as the temperature decreases or as the hydrogen content in the diluent gas increases. Qualitatively these results are in good agreement with the literature. The results of Böcker and Hausner⁴² presented in Fig. 2.4 (p. 27) show the composition of SiC powder produced from the thermal decomposition of CH_3SiH_3 in an argon diluent. Note that at lower temperatures the carbon content in the powder is below the theoretical 30 wt % for SiC . The carbon content increases with increasing temperature.

Alternatively the powder possesses excess silicon and the silicon concentration decreases as the temperature increases. At a temperature of ≈ 1900 K the carbon content reaches a level approximately equal to the theoretical value for SiC. It is then constant for temperatures greater than 1900 K. These last results are qualitatively the same as those calculated in this study. Thus the equilibrium thermodynamic calculations result in a trend which has previously been observed experimentally. The calculated transition temperature from a codeposit of SiC + Si to single phase SiC, in a pure argon diluent, is lower than Böcker's result. The difference may occur because the present calculations were made with a $C^{H_3SiH_3}/Ar = 5.8 \times 10^{-3}$ while Bocker's experimental results were made with $CH_3SiH_3/A = 0.11$. Another possibility is that the reactant gas, in Bocker's experiment, did not reach the actual temperature monitored on the outer surface of the graphite tube.

The calculated results of (1) the existence of a SiC + Si two phase field and (2) the increase in Si content as the hydrogen content in the diluent gas increases are also in agreement with experimental results presented in this work. X-ray diffraction spectra for two coatings, one formed in pure argon diluent (Fig. 4.22, p. 96) and another in pure hydrogen diluent, (Fig. 4.23, p. 98), formed at the same temperature confirm the calculations. No silicon was observed, by x-ray diffraction, in the coating deposited in pure argon (Fig. 4.22, p. 96). Results of calculations show the Si/SiC mole ratio for these conditions is $\approx 1 \times 10^{-4}$. This small concentration would not be observable with normal x-ray diffraction techniques which are limited

to approximately a 2 wt % detection limit. Silicon was observed in the coating deposited in pure hydrogen diluent as is shown in Fig. 4.23 (p. 98). This trend was also confirmed by results of two other experiments performed under identical conditions but with hydrogen contents in the diluent gas of 8.6 and 77 mol %. No silicon was observed in the 8.6 mol % H_2 . Silicon was observed in the 77 mol % H_2 coating and the x-ray diffraction peaks were less intense than that of the coating deposited in pure hydrogen.

Consider the effect of C_2H_2 addition to the $CH_3SiH_3 - (Ar - H_2)$ system. Again the two major product gaseous species are argon and hydrogen. These are the major species since argon does not take part in the reactions and the remaining gaseous species are highly unstable for the conditions evaluated in these studies. However CH_4 and SiH_4 are the minor gaseous species with the highest partial pressure for most of the conditions evaluated. Monitoring of the CH_4 partial pressure may be useful in revealing the reactions which are taking place in the CVD reaction chamber. Addition of C_2H_2 to the system can influence the type and relative concentration of condensed phases. The computed CVD phase diagram which summarizes these results is shown in Fig 4.7 (p. 65). The addition of C_2H_2 to the system can result in the codeposition of $SiC + C$ for low hydrogen contents in the diluent gas. At high hydrogen content in the diluent gas, the addition of a small amount of C_2H_2 can change the composition of the condensed phase from codeposited $SiC + Si$ to single phase SiC . These results were evaluated experimentally. Two experiments were performed with controlled amounts of C_2H_2 added to the $C_3SiH_3 - (Ar - H_2)$ system. The experimental

conditions were similar to two previous experiments except for the C_2H_2 addition and are shown in Table 4.6 (p. 100). The experiments matched the calculations where $C_2H_2/SH_3SiH_3 = 3.4 \times 10^{-3}$ and $CH_3SiH_3/diluent = 5.8 \times 10^{-4}$. Two types of diluent gases were used, pure argon, and an Ar — H_2 mixture with a hydrogen content of 77 mol %. The coatings were evaluated by x-ray diffraction, Raman spectroscopy and quantitative electron microprobe analyses. The results for the pure argon diluent will be discussed first. Addition of C_2H_2 in this case clearly resulted in a coating which contained excess carbon. A comparison of the Raman spectra shown in Fig. 4.24 (p. 101) and Fig. 4.25 (p. 102) indicate excess carbon is present in the coating deposited with the C_2H_2 addition. Quantitative electron microprobe results were also in agreement. The silicon content of the coating deposited in argon without C_2H_2 was nearly identical, within experimental error, to the silicon content of a single crystal SiC. The silicon content of the coating produced with the C_2H_2 addition was measured to be 64.8 ± 0.9 wt %. This indicates the presence of excess carbon in the coating. If all the C_2H_2 and CH_3SiH_3 decomposed and deposited on the substrate particles, then the silicon content would be 68.3 wt %. This is based upon the experimental gas flow rates. The 68.3 wt % Si value is lower than the 70 wt % theoretical value for pure SiC but slightly higher than the measured 64.8 wt %. However the C_2H_2 may not decompose at the same rate, temperature, or location in the fluidized-bed. If one assumes that all the C_2H_2 is decomposed and deposited onto the substrate but the CH_3SiH_3 is deposited at the experimentally measured efficiency, then the silicon content would be

67.2 wt %. This is still slightly higher than the experimental which does contain some error value but still in excellent agreement with the thermodynamic calculations. The results for the two experiments performed at a hydrogen diluent content of ≈ 77 mol % are also in agreement with the equilibrium thermodynamic calculation. Comparison of the Raman spectra presented in Fig. 4.26 (p. 104) and 4.27 (p. 105) clearly show the decrease in the silicon content as C_2H_2 is added to the system. The quantitative electron microprobe measurements also agree. The silicon content of the coating deposited with no C_2H_2 addition was 71.9 wt %. Addition of C_2H_2 to the system decreased the silicon content to approximately that of the single crystal SiC which is in agreement with the calculations.

