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NOVEL PRECURSOR APPROACHES FOR CMC DERIVED BY POLYMER PYROLYSIS

Prepared by

W. R. Schmidt

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13. ABSTRACT *(Maximum 200 words)*

A family of reactive endblocked poly(methylvinylsilane), PMVS, polymers was developed for fabricating fiber-reinforced silicon carbide ceramic matrix composites (CMCs). Control of reaction conditions was optimized to synthesize a baseline PMVS in multiple batches and sufficient quantity to examine modifications of the polymer chemistry during processing and pyrolysis.

The conversion of PMVS to carbon-rich nanocrystalline silicon carbide ceramic was studied using a variety of analytical techniques, including thermal analysis, infrared and nuclear magnetic resonance spectroscopy, X-ray diffraction, and electron microscopy.

The excess C in PMVS ceramic chars was effectively scavenged with an added Si source. Perhydropoly(silazane), PHPS, provided a polymer precursor source of Si_3N_4 and excess Si. Blends of PHPS and PMVS had higher char yields (70-85%) than either component polymer and generated novel nanocrystalline ceramics with heating to 1600 °C. Crystal growth was inhibited in chars derived from these blends. Added elemental Si reacted with the excess C and enhanced crystal growth of SiC above the melting point of Si.

Representative CMCs with good mechanical properties were fabricated using several PMVS-based matrix sources. The CMCs showed load vs. deflection curves typical of non-brittle failure and tensile specimens showed fibrous failure.

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Novel Precursor Approaches for CMC Derived by Polymer Pyrolysis

FINAL TECHNICAL REPORT

Contract F49620-91-C-0017

Reported by Wayde R. Schmidt
Wayde R. Schmidt

Approved by John J. Brennan
John J. Brennan

DATE: 15 February 1994

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I. INTRODUCTION

Current DoD technology thrusts such as the Integrated High Performance Turbine Engine Program depend on the development of high temperature low density materials. Fiber reinforced ceramics are projected to play a major role because of their high temperature capacity and superior mechanical properties on a density normalized basis at elevated temperature. Chemical vapor infiltration (CVI) and hot pressing of powder infiltrated tape materials have been the dominant methods used for fabricating ceramic matrix composites over the last 15 years. However, the high cost of CVI and scaling issues with hot pressing techniques are formidable barriers to widespread application.

More recently, the conversion of preceramic polymers as a matrix synthesis process has been considered. This approach offers several advantages relative to the other processes for the fabrication of ceramic composites. First, a range of useful composite matrices can be prepared based on carbide, oxide and nitride precursors. Second, fillers and other additives may be easily incorporated into the composite, thus enabling the synthesis of multi-phase compositions. Third, reproducible matrix characteristics can be anticipated by controlling polymer chemistry and composite fabrication cycles. Finally, the utilization of preceramic polymers is adaptable to complex shape configurations.

In previous AFOSR-funded activities [1-3], the United Technologies Research Center studied poly(methylvinylsilane) (PMVS) polymers as a family of precursor materials which were amenable to ambient pressure processing of SiC-based ceramic matrix composites (CMCs). While carbon fiber-reinforced composites with impressive mechanical properties were demonstrated using commercially available polymers, careful studies of the matrix chemistry on the microstructural level showed that excess oxygen was absorbed during processing, and pyrolysis products were carbon rich. These characteristics are undesirable from the viewpoint of developing composites with high temperature oxidative stability.

The subject program focused on innovative precursors and novel processing approaches to achieve controlled stoichiometry and microstructures in CMCs. During the first year of the program, PMVS polymers were studied with modifications to reduce the susceptibility to oxygen absorption by removing Si-H containing reagents during the polymer synthesis, and to improve the ceramic char yield by introducing reactive endgroups into the polymer structure [2]. In the second year, a baseline PMVS polymer was prepared based on the first year's work and, in an attempt to optimize the ceramic conversion chemistry, the effects of curing methods, polymer blending, and reactive atmosphere pyrolysis on the ceramic yield and on the composition of the derived ceramic phase were studied [3]. The third and final year of the program, which is the subject of this report, emphasized a detailed examination of the conversion of PMVS to nanocrystalline β-SiC, as well as improvements made to the stoichiometry of the ceramic phase by blending the C-rich PMVS polymer with sources of excess Si which would scavenge the C at high temperatures to form additional SiC.

II. EXPERIMENTAL METHODS

A. General Methods

The polymeric source of C-rich SiC was a reactive endblocked poly(methylvinylsilane), PMVS. This polymer was synthesized by Dr. John Wesson at UTRC using a modified sodium-coupling reaction of the component chlorosilanes [2,3]. It was obtained as a transparent, pale yellow viscous liquid. Perhydropoly(silazane), PHPS, was purchased from Tonen Corporation (product designated as PHPS-1) and used as the polymeric precursor to Si-rich Si_3N_4 in the polymer blending studies. Submicron silicon powder was purchased from Dr. John Haggerty at the Massachusetts Institute of Technology, and used as an alternative source of silicon in blends with PMVS. Blends of PMVS and either PHPS or submicron silicon powder were prepared so that the molar amount of added silicon was equal to the level of excess carbon remaining in the PMVS ceramic char after pyrolysis to 1000 °C. A range of blends, containing several ratios of moles of added Si (from PHPS or submicron Si) per mole of excess C (from PMVS), were prepared to examine the effect of added Si on the thermal behavior and crystallinity of the PMVS ceramic residue. These blend compositions are summarized in Table I. Samples identified as PMVS only, PHPS/PMVS Blend A (Si/C equal to 0), and submicron Si/PMVS Blend Si-0 (Si/C equal to 0) are equivalent.

Polymer synthesis, sample manipulation, and polymer blending were performed in an inert N_2 atmosphere. When practical, samples and blends were prepared and handled in a N_2-filled glovebox, with N_2 purified in-line over an activated copper catalyst and dried over 3 Å molecular sieves. Homogeneous PHPS/PMVS liquid polymer blends were prepared by mechanically mixing appropriate weights of the components. Submicron silicon/PMVS blends were prepared by weighing the appropriate amounts of the components, adding approximately 50 mL of anhydrous ether to dissolve the PMVS, mechanically stirring to homogeneously distribute the silicon powder, followed by removal of the ether by rotary evaporation with applied heat. In this manner, the silicon powder was uniformly coated with viscous PMVS polymer.

TABLE I.

BLEND COMPOSITIONS BASED ON EXCESS CARBON REMAINING IN CHAR FOLLOWING PYROLYSIS OF PMVS TO 1000 °C IN ARGON

PHPS/PMVS BLENDS			SUBMICRON Si/PMVS BLENDS		
Blend Code	*Wt% PMVS*	*Moles of added Si per mole of excess C*	*Blend Code*	*Wt% PMVS*	*Moles of added Si per mole of excess C*
A	100.0	0	Si-0	100.0	0
B	50.0	0.25	Si-2	98.7	0.05
C	33.3	0.50	Si-4	97.6	0.1
D	20.0	1.0	Si-5	94.2	0.25
E	14.4	1.5	Si-6	89.0	0.5
F	11.2	2.0	Si-3	80.2	1.0
G	2.5	10.0	Si-1	61.8	2.5
H	0.0	∞			

Transmission infrared spectra were recorded with a Bruker Model 98 Fourier Transform Infrared (FTIR) Spectrophotometer integrated with OPUS computer hardware and operating software. The FTIR utilized either an evacuated optical chamber coupled with a DTGS detector, or a microscope accessory coupled with a liquid N_2-cooled MCT detector. Both detectors were operated at 2 cm^{-1} resolution. Liquid samples were examined as smears between KBr windows. Preceramic and ceramic solid samples were finely ground, diluted with spectroscopic grade KBr, and pressed as transparent disks. Samples for IR study were transferred from the glovebox to the spectrophotometer in N_2-filled bags to minimize exposure to air and moisture.

Low temperature (20-1000 °C) thermogravimetric analysis (TGA) was performed on the as-synthesized PMVS and various PHPS/PMVS and submicron Si/PMVS blends in flowing argon

(50 cc/min) with a DuPont Instruments integrated 9900 Computer/Thermal Analyzer configuration using a Model 951 Thermogravimetric Analyzer. Typical heating rates were 2, 5, or 10 °C/min. Simultaneous TGA/DTA (differential thermal analysis) experiments were performed on the 1000 °C ceramic char materials by Mr. Ed Whalen at Harrop Industries, Columbus, Ohio. Experiments were run on these samples from 20-1600 °C in either flowing argon or nitrogen at a heating rate of 10 °C/min. Residues (1600 °C) from these experiments were returned to UTRC for further characterization by X-ray diffraction, TEM, and solid state NMR analytical techniques.

X-ray powder diffraction (XRD) specimens were prepared by finely grinding the samples in either an alumina or boron carbide mortar and pestle. Ground powders were placed on a low background specimen holder which had been lightly coated with petroleum jelly. Diffraction measurements were obtained using Cu Kα radiation with a SIEMENS D500 diffractometer, equipped with a diffracted beam monochromator, and operated at 40 kV and 20 mA. Data were digitally recorded in a step scan from 2Θ values of 10 to 80°, with a count time of 1.5 seconds at each step. A 0.05° receiving slit and a 1° divergence slit were used for all data. Digitized data were plotted as connected scatter plots using Jandel Scientific's Sigmaplot Software.

Scanning electron microscopic (SEM) examination was performed on the ceramic matrix composite samples using an AMRAY 1850 Field Emission Microscope operating from 5-20 keV. Samples were coated with carbon prior to examination to minimize charging. Powder samples for transmission electron microscopic (TEM) examination were finely ground and collected on holey carbon film (Pella #132 Lacey Carbon Film) prior to analysis. Samples were examined using an EM 400T Transmission Electron Microscope, operating at an accelerating voltage of 120 keV, at magnifications of 10,000-130,000X. Documentation of particle microstructures was performed at 60,000X using bright-field/dark-field techniques. Selected Area Electron Diffraction (SAED) and Energy Dispersive X-ray Spectroscopy (EDS, Kevex Delta 4 Model) were employed when necessary. Only particles that were both representative of the general morphology of the powder sample and transparent to the electron beam were chosen for TEM study.

B. NMR Methods

Solid state NMR experiments were performed on a Chemagnetics CMX instrument operating at 71 MHz for ^{29}Si and 90 MHz for ^{13}C. All spectra are reported relative to tetramethylsilane (TMS). 90° pulse widths were 6 μseconds. Single pulse experiments were performed with 30° pulses and 15 second repetition times during signal averaging to overcome long spin-lattice relaxation times. Cross-polarization spectra were obtained with a contact time of 5 milliseconds and spin-locking fields of 42 kHz. Samples were stored and packed in PENCIL rotors in a glove box under N_2. All experiments were performed with magic angle spinning (MAS) at speeds in the vicinity of 4 kHz with N_2 as the drive gas. Cyclops phase cycling was used in all experiments. All single pulse ^{13}C spectra were performed with background subtraction to remove signals from probe polymer materials.

C. Pyrolysis Methods

The conversion of polymeric PMVS to SiC-containing ceramic was studied by heating portions of PMVS to various temperatures and characterizing the intermediate samples by FTIR, NMR, TEM and XRD techniques. For pyrolysis experiments to 1000 °C, portions of polymer were poured into fused silica boats, loaded into an "O" ring-sealed fused silica furnace tube equipped with gas inlet and outlet valves, sealed by clamping, and placed in a programmable Lindberg furnace. Samples were heated at a rate of 2 °C/min in purified/dried flowing argon, held at 200, 400, 600, 800, or 1000 °C for 1 hour, cooled at 2 °C/min in flowing argon, and removed and stored in the glovebox prior to analysis. Portions of PMVS, previously pyrolyzed at 1000 °C in argon, were heated further to 1200, 1400, or 1600 °C in argon in a molybdenum foil-lined alumina boat within an alumina tube. All PMVS blend samples were pyrolyzed to 1000 °C for 1 hour and cooled in argon at heating and cooling rates of 2 °C/min. Portions of the resulting chars were submitted for simultaneous TGA/DTA analysis by Harrop Industries, XRD, and solid state NMR study.

D. Composite Fabrication Methods

Ceramic matrix composites with different matrix compositions were fabricated using the Polymer Impregnation-Pyrolysis (PIP) process. The composite sample codes and the corresponding matrix sources were: (1) AF-93-01, as-synthesized PMVS; (2) AF-93-02, PHPS/PMVS Blend D; and (3) AF-93-03, submicron Si/PMVS Blend Si-3. The blended samples were chosen so that the amount of added Si was approximately equal to the stoichiometric level of excess C (Si/C equal to 1.0, Table I). Three 7.9 cm by 4.1 cm CMCs with 12 plies of BN-coated Nicalon™ Si-C-O fiber in a plain weave architecture were fabricated using the following process:

STEP 1: Fiber cloth was prepregged by painting the cloth with a solution/dispersion containing the appropriate matrix source in approximately 60 mL of anhydrous ether, followed by evaporation of the solvent;

STEP 2: Prepregged fiber cloth plies were stacked in a die, vacuum bagged, and press-cured with gradual heating to 300 °C;

STEP 3: Cured "green" composites were pyrolyzed in flowing argon to 1000 °C at a heating rate of 2 °C/min, held at 1000 °C for 1 hour, and cooled in argon at a rate of 2 °C/min;

STEP 4: Pyrolyzed composites were re-infiltrated with the appropriate polymer matrix source under vacuum, and cured in an autoclave under 100 psi overpressure of N_2 at 300 °C;

STEP 5: Infiltrated composites were re-pyrolyzed to 1000 °C in argon;

STEPS 4 AND 5 WERE REPEATED FOR A TOTAL OF 5 PYROLYSIS CYCLES.