Thermodynamic equilibrium analyses of the $CH_3SiH_3 - C_2H_2 - (Ar - H_2)$ system agree with experimental results. This points to the importance of the free energy concept in the evaluation of chemical vapor deposition reactions.

The calculated efficiency for the decomposition of CH_3SiH_3 was always greater than 97% for the entire range of conditions evaluated in this study. The experimental coating efficiency, however, is a measure of the fraction of available SiC which is deposited onto the substrate particles. A certain amount of SiC is always deposited on the fluidization assembly surfaces. SiC powder is also formed and exhausted from the system. Thus the experimental coating efficiency is always less than the theoretical value. The experimental coating efficiency versus coating temperature plot presented in Fig. 4.15 (p. 85) show that the CVD of SiC occurs at lower temperatures whenever

pure argon is used as the diluent gas. The presence of hydrogen diluent gas delays the decomposition reactions so that higher temperatures are required. However, rather high efficiencies, >70%, are obtained in both cases at coating temperatures of 1180 and 1280 K. The coating efficiency for the 873 K experiment performed in pure argon was less than 1%. In addition, no powder formation was observed by viewing the fluidization assembly. The lack of CH_3SiH_3 decomposition may be related to the increase in free energy required for nucleation and growth in the gas phase or to kinetic factors. Perhaps intermediate reactions cannot occur quickly enough at these low temperatures during the relatively short residence time in the CVD system. If this were the case perhaps lowering the gas flow rates would increase the coating efficiency.

The morphology of the SiC coatings indicates that CH_3SiH_3 decomposes in the gas phase by a nucleation and growth mechanism. The coating porosity increases (Fig. 4.12, p. 77) as the temperature is increased from 1073 to 1280 K. The scanning electron micrographs imply a similar mechanism. The micrographs presented in Fig. 4.14 (p. 79) show the surface of the coating produced at 1073 K in an argon diluent to be rather smooth. Small particles can be seen on the surface and a sintering mechanism is implied. The morphology of the surface changes to a "powdery" appearance for coatings deposited at 1280 K. Coatings deposited at still higher temperatures (1685 K), however, have a globular morphology. Sintering of the particles may have occurred at 1685 K and a grain growth mechanism may be dominant at this higher temperature. These results are also in agreement with the results of

Spielmann,³⁸ and Böcker and Hausner.⁴² Spielmann³⁸ found that CH_3SiH_3 decomposed prior to contacting a single crystal substrate. More decomposition occurred when the CH_3SiH_3 was mixed with a diluent gas than when it was flowed into the system at a low pressure with no diluent gas. The CH_3SiH_3 mixed with argon diluent may have been heated to higher temperatures due to the improved thermal conductivity of the gas phase. These results are also consistent with the Böcker and Hausner⁴² results which show that SiC powder can be produced from the thermal decomposition of CH_3SiH_3 .

The crystallinity of the SiC deposits was found to be a function of temperature and hydrogen content in the diluent gas. Amorphous deposits were formed at or below 1073 K irrespective of hydrogen content in the diluent gas. Crystalline deposits were formed at coating temperatures of 1180 K and above. The formation of amorphous deposits may be due to kinetic factors, low diffusion coefficients, or perhaps even to incomplete decomposition. Cubic β -SiC is calculated to form at all conditions in this study. This is because the free energy of formation for β -SiC is always taken to be more negative than that of α -SiC. Experimentally β -SiC is the major phase observed but a small amount of α -SiC is also present. The coatings were isotropic since the peak heights of the x-ray diffraction spectra were nearly identical to patterns of standard powdered SiC specimens. The crystallite size measurements show similar behavior to the coating efficiency data. The 9 nm crystallite size reported in this work for SiC coatings deposited at 1280 K in pure argon diluent are remarkably close to those reported by Böcker and Hausner,⁴² 5 nm, for SiC powder produced at the

same temperature. The crystallite size of as-produced coatings was dependent upon the hydrogen content in the diluent gas. Smaller crystallite sizes were measured for coatings deposited at higher hydrogen content in the diluent gas. SiC crystallite growth may be limited by the presence of "excess" silicon precipitates if the SiC crystals are pinned by the precipitates. If the silicon concentration of the SiC coating is taken to be ≈ 1 mol % and the precipitates as cubes with an edge dimension of ≈ 1 nm then the relative spacing between the "excess" silicon precipitates is ≈ 5 nm. A larger silicon content would result in a smaller spacing between the "excess" silicon precipitates resulting in a decrease in the SiC crystallite size.

Annealing amorphous SiC coatings at 1173 K crystallized the material. Densification occurs upon crystallization as shown by the scanning electron micrographs presented in Fig. 4.19 and 4.20 (p. 93). All SiC coatings had approximately the same crystallite size after a 1523 K, 3 h anneal in an argon atmosphere. However specimens formed in diluent atmospheres rich in hydrogen always had a larger crystallite size than those formed in pure argon when annealed at 1723 K for 3 h. The coatings deposited in diluents rich in hydrogen are also the coatings with high silicon content. The larger crystallite size is perhaps related to the silicon content. Silicon is molten above 1685 K and thus may aid in the growth of crystallites due to the increase in the liquid phase diffusion coefficients.