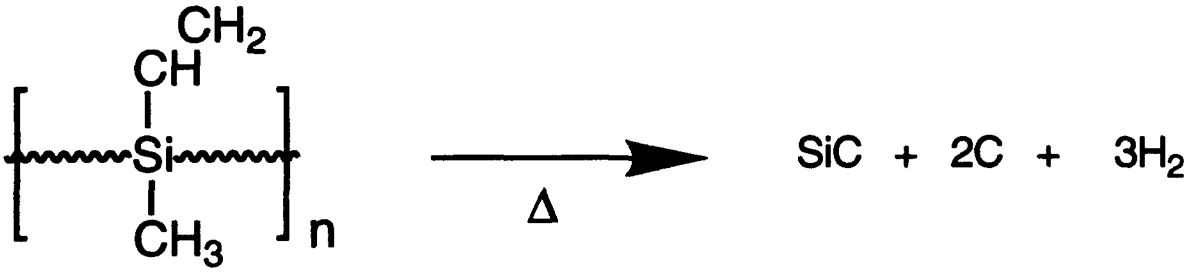
E. Mechanical Test Methods

Fabricated composite panels were machined into parallel-sided samples approximately 7.9 cm long by 0.75 cm wide by 0.33 cm thick for three-point flexural and tensile testing. Flexural tests were performed in air at either 22 °C or 1000 °C, using a lower span of 6.35 cm and a crosshead rate of 0.127 cm/min. Strains were measured with a deflectometer. Tensile tests were performed in air at 22 °C using a gauge length of 1.27 cm and a crosshead rate of 0.127 cm/min. Strain measurements were made using an extensometer.

III. RESULTS

A. Conversion of PMVS to C-rich SiC

Poly(methylvinylsilane), PMVS, has the approximate formula $[\text{Si(CH=CH}_2\text{)CH}_3]_n$, and theoretically converts to SiC, excess carbon, and hydrogen gas with heating according to Reaction 1:



$$\left[\text{Si}(\text{CH=CH}_2)(\text{CH}_3)\right]_n \xrightarrow[\Delta]{} \text{SiC} + 2\text{C} + 3\text{H}_2$$

REACTION 1

Although elemental analysis has shown that PMVS produces excess carbon following pyrolysis [2,3], the actual conversion process of polysilanes containing vinyl and methyl functionality is known to be quite complicated [4,5]. The thermogravimetric analysis curve of PMVS (Figure 1), shows two major regions of weight loss: (1) 50-150 °C, where approximately 5% of the original sample weight was lost; and (2) 350-700 °C, where an additional 50% of the original weight was lost, resulting in a final ceramic char yield of approximately 45%.

Samples of PMVS that were isolated at intermediate temperatures between 200 °C and 1600 °C varied in both appearance and chemical structure. The samples ranged in morphology from a clear viscous liquid (PMVS) to brittle, black glassy solids (PMVS heated from 1000-1600 °C). Table II summarizes the appearance of the isolated PMVS samples.

TABLE II.

SAMPLE MORPHOLOGY OF PMVS PYROLYZED TO VARIOUS TEMPERATURES IN ARGON FOR 1 HOUR

Maximum Pyrolysis Temperature	*Description of Sample Morphology*
25 °C (as synthesized)	transparent, pale yellow viscous liquid
200 °C	translucent, white rubbery solid
400 °C	nonporous, yellow glassy solid
600 °C	nonporous, orange/brown glassy solid
800 °C	nonporous, brown/black glassy solid
1000 °C	nonporous, black glassy solid
1200 °C	nonporous, black glassy solid
1400 °C	nonporous, black glassy solid
1600 °C	nonporous, black glassy solid