The results and discussion of the chemical vapor deposition of SiC from CH_3SiH_3 points to the value of the thermodynamic equilibrium calculations and the free energy concept.

Coating of Nuclear Waste Ceramics

The coated particle concept for the solidification of high-level-nuclear waste has been evaluated. The chemical vapor deposition process was used and substrates of Cs-loaded zeolite and ceramic waste forms with waste loadings greater than 70 wt % were successfully coated. Coatings of SiC and pyrocarbon were applied in fluidized-bed coatiers. Leach testing of the coated particles showed them to be highly leach resistant; leach rates were lower than any other nuclear waste form.

The multibarrier approach to the solidification and disposal of nuclear waste has been evaluated by other researchers. Although substrate materials used in earlier studies were not optimal for the chemical vapor deposition process, those experiments provided significant insight into the properties of substrates that are most important to the coating process. Sol-gel technology has been used to produce crystalline ceramic substrates.

Cesium loaded zeolite has been used many times for storage of cesium. Recent work by various researchers have shown that Cs-loaded zeolites can be heat-treated to fix a certain fraction of the cesium.⁶⁵ Thus Cs-loaded zeolite was chosen as a substrate for the coated particle concept. Cs-loaded zeolite was heat treated in air to remove gaseous volatiles, and water of hydration, and to stabilize the material. It was then coated with SiC or pyrocarbon. The SiC coated Cs-loaded zeolite particles were not leach tested since this development occurred near the end of the research program. However,

the pyrocarbon coated substrate was found to be highly leach resistant. It possesses the lowest cesium leach rates for any reported Cs-bearing waste form.

Coating of gel-derived substrates with high waste loading was also evaluated. The substrate particles were compatible with SiC coatings chemically vapor deposited from methylsilane. The SiC coated particles were later overcoated with pyrocarbon at temperatures of up to 1473 K. Leach testing showed the 70/30 substrate particles coated with SiC and overcoated with pyrocarbon to be highly leach resistant and all measurements were at or below state-of-the-art detection limits. Coatings of SiC were also applied to substrate particles of high waste loading (90/10 composition) from the decomposition of CH_3SiH_3 in a nitrogen diluent atmosphere. A nitrogen diluent atmosphere was evaluated since processing costs would be lower if nitrogen were used rather than argon. Typical coating conditions were used which were similar to Run 91 for the low density buffer and to Run 84 for the high density coating. However, the nitrogen diluent gas flow rate was increased by a factor of ≈ 1.5 as compared to that of argon. The low density buffer coating was deposited at 1280 K to prevent fracture of the dense coating. The coating was determined to be SiC from x-ray diffraction data, however, further analyses are required to completely evaluate the phases and composition of the coating. The x-ray diffraction results indicate that the $\text{CH}_3\text{SiH}_3 - \text{N}_2$ system did not reach thermodynamic equilibrium since the thermodynamic calculations predicted $\text{Si}_3\text{N}_4 + \text{C}$ to codeposit under these conditions. Equilibrium may not have been reached due to kinetic

factors. There may not have been sufficient time for the CH_3SiH_3 to react with the nitrogen diluent. These particles were also overcoated with pyrocarbon from the thermal decomposition of propylene at 1473 K. The hydrogen concentration in the product gases was kept lower than the 4% explosive limit to increase the safety aspects of the coating procedures. An outer SiC coating may also be applied to prevent the oxidation of the pyrocarbon layer in case the particles are subjected to temperatures greater than ≈ 1073 K in air.

Chemical vapor deposition processes have been found to be very useful in coating of alternative waste form substrates. The process uses relatively simple equipment such as fluidized-bed coaters and can utilize much information developed for the coating of HTGR fuel. Substrates of high waste loading as well as Cs-loaded zeolite have been successfully coated and leach testing has shown them to be the most leach resistant nuclear waste form. The development of a generic Cs-bearing nuclear waste form can be applied to any number of alternative waste form processes including that of borosilicate glass. One of the key items in this research was the research and development of the chemical vapor deposition of SiC from methylsilane.

CHAPTER VI

SUMMARY AND CONCLUSIONS

The chemical vapor deposition (CVD) of silicon carbide from methylsilane and coating of nuclear waste ceramics were evaluated. Both thermodynamic equilibrium calculations and SiC deposition experiments were performed. The variables studied included temperature, hydrogen content in the diluent gas (either argon or nitrogen), and addition of C_2H_2 . The substrates which were coated included pyrolytic carbon coated alumina, Cs-loaded zeolite, and sol-gel-derived alternative nuclear waste ceramics of high waste loading.

The theoretical and experimental observations were performed with a mole ratio of CH_3SiH_3 /diluent = 4.8×10^{-3} and a total system pressure of 1.01×10^5 Pa.

1. The thermodynamic equilibrium calculations for the CH_3SiH_3 - Ar system indicated that SiC + Si are codeposited up to a temperature of ≈ 1450 K. Single phase SiC is calculated to form above ≈ 1450 K. The Si/SiC mole ratio for the condensed phase is $\approx 1 \times 10^{-5}$ at 973 K and decreases as the temperature is increased.
2. The calculated results for the CH_3SiH_3 - H_2 system are similar to the above except SiC + Si is calculated to form over the entire 973 to 1600 K temperature range. The Si/SiC mole ratio is $\approx 1 \times 10^{-2}$ at 973 K and decreases with increasing temperature.
3. Addition of C_2H_2 to the CH_3SiH_3 - (Ar - H_2) system can influence the types and concentration of phases present in the condensed phase.

4. The major carbon and silicon gaseous product species calculated to occur are CH_4 and SiH_4 respectively.
5. Amorphous SiC is deposited at or below ≈ 1073 K and crystalline SiC is deposited at temperatures greater than ≈ 1180 K.
6. For the 973 to 1280 K temperature range, the coating efficiency generally increases and coating density generally decreases with increasing temperature. Silicon carbide coating densities of $\approx 98\%$ of theoretical and coating efficiencies $> 75\%$ can be achieved at a temperature of ≈ 1180 K in a fluidized-bed coater.
7. The silicon content of the SiC coating increases with increasing hydrogen content in the diluent gas. This result is in agreement with the thermodynamic calculations.
8. Addition of C_2H_2 to the $\text{CH}_2\text{SiH}_3 - (\text{Ar} - \text{H}_2)$ system affected the types and content of phases present in the coating. Results were in agreement with thermodynamic calculations.
9. Cs-loaded zeolite can be coated with either pyrolytic carbon, SiC, or both. The cesium leach rate of pyrolytic carbon coated zeolite is below detection limits and is at least three orders of magnitude lower than that for borosilicate glass.
10. Substrates of high waste loading were coated with SiC and overcoated with pyrolytic carbon. SiC coatings were deposited from the $\text{CH}_3\text{SiH}_3 - \text{Ar}$ and $\text{CH}_3\text{SiH}_3 - \text{N}_2$ systems. Formation of SiC from the $\text{CH}_3\text{SiH}_3 - \text{N}_2$ system indicates the system did not reach equilibrium since $\text{Si}_3\text{N}_4 + \text{C}$ are calculated to codeposit. Substrate particles were overcoated with propylene at a

temperature of 1473 K. The hydrogen concentration was held below the 4% explosive limit to increase safety aspects.

These observations lead to the following conclusions:

1. The free energy concept and thermodynamic equilibrium calculations are of great value for the evaluation of both the condensed and gaseous phase compositions present during chemical vapor deposition.
2. Impermeable SiC coatings can be applied onto nuclear waste ceramics from the thermal decomposition of methylsilane (CH_3SiH_3) in fluidized-bed coaters.
3. Coating of Cs-loaded zeolite and other nuclear waste ceramics can provide increased leach resistance.

REFERENCES

REFERENCES

1. Interagency Review Group on Nuclear Waste Management, Report to the President by the Interagency Review Group on Nuclear Waste Management, Washington, D.C. (March 1979).
2. A. M. Platt, and J. L. McElroy, Management of High-Level Nuclear Wastes, PNL-SA-7022, Battelle Pacific Northwest Laboratories, Richland, WA (December 1978).
3. M. J. Plodinec, "Development of Glass Compositions for Immobilization of Savannah River Plant Waste," p. 31 in Scientific Basis for Nuclear Waste Management, G. J. McCarthy, ed., Plenum Press, N.Y. (1979).
4. A. E. Ringwood, S. E. Kesson, N. G. Ware, W. Hiberson, and A. Major, "Immobilization of High Level Nuclear Reactor Wastes in SNYROC," Nature (London), 278(5701), pp. 219-23 (1979).
5. R. Roy, "Rational Molecular Engineering of Ceramic Materials," J. Am. Ceram. Soc., 60(7-8), 350-63 (1977).
6. G. J. McCarthy, "High-Level Waste Ceramics: Materials Considerations, Process Simulation and Product Characterization," Nucl. Technol., 32, pp. 92-105 (1977).
7. A. E. Ringwood, Safe Disposal of High Level Nuclear Reactor Wastes: A New Strategy, Australian National University Press, Canberra (1978).
8. P. E. D. Morgan, D. E. Clarke, C. M. Jantzen, and A. B. Harker, "High Alumina Tailored Nuclear Waste Ceramics," J. Am. Ceram. Soc., 64(5), pp. 249-58 (1980).
9. A. B. Harker, D. R. Clarke, C. M. Jantzen, and P. E. D. Morgan, "The Effect of Interfacial Material on Tailored Ceramic Nuclear Waste Form Dissolution," Surfaces and Interfaces in Ceramics and Ceramic-Metal Systems, Berkeley, CA (July 1980).
10. G. J. McCarthy, W. B. White, and D. E. Pfoertsch, "Synthesis of Nuclear Waste Monazites, Ideal Actinide Hosts for Geologic Disposal," Mater. Res. Bull., 13, p. 1239 (1978).