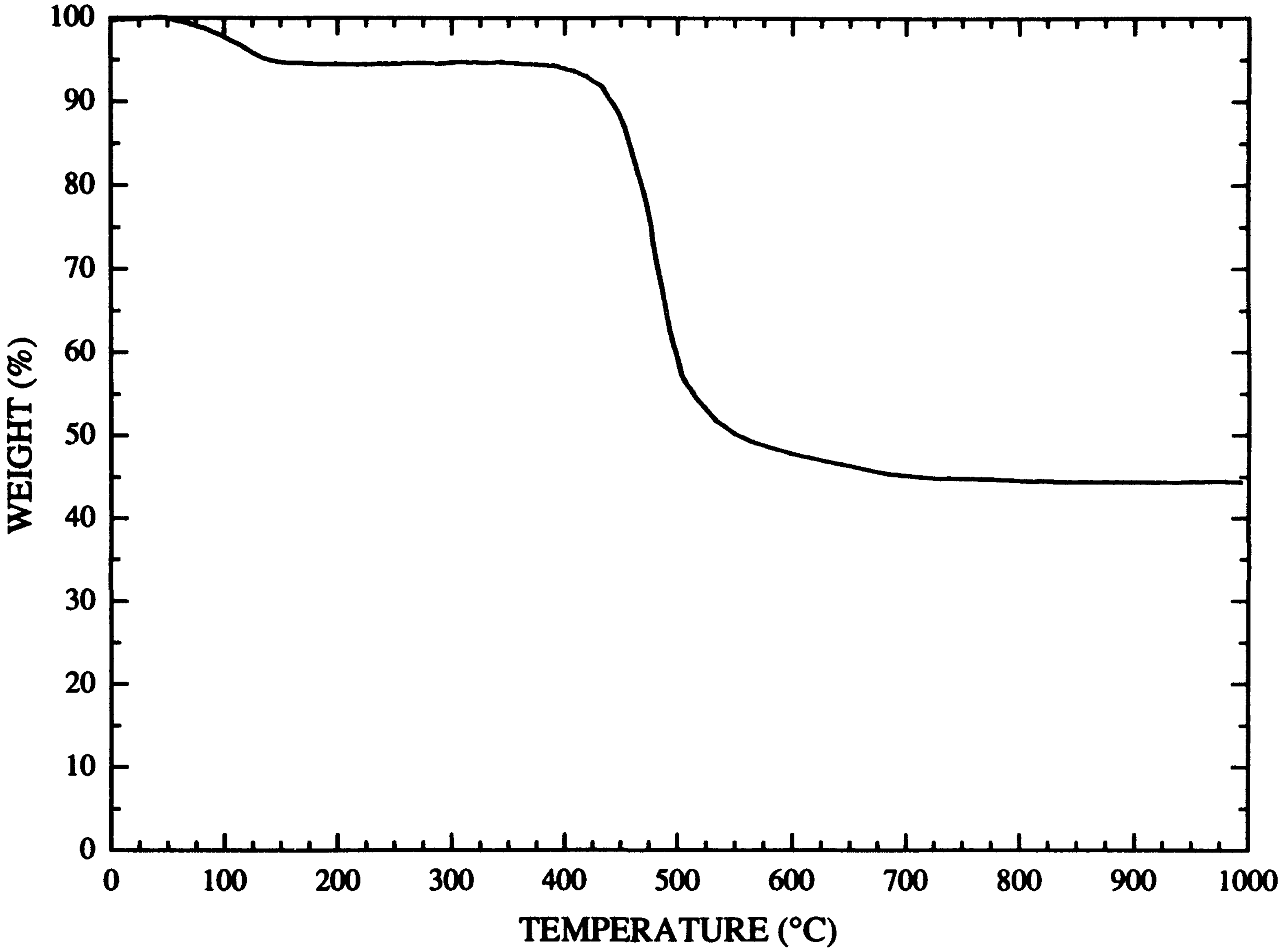


Figure 1. Thermogravimetric Analysis Curve of PMVS Heated in Argon at 2 °C/min.

Changes in the chemical structure of PMVS during the polymer-to-ceramic conversion were examined by FTIR and NMR spectroscopy. FTIR spectroscopy provided a means to identify changes in the types and relative amount of specific functional groups in the polymer, based on the location and intensity of vibrational bands in the spectra. NMR spectroscopy was used as a complementary analytical technique to probe the types of bonding environments around specific nuclei, especially ^{13}C or ^{29}Si. Figure 2 shows a series of infrared spectra for the PMVS samples heated to various temperatures. The presence of a broad band between 3200 cm^{-1} and 3400 cm^{-1} in some spectra can probably be attributed to the absorption of water on the preceramic samples due to handling [4,6]. On heating to 200 °C, there is a decrease in the intensity of peaks associated with vinyl functionality (3048 cm^{-1}, asym. $=CH_2$; 1397 cm^{-1}, $SiCH=CH_2$ deform.) [4], and a broadening of the band associated with $Si\text{-}CH_2\text{-}Si$ bonding (1048 cm^{-1}) [4]. The spectrum obtained following further heating of the sample to 400 °C shows the absence of vinyl functionality, a greatly broadened C-H stretching band (3200-2800 cm^{-1}), and the presence of a new broad peak, indicative of Si-H bonding (2078 cm^{-1}) [4]. Additional heating to 600 °C causes the peaks attributed to C-H and Si-H bonding to decrease in intensity, and the large number of peaks from 1100-500 cm^{-1} to condense into two major bands. At 800 °C, the IR spectrum indicates that most of the C-H and Si-H functionality are gone. By 1000 °C, the presence of a single strong band characteristic of the Si-C stretch (centered near 800 cm^{-1}), indicates that SiC ceramic was formed [4,7].

Solution and solid state ^{13}C and ^{29}Si NMR spectroscopic techniques were used to examine spectral changes, as a function of temperature, of samples isolated during the conversion of PMVS to SiC ceramic. Figure 3 shows a series of ^{13}C solid state MAS NMR spectra for samples of PMVS pyrolyzed from 200-1000 °C. For specific peak assignments, an asterisk (*) preceding an atom is used to identify that atom which generates a particular peak in the spectrum. A methyl group, $-CH_3$, is abbreviated as Me. The ^{13}C spectrum of the 200 °C sample shows two sharp resonances indicative of vinyl groups ($R_3Si{*}CH={*}CH_2$) centered near 131.7 and 139.3 ppm, and a major peak from a variety of methyl functionality from 1 to -10 ppm ($RSi{*}Me_3$ end groups from 1 to -2 ppm; mixture of $R_3SiSi({*}Me_2)SiR_3$ and $R_2Si(CH=CH_2){*}Me$ groups from -5 to -10 ppm) [4,8]. A small peak near 11 ppm is attributed to a poly(carbosilane) fraction, $R_3Si\text{-}{*}CH_2CH_2\text{-}SiR_3$ [4]. The spectrum of the sample heated to 400 °C shows no indication of remaining vinyl functionality. An increase in the intensity of the peak near 11 ppm indicates that the amount of poly(carbosilane) fraction has increased slightly, while the resonance due to the methyl functionality has broadened slightly and shifted to 0.8 ppm. Further heating to 600 °C causes the spectral peaks to coalesce into a broad peak now located at 3.8 ppm, between the original positions of the poly(carbosilane) peak and the methyl-functionality peaks. Spectra of samples heated at 800

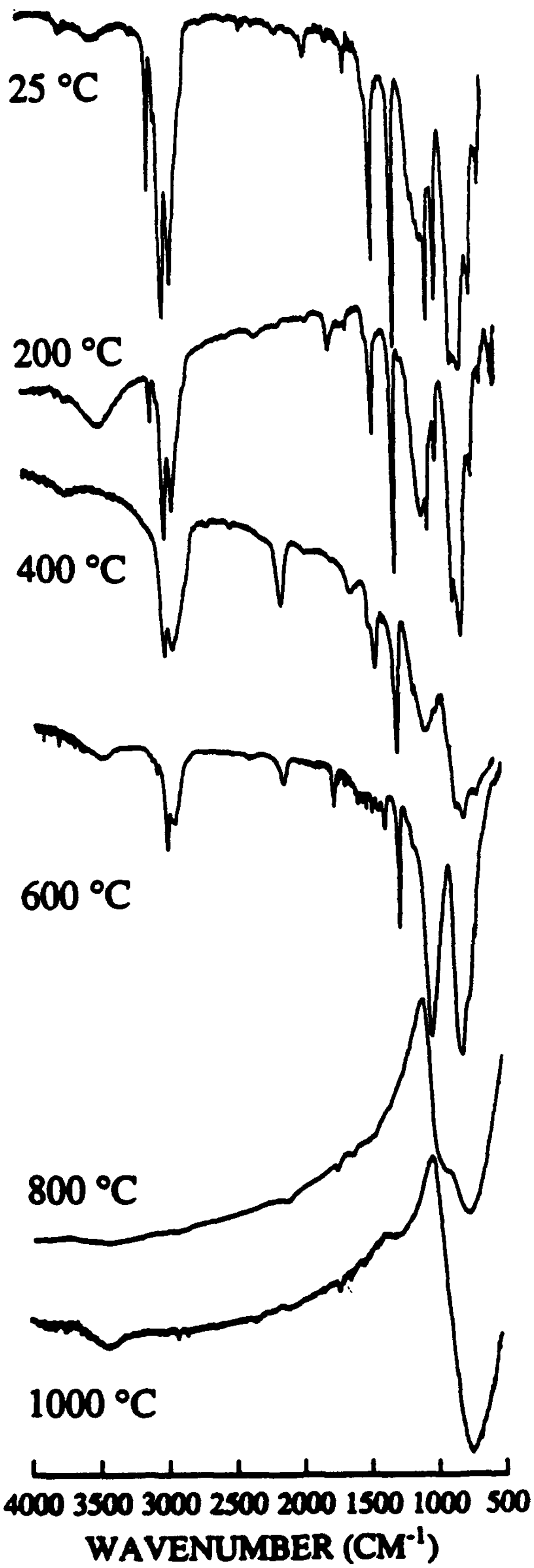


Figure 2. **Transmission Infrared Spectra of Isolated PMVS Samples Heated in Argon to Various Temperatures.**

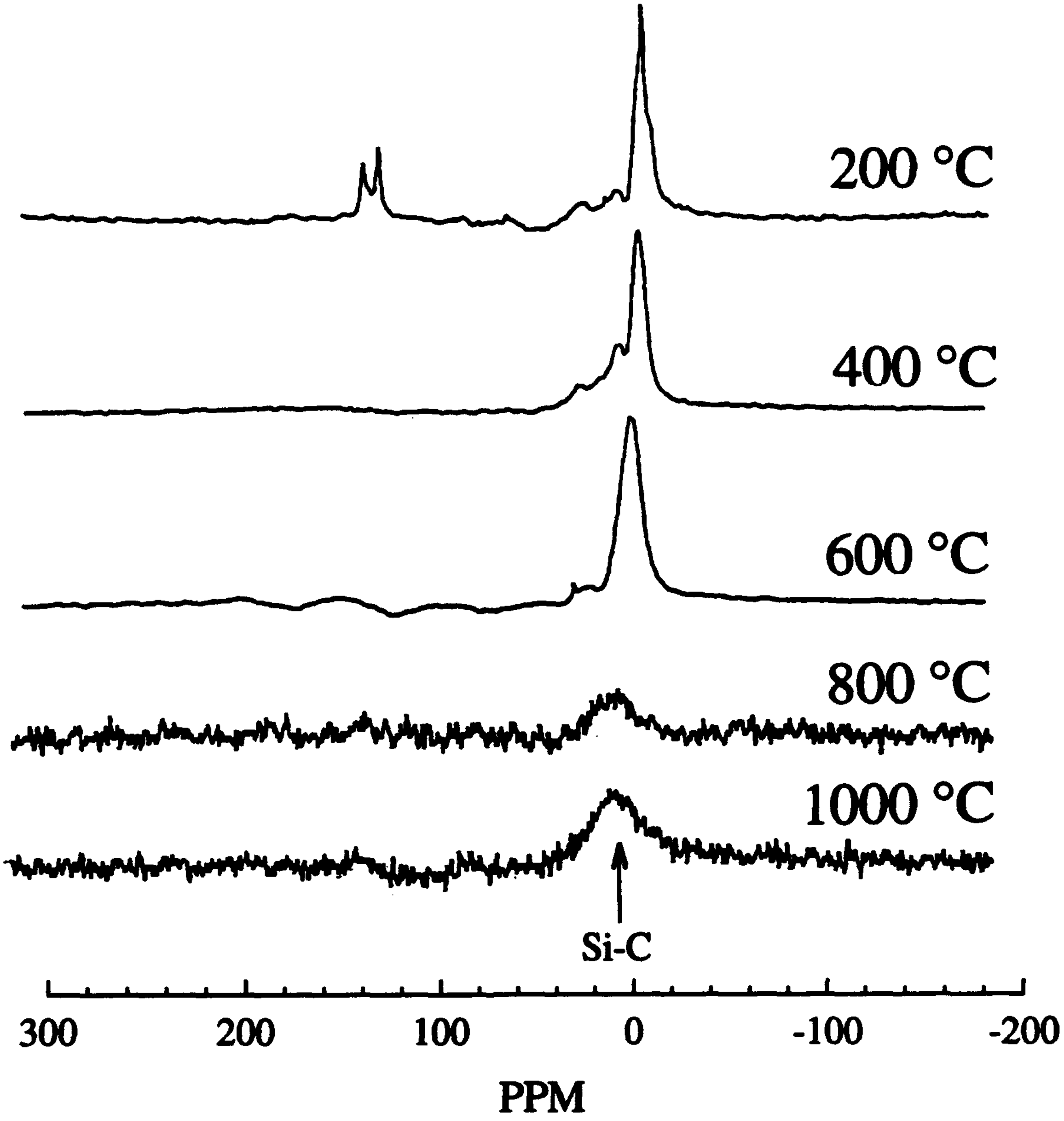


Figure 3. Solid-state ^{13}C MAS NMR Spectra of Isolated PMVS Samples Heated in Argon to Various Temperatures.

°C and 1000 °C show a single, broad peak with significantly reduced intensity, centered near 15.8 ppm. With further heating from 1200 °C to 1600 °C (not shown), this peak continues to broaden and it shifts from 17.5 ppm at 1200 °C to 19.6 ppm at 1600 °C. A single, main peak near 20 ppm confirms the formation of crystalline SiC [4,9-11].

The solid state ^{29}Si MAS NMR spectra of PMVS isolated after heating from 200-1000 °C show a similar series of changes in the types of silicon environments (Figure 4). After heating at 200 °C, the relatively large number of peaks in the spectrum indicate a wide variety of different silicon environments. These peaks can be attributed to the following silicon types: (1) $R_3Si{*}Si(Me_2)SiR_3$, $R_3Si{*}Si(CH{=}CH_2)MeSiR_3$, and extended $-({*}SiMe_2)_n-$ chains from -40 to -55 ppm; (2) $R_3Si{*}SiMe_3$ end groups from -10 to -20 ppm; and (3) $Me_3{*}SiCH_2Si(Me_2)SiR_3$ poly(carbosilane) units and extended $-(CH_2)_n-$ chains from 20 to 0 ppm [4,8]. Spectra of samples heated from 400 °C to 1000 °C show a reduction in the types of silicon environments, with a single, broad peak remaining above 600 °C. Although the peak centered at -4.3 ppm is relatively broad in the 800 °C spectrum, the peak sharpens and shifts to lower frequencies with increased processing temperature, finishing near -15.9 ppm in the spectrum of the sample heated to 1600 °C. This value is in good agreement with the reported values of -18 ppm for the single peak of β-SiC and -14, -20, and -25 ppm for the three peaks observed for α-SiC [4,9,10,12,13].