11. L. A. Boatner, G. W. Beall, M. M. Abraham, C. B. Finch, R. J. Floran, P. G. Huray, and M. Rappaz, "Lanthanide Orthophosphates for the Primary Immobilization of Actinide Wastes," presented at the International Symposium on the Management of Alpha Contaminated Wastes, Vienna, Austria (June 1980).
12. P. G. Huray, M. T. Sparr, S. E. Nave, and J. M. Legan, "The Application of ^{57}Fe Mössbauer Spectroscopy to the Characterization of Nuclear Waste Forms," pp. 59-73 in Scientific Basis for Nuclear Waste Management, S. V. Topp, ed., North Holland (1980).
13. B. C. Sales, C. W. White, and L. A. Boatner, "A Comparison of the Corrosion Characteristics of Synthetic Monazite and Borosilicate Glass Containing Simulated Nuclear Defense Waste," Nucl. and Chem. Waste Manag., 4(4), pp. 281-9 (1983).
14. R. F. Harker, and R. C. Ewing, Naturally Occurring Crystalline Phases: Analogues for Radioactive Waste Forms, Pacific Northwest Laboratory Report, PNL-3505 (1981).
15. R. W. Kidd, M. F. Browning, and J. M. Rusin, "Chemically Vapor Deposited Coatings for Multibarrier Containment of Nuclear Waste," pp. 563-77 in Proceedings of the Seventh International Conference on Chemical Vapor Deposition 1979, T. O. Sedgwich and H. Lydtin, eds., Los Angeles, CA (October 1979).
16. J. M. Rusin, R. O. Lokken, J. M. Lukacs, R. R. Sump, M. F. Browning, and G. J. McCarty, Multibarrier Waste Forms Part I: Development, PNL-2668-1, Battelle Pacific Northwest Laboratories, Richland, WA (September 1978).
17. J. M. Rusin, W. J. Gray, and J. W. Wald, Multibarrier Waste Forms Part II: Characterization and Evaluation, PNL-2668-2, Battelle Pacific Northwest Laboratories, Richland, WA (August 1979).
18. R. O. Lokken, Multibarrier Waste Forms Part III: Process Considerations, PNL-2668-3, Battelle Pacific Northwest Laboratories, Richland, WA (October 1979).
19. J. M. Rusin, J. W. Shade, R. W. Kidd, and M. F. Browning, "Chemically Vapor Deposited Coatings for Multibarrier Containment of Nuclear Wastes," pp. 248-61 in Alternate Nuclear Waste Forms and Interactions in Geologic Media, L. A. Boatner and G. C. Battle, Jr., eds., CONF-8005107, U.S. Department of Energy, Washington, D.C. (1980).

20. J. M. Rusin et al., Chemically Vapor Deposited Coatings for Multibarrier Containment of Nuclear Wastes, PNL-SN-8863 (1980).
21. W. Neumann and O. Kofler, "Coating of Waste Containing Ceramic Granules," pp. 150-54 in Ceramic In Nuclear Waste Management, T. D. Chikalla and J. E. Mendel, eds., CONF-790420, U.S. Department of Energy, Washington, D.C. (April 1979).
22. P. A. Hass, J. M. Begovich, A. D. Ryon, and J. S. Vavruska, "Chemical Flowsheet Conditions for Preparing Urania Spheres by Internal Gelation," Ind. Eng. Chem. Prod. Res. Div., 19[3], pp. 459 (1980).
23. J. B. W. Kanij, A. J. Noothout, and O. Vatocik, "The KEMA U(VI)-Process for the Production of UO_2 Microspheres," pp. 185-95 in Sol-Gel Processes for Fuel Fabrication, International Atomic Energy Agency, Vienna (1974).
24. Oak Ridge National Laboratory, Assessment of Gel-Sphere-Pac Fuel for Fast Breeder Reactors, ORNL-5468, Oak Ridge National Laboratory, Oak Ridge, TN (1978).
25. R. W. Dayton, J. H. Oxley, and C. W. Towley, "Ceramic Coated Particle Nuclear Fuels," J. Nucl. Mater., 11, pp. 1-31 (1964).
26. R. L. Beatty, Pyrolytic Carbon Deposited from Propane in a Fluidized Bed, ORNL-TM-1649 (M.S. Thesis, University of Tennessee) (January 1967).
27. T. D. Gulden, "Deposition and Microstructure of Vapor-Deposited Silicon Carbide," J. Am. Ceram. Soc., 51, pp. 424-7 (1968).
28. L. H. Ford, N. S. Hibbert, and D. G. Martin, "Recent Developments of Coatings for GCFR and HTGCR Fuel Particles and their Performance," J. Nucl. Mat., 45, pp. 139-49 (1972).
29. E. Gyarmati, and H. Nickel, Stationary and Dynamic Deposition of Silicon Carbide on Coated Fuel Particles, JUL-900-RW, ORNL-TR-2733 (1972).
30. J. I. Federer, "Parametric Study of SiC Coatings Deposited in a Fluidized Bed," Thin Solid Film, 40, pp. 89-96 (1977).

31. R. L. R. Lefevre, and M. S. T. Price, "Coated Nuclear Fuel Particles: The Coating Process and Its Model," Nucl. Technol., 35, pp. 263-78 (1977).
32. E. Pollman, J. Pelissier, C. S. Yust, and J. K. Kaae, "Transmission Electron Microscopy of Pyrocarbon Coatings," Nucl. Technol., 35, pp. 301-9 (1977).
33. D. P. Stinton, and W. J. Lackey, "Effect of Deposition Conditions on the Properties of Pyrolytic SiC Coatings for HTGR Fuel Particles," Am. Ceram. Soc. Bull., 57(6), pp. 562-73 (1978).
34. W. J. Lackey, R. E. Blanco, and A. L. Lotts, "Application of Sol-Gel Technology to Fixation of Nuclear Reactor Waste," Nucl. Technol., 49(2), pp. 321-24 (1980).
35. British Patent 859,947, Wacker-Chemie G.M.B.H., F.R. Germany, "Process for the Manufacture of Very Pure Crystalline Silicon Carbide," (1959).
36. H. J. Spangenberg, H. Kriegsmann, "Zur Thermodynamik der Methylsilane $\text{CH}_3\text{-SiH}_3$ und $\text{CH}_3\text{-SiD}_3$," Z. Phys. Chem. Bd 224, Heft 3/4, pp. 273-7 (1963).
37. G. P. Van der Kelen, O. Volders, H. van Onckelen, and Z. Eeckhaut, "The Mass Spectra of Silane and the Methylsilanes," Zeit. fur Anorg. Allg. Chemie, 338, pp. 105-12 (1965).
38. Von Werner Spielmann, "Epitaxiales Wachstum von SiC mit Hilfe von Methylsilan oder Silan und Propan im Vakuum," Zeits. Angew. Physik., 19, pp. 93-4 (1965).
39. J. J. Kohanek, P. Estacio, and M. A. Ring, "Pyrolysis of Methylgermane and Methylsilane," Inorg. Chem., 8(11), pp. 2516-7 (1969).
40. M. A. Ring, M. J. Puentes, and J. E. O'Neal, "Pyrolysis of Monosilane," J. Am. Chem. Soc., 92(16), pp. 4845-8 (1970).
41. P. S. Skell, and P. W. Owen, "Chemistry of Atomic Silicon. III. Reactions of Electron Bombardment Produced Silicon Vapor with Silanes," J. Am. Chem. Soc., 94(15), pp. 5434-8 (1972).
42. W. Böcker and H. Hausner, "Verfahren zur Herstellung von Silicium Carbidpulvern aus der Gasphase," Ber. Dt. Keram. Ges., 55(4), pp. 233-7 (1978).