X-ray powder diffraction measurements suggest that PMVS samples heated to 800 °C or 1000 °C for 1 hour in argon are essentially amorphous (Figure 5). With increased heating to 1200 °C, three broad peaks are evident near 2Θ values of 36°, 61° and 72°, which correspond to the (111), (220), and (311) planes of β-SiC, respectively. Further heating to 1400 °C and 1600 °C causes these peaks to sharpen significantly. The average crystal size was calculated from peak broadening measurements of the peak for the (111) plane, using the Scherrer formula [14]. The inset plot in Figure 5 shows that crystal size gradually increases with higher processing temperature; from about 1 nm at 800 °C to 4 nm at 1400 °C. Heat treatment at 1600 °C causes a further increase in the average crystal size to nearly 20 nm. An additional broad peak, centered near a 2Θ value of 25°, is evident in the diffraction patterns of PMVS heated to 1400 °C and 1600 °C. This peak is attributed to the presence of poorly crystalline graphitic carbon in the ceramic char.

TEM examination of PMVS samples that were heated to 1000 °C and 1600 °C for 1 hour in argon shows a homogeneous distribution of equiaxed, nanometer-sized crystals. Representative dark-field photomicrographs of these samples, with the corresponding SAED patterns, are shown

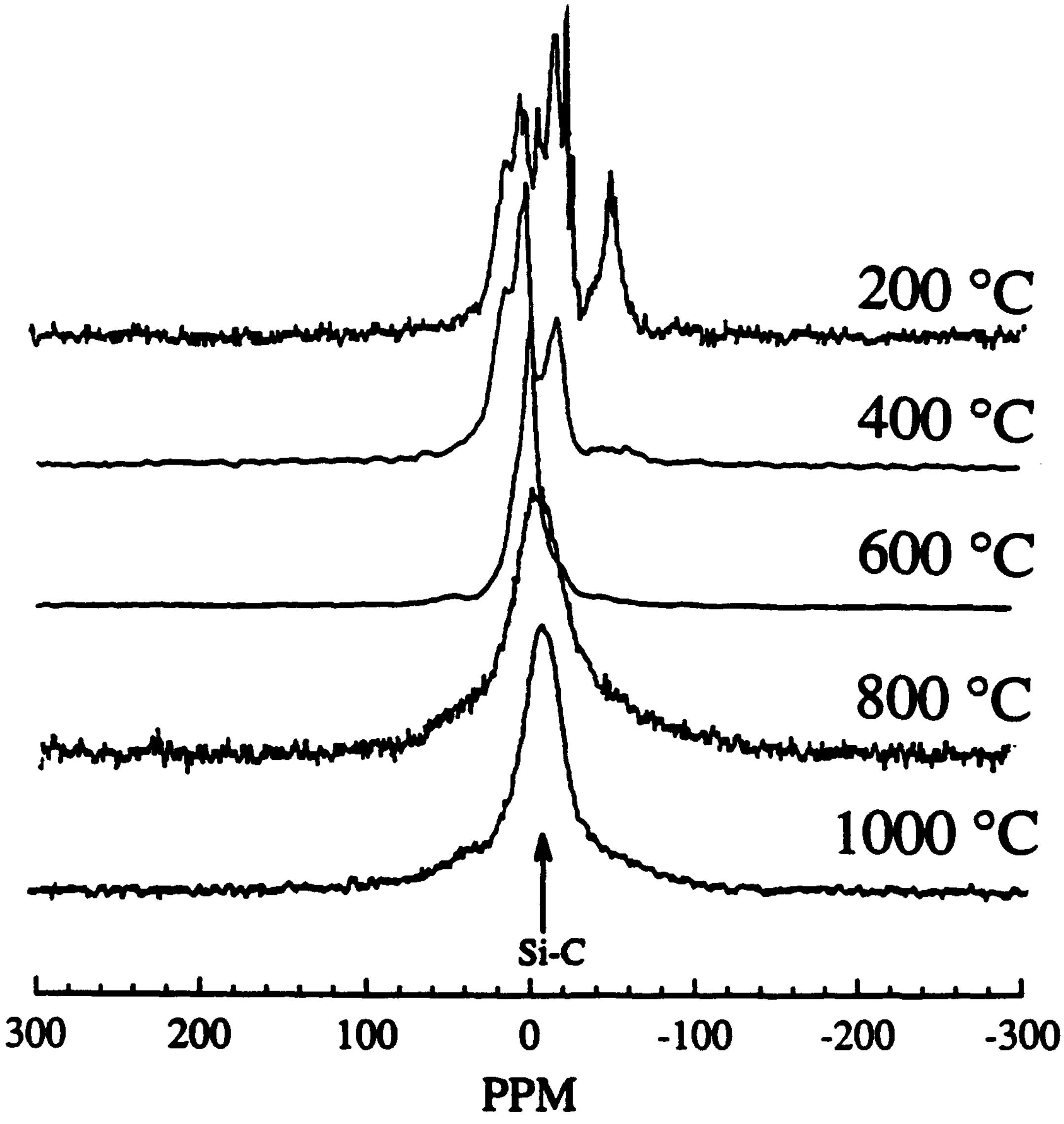


Figure 4. **Solid-state ^{29}Si MAS NMR Spectra of Isolated PMVS Samples Heated in Argon to Various Temperatures.**