43. V. G. Fritz, J. Maas, and A. Hornung, "Zur Bildung von Carbosilanen aus Methylsilanen," Z. Anorg. Allg. Chem., 460, pp. 115-43 (1980).
44. J. Schlichting, "Review, Chemical Vapor Deposition of Silicon Carbide," Powder Metall. Int., 12(4), pp. 196-200 (1980).
45. H. E. O'Neal, and M. A. Ring, "An Additivity Scheme for the Estimate of Heats of Formation, Entropies, and Heat Capacities of Silanes, Polysilanes, and their Alkyl Derivatives," J. Organometallic Chemistry, 213, pp. 419-34 (1981).
46. U. S. Patent 4,376,792, P. Angelini, W. J. Lackey, D. P. Stinton, R. E. Blanco, W. D. Bond, and W. D. Arnold, U.S.A., U.S. Department of Energy, "Method and Article for Primary Containment of Cesium Wastes," (1983).
47. U. S. Patent 4,459,338, P. Angeline, C. E. DeVore, W. J. Lackey, R. E. Blanco, and D. P. Stinton, U.S.A., U.S. Department of Energy, "Method of Disposition of Silicon Carbide Layers on Substrates and Product," (1984).
48. G. J. McCarthy, Quarterly Progress Report, Research and Development Activities, Waste Fixation Program, PNL Report, BNWL-1932 (September 1975).
49. A. E. Ringwood, S. E. Kesson, N. G. Ware, W. O. Hibberson, and A. Major, "The Synroc Process. A Geochemical Approach to Nuclear Waste Immobilization," Geochem. J., 13(4), pp. 141-65 (1979).
50. V. M. Oversby, Properties of SYNROC-C Nuclear Waste Form: A State-of-the-Art Review, UCRL-53326, Lawrence Livermore National Laboratory, Livermore, CA (September 1982).
51. J. A. Stone, S. T. Goforth, Jr., and P. K. Smith, Preliminary Evaluation of Alternative Forms for the Immobilization of Savannah River Plant High-Level Waste, DuPont Savannah River Laboratory, Aiken, S.C., BP-1545.
52. J. R. Wiley, and R. M. Wallace, Removal of Cesium from Savannah River Plant Waste Supernate, DP-1388 (July 1975).
53. F. J. Ryerson, Synroc D: Microstructure and Mineral Chemistry, Lawrence Livermore National Laboratory Report, UCRL-88458 (Dec. 1982).

54. C. Hoenig, R. Otto, J. Campbell, Densification Studies of Synroc D for High-Level Defense Waste, Lawrence Livermore National Laboratory Report, UCRL-53392 (March 1983).
55. W. D. Arnold, W. D. Bond, and S. M. Robinson, "Preparation of Gel Spheres Containing Simulated High-Level Radioactive Waste," Rad. Waste Manag. and the Nucl. Fuel Cycle, 3(1), pp. 57-74 (1982).
56. W. J. Gray, "Reaction of Graphite with Water and Its Implications for Radioactive Waste Storage," Radioactive Waste Management, 1(1), pp. 105-9 (1980).
57. P. Angelini, D. P. Stinton, J. S. Vavruska, A. J. Caputo, and W. J. Lackey, "Sol-Gel Technology Applied to Alternative High-Level Waste Forms Development," pp. 242-7 in Alternate Nuclear Waste Forms and Interactions in Geologic Media, L. A. Boatner and G. C. Battle, Jr., eds., CONF-8005107, U.S. Department of Energy, Washington, D.C. (1980).
58. W. J. Lackey, P. Angelini, F. L. Layton, D. P. Stinton, and J. S. Vavruska, "Sol-Gel Technology Applied to Glass and Crystalline Ceramics," pp. 391-417 in Waste Management '80, Vol. 2, R. G. Post, ed., University of Arizona, Tucson, (1980).
59. P. Angelini, W. D. Bond, A. J. Caputo, J. E. Mack, W. J. Lackey, D. A. Lee, and D. P. Stinton, "Sol-Gel Technology Applied to Crystalline Ceramic Nuclear Waste Forms," pp. 173-80 in Scientific Basis for Nuclear Waste Management, J. G. Moore, ed., Plenum Press, N.Y. (1981).
60. D. P. Stinton, P. Angelini, A. J. Caputo, and W. J. Lackey, "Coating of Crystalline Nuclear Waste Forms to Improve Inertness," J. Am. Ceram. Soc., 65(8), (August 1982).
61. D. M. Stachan, B. O. Barnes, R. P. Turcotte, "Standard Leach Tests for Nuclear Materials," p. 347 in Scientific Basis for Nuclear Waste Management, J. G. Moore, ed., Plenum Press, N.Y. (1980).
62. J. I. Nelson, and B. W. Mercer, "Ion Exchange Separation of Cesium from Alkaline Waste Supernatant Solutions," Technical Report No. HW-76449, United States Atomic Energy Commission, Hanford, WA (1963).