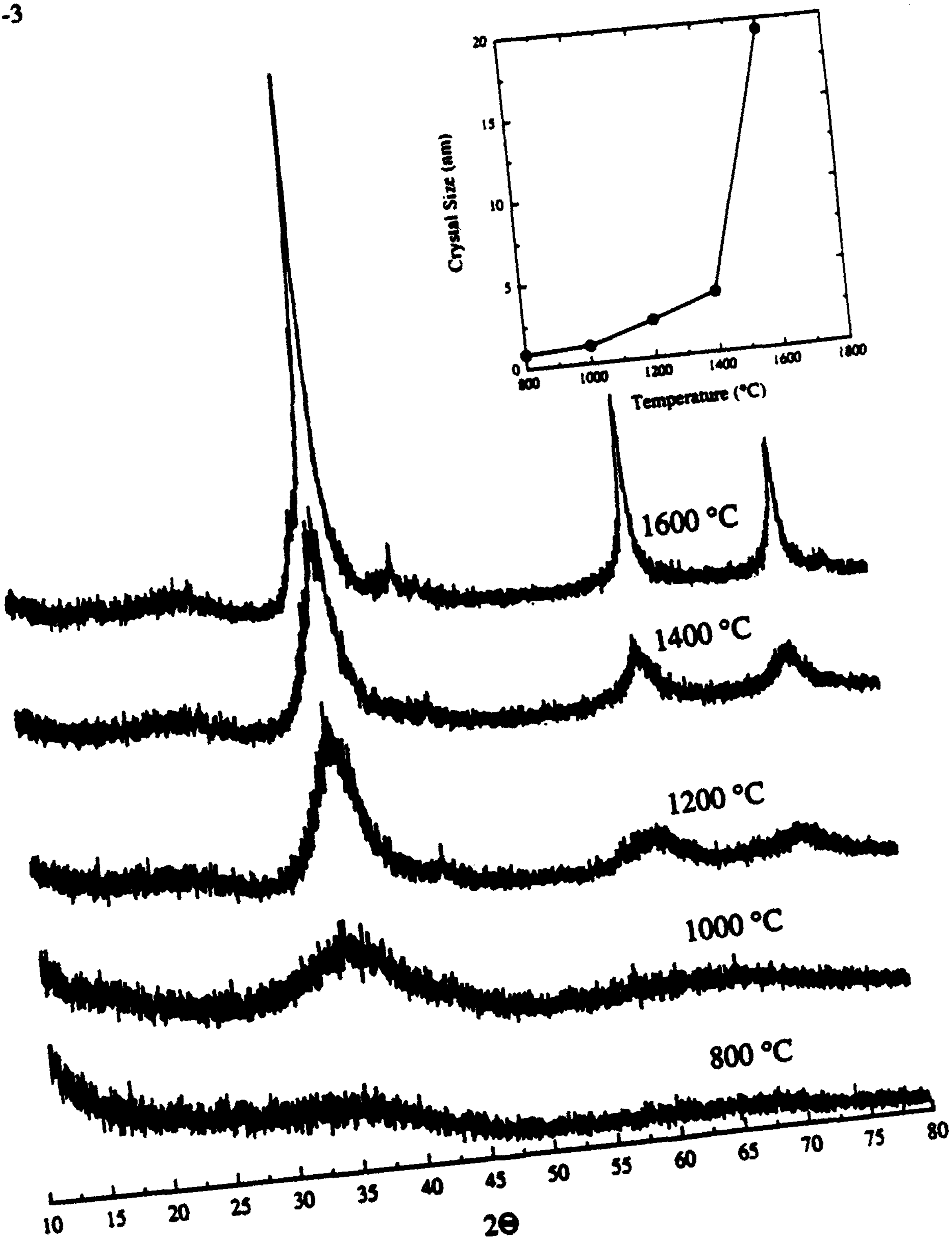
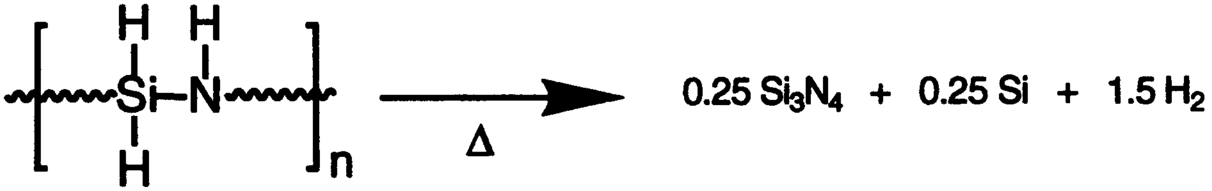


Figure 5. X-ray Diffraction Patterns of PMVS Heated in Argon to Various Temperatures for 1 Hour. Inset Plot Shows the Dependence of Crystal Size on Temperature.

in Figure 6. The measured sizes of typical crystal grains are consistent with X-ray diffraction measurements of peak broadening (Figure 5, inset plot). Electron diffraction patterns for the observed crystal orientation were indexed to the major planes of β-SiC. A comparison of the SAED images of samples heated to either 1000 °C or 1600 °C shows that the electron diffraction lines for the 1600 °C sample are significantly sharper and the intensity of the amorphous halo is lower.

B. Blending Studies of PHPS with PMVS

In an effort to convert the excess C produced during the pyrolysis of PMVS to additional SiC ceramic, perhydropoly(silazane), PHPS, was added as a source of excess Si. PHPS has an average structure of $[SiH_2NH]_n$, and theoretically decomposes in an inert atmosphere to Si-rich Si_3N_4 with loss of volatile hydrogen gas according to Reaction 2:



REACTION 2

Thermogravimetric analysis curves of PMVS, PHPS, and blends of the two polymers heated at 2 °C/min in argon are shown in Figure 7. The PHPS used in this study shows a single, gradual weight loss over the temperature range 100-400 °C, with a final ceramic char yield of 57%. In comparison, each blend of PHPS and PMVS shows a complex weight loss behavior from 20-500 °C, which appears to contain aspects of both the PHPS and PMVS TGA curves. The char yields of the PHPS/PMVS blends range from 70-82%, depending on the relative ratio of added Si to excess C (Table I), and are significantly higher than the char yields of either component polymer.

The as-received PHPS polymer was analyzed by liquid ^{13}C and ^{29}Si NMR spectroscopy. No carbon peaks were observed in the ^{13}C spectrum, which is consistent with the absence of C in the base structure of the polymer (Reaction 2). The ^{29}Si spectra (not shown) have a major peak centered near -33.6 ppm and a minor peak near -49.5 ppm. The presence of two peaks indicates that there are two types of chemically distinct Si environments in the polymer structure.