63. J. S. Buckingham, "Laboratory Evaluation of Zeolite Material for Removing Radioactive Cesium from Alkaline Waste Solutions," Technical Report No. ARII-SA-49, United States Atomic Energy Commission, Hanford, WA (1970).
64. DOE-SDS Task Force, "Evaluation of Increased Cesium Loading on Submerged Demineralizer System (SDS) Zeolite Beds," Technical Report No. DOE/NE-0012, United States Department of Energy, Washington, DC (May 1981).
65. S. Komarneni, and R. Roy, "Zeolites for Fixation of Cesium and Strontium from Radwastes by Thermal and Hydrothermal Treatment," Nucl. Chem. Waste Management, 2[4], pp. 259-64 (1981).
66. S. Komarneni, G. L. Palau, and K. K. S. Pillay, "Radiation Effects on a Zeolite Ion Exchanger and a Pollucite," Nucl. and Chem. Waste Management, 4(4), pp. 335-8 (1983).
67. K. K. Yee, "Protective Coatings for Metals by Chemical Vapour Deposition," Int. Met. Rev., 1, pp. 226-42 (1978).
68. C. Greskovich, and J. H. Rosolowski, "Sintering of Covalent Solids," J. Am. Ceram. Soc., 59(7), pp. 336-43 (1976).
69. J. E. Spruiell, "Chemical Vapor Deposition of Silicon Carbide from Silicon Tetrachloride-Methane- H_2 ," pp. 279-95 in Chemical Vapor Deposition, J. M. Blocher, Jr., J. C. Withers, eds., (1970).
70. U. S. Patent 3,011,912, P. J. Gareis, and P. H. Mohr, Union Carbide Corporation, "Process for Depositing Beta Silicon Carbide," (1961).
71. J. I. Federer, Deposition of Silicon Carbide Coatings on Particles in a Fluidized Bed Using Silane and Tetramethylsilane - A Feasibility Study, ORNL/TM-6185 (1978).
72. K. E. Knipschild, and D. A. Lee, Thermal Analysis of Synroc Gel Microspheres, ORNL/TM-7930 (1981).
73. F. L. Layton, Laboratory Procedures for the Analysis of HTGR Fuels and Materials, ORNL/GCR-78/12 (1978).
74. D. M. Hewett, and W. R. Laing, Nucl. Technol., 21, p. 149 (1974).

75. P. Krautwasser, G. M. Begun, and P. Angelini, "Raman Spectral Characterization of Silicon Carbide Nuclear Fuel Coatings," J. Am. Ceram. Soc., **66**(6), pp. 424-34 (1983).
76. G. Eriksson, "Thermodynamic Studies of High Temperature Equilibria, III. SOLGAS, A Computer Program for Calculating the Composition and Heat Condition of an Equilibrium Mixture," Acta Chem. Scand., **25**(7), pp. 2651-8 (1971).
77. T. M. Besmann, Solgasmix-PV, A Computer Program to Calculate Equilibrium Relationships in Complex Chemical Systems, ORNL/TM-5775.
78. W. B. White, W. M. Johnson, and G. B. Dantzig, "Chemical Equilibrium in Complex Mixtures," J. Chem. Phys., **28**(5), pp. 751-5 (1958).
79. A. I. Kingon, L. J. Lutz, P. Liaw, and R. F. Davis, "Thermodynamic Calculations for the Chemical Vapor Deposition of Silicon Carbide," J. Am. Ceram. Soc., **66**(1), pp. 558-66 (1983).
80. T. M. Besmann, and K. E. Spear, "Analysis of the Chemical Vapor Deposition of Titanium Diboride I. Equilibrium Thermodynamic Analysis," J. Electrochemical Soc., **124**(5), pp. 786-90 (1977).
81. T. M. Besmann, and K. E. Spear, "Analysis of the Chemical Vapor Deposition of Titanium Diboride, II Modeling the Kinetics of Deposition," J. Electrochemical Soc., **124**(5), pp. 790-7 (1977).
82. D. R. Stull, and H. Prophet, "JANAF Thermochemical Tables," Second Edition, U.S. Government Printing Office, Washington, DC (1971).
83. D. P. Stinton, W. J. Lackey, and P. Angelini, "Immobilization of Radioactive Cesium in Pyrolytic-Carbon-Coated Zeolite," J. Am. Ceram. Soc., **66**(6), pp. 389-392 (June 1983).

APPENDICES

APPENDIX A

Table A.1. Composition of simulated SRP^a waste matrix additives, and product

Component	SRP ^a Waste (wt %)	Simulated high-level waste-loaded SRP forms					
		SYNROC-D ^b		70/30 ^c		90/10 ^d	
		Matrix (wt %)	Product (wt %)	Matrix (wt %)	Product (wt %)	Matrix (wt %)	Product (wt %)
Fe ₂ O ₃	49.9		27.4		35.8		44.9
Al ₂ O ₃	9.8	33.6	20.6		7.0		8.8
MnO ₂	13.7		7.5		9.9		12.4
U ₃ O ₈	4.5		2.5		3.2		4.1
CaO	3.7	10.3	6.7	18.0	7.7		3.3
NiO	6.2		3.4		4.4		5.6
SiO ₂	1.2	15.8	7.8	21.2	6.7		1.1
Na ₂ O	7.0		3.8	9.9	7.9		6.3
Na ₂ SO ₄	1.3		0.7		0.9		1.2
Ce ₂ O ₃	1.1		0.6		0.8		0.9
Nd ₂ O ₃	1.1		0.6		0.8		0.9
SrO	0.5		0.3		0.4		0.5
TiO ₂		31.8	14.3	39.1	11.0		
ZrO ₂		8.5	3.8	11.8	3.3	100	10.0
Mo ₂ O ₃					0.2		

^aComposite Savannah River Plant (SRP) waste with aluminum removal normalized to compensate for removal of zeolite and addition of Ce₂O₃, SrO, and Nd₂O₃.

^bSYNROC-D (~70 wt % composite SRP waste without aluminum removal plus 30 wt % additives).

^c70/30 (~70 wt % composite SRP waste with aluminum removal plus 30 wt % additives).

^d90/10 (~90 wt % composite SRP waste with aluminum removal plus 10 wt % ZrO₂).

APPENDIX B

Table B.1. SiC crystallite size determined by x-ray diffraction

Run number	Coating conditions		Annealing condition		SiC crystallite size (nm)			
	Temperature (K)	H ₂ in diluent ^a gas (mol %)	Temperature (K)	Time (h)	Diffraction line			Standard deviation (nm)
					2 θ 35.7° (111)	2 θ 60.1° (220)	2 θ 72.4° (311)	
52	873	0	b	b	c	c	c	e
60	973	0	b	b	c	c	c	e
82	973	0	b	b	c	c	c	e
"	"	"	973	24	c	c	c	e
"	"	"	1173	3	3.1	4.8	4.1	4.5
"	"	"	1523	3	c	2.6	2.2	12.4
45	1073	0	b	b	c	c	c	e
"	"	"	1073	24	c	6.5	4.3	5.4
"	"	"	1173	3	c	6.0	5.8	5.9
90	1073	8.6	b	b	c	c	c	e
"	"	"	1073	24	c	c	c	e
"	"	"	1173	3	c	4.8	4.7	4.8
76	1073	75.4	b	b	c	c	c	e
75	1073	100	b	b	c	c	c	0.
77b	"	"	1723	3	c	6.0	9.4	27.7
84	1073	0	b	b	c	c	c	1.7
"	1173	0	b	b	d	9.4	8.7	e
"	"	"	1173	24	d	9.4	7.8	9.1
"	"	"	1523	3	d	12.3	10.3	8.6
"	"	"	1723	3	d	19.2	17.2	11.3
89	1180	8.6	b	b	d	10.4	7.8	18.2
"	"	"	1523	3	d	12.3	11.9	9.1
88	1180	75.4	b	b	d	5.2	4.7	12.1
"	"	"	1173	24	5.2	5.1	5.2	5.0
"	"	"	1523	3	11.8	10.2	10.3	5.1
								10.2
								0

Table B.1. (continued)

Run number	Coating conditions		Annealing condition		SiC crystallite size (nm)				
	Temperature (K)	H ₂ in diluent ^a gas (mol %)	Temperature (K)	Time (h)	Diffraction line			Average (nm)	Standard deviation (nm)
					2 θ 35.7° (111)	2 θ 60.1° (220)	2 θ 72.4° (311)		
85	1180	100	b	b	d	3.1	3.1	3.1	0
"	"	"	1173	24	d	3.4	4.9	4.2	0.8
"	"	"	1523	3	d	8.9	10.9	9.9	1.0
"	"	"	1723	3	d	21.2	23.3	22.3	1.1
92	1280	0	b	b	d	9.2	8.5	8.8	0.3
"	"	"	1273	24	d	9.4	8.5	8.9	0.4
"	"	"	1723	3	d	13.6	13.1	13.3	0.2
99	1280	100	b	b	d	3.8	3.7	3.8	0.1
"	"	"	1273	24	d	4.4	4.5	4.4	1
"	"	"	1723	3	d	26.0	27.3	26.7	7

^aDiluent is Ar-H₂ system.

^bNot annealed.

^cNot measurable.

^dInterference with diffraction line from Al₂O₃.

^eAmorphous.

VITA

Peter Angelini was born on December 27, 1945 in Mosciano S'Angelo, Italy. His parents are Joseph and Dolly Angelini who reside in Weirton, West Virginia. He has one brother, Walter, who also resides in Weirton, West Virginia with his family.

He graduated from St. Paul Elementary School, and Madonna High School in Weirton, West Virginia; West Virginia University in 1967 with a Bachelor of Science in Physics; University of Tennessee in 1974 with a Master of Science in Physics; University of Tennessee in 1985 with a Doctor of Philosophy in Metallurgical Engineering.

He accepted a position at the Oak Ridge National Laboratory in 1967 and is a research staff member in the Metals and Ceramics Division. His research areas have been on the processing and determination of physical properties of actinide oxides for radio-isotopic heat sources, sol-gel derived High Temperature Gas-Cooled Reactor fuel, chemical vapor deposition of SiC onto gel-derived particles for the Alternative Nuclear Waste Programs, and transmission electron microscopy of structural ceramics for the Basic Energy Sciences.

He has received two Industrial Research, IR-100, awards, and four U.S. patents. He is a member of the American Ceramic Society, American Society for Metals, and the Electron Microscopy Society of America and is involved in various civic organizations.

He was married to Susan E. Black, daughter of Clifford and Colleen Black of Oak Ridge, in 1969 and has three children, Bibiana, Isabella, and Joseph Angelini. He resides with his spouse and children in Oak Ridge, Tennessee, U.S.A.