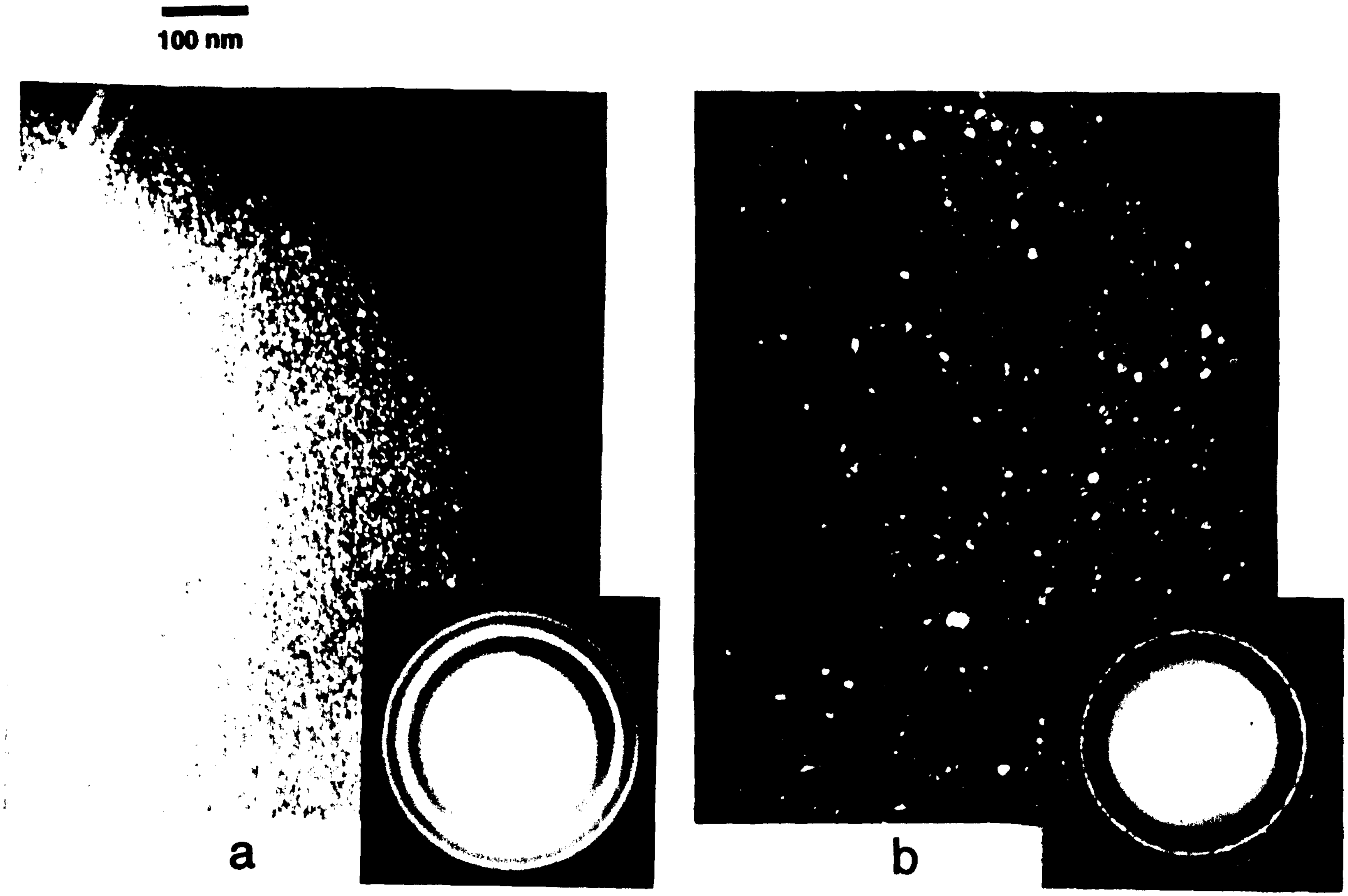


Figure 6. Dark Field Transmission Electron Micrographs of PMVS Heated in Argon to a) 1000 °C or b) 1600 °C for 1 Hour,

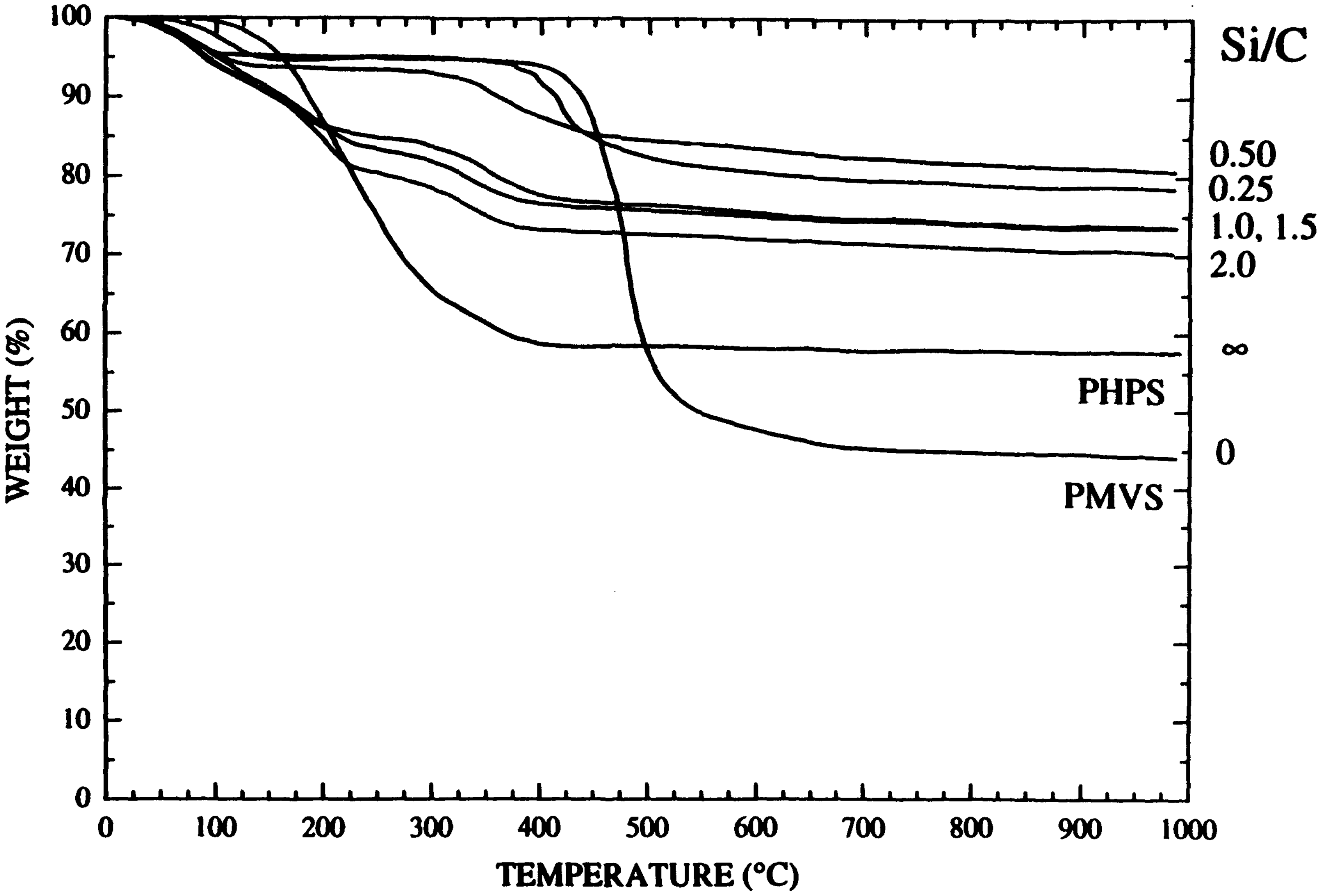


Figure 7. Thermogravimetric Analysis Curves of PHPS, PMVS, and PHPS/PMVS Blends (Table I) Heated in Argon at 2 °C/min.

Solid state ^{13}C MAS NMR spectra of the PHPS/PMVS blends heated to 1600 °C in argon in the DTA experiments (not shown) consist of single peaks, centered near 22 ppm, for the C environment expected in SiC [4,9-11]. The peak is relatively sharp for Blend A (PMVS only), but broadens, and the peak shifts toward 26 ppm as the amount of PHPS is increased in Blends B-F. The spectrum of Blend H (PHPS only) shows no peak, which is consistent with the absence of carbon in that sample.

A series of solid state ^{29}Si MAS NMR spectra are shown in Figure 8 for the PHPS/PMVS polymer blends which were heated to 1000 °C in argon (Table I). Each spectrum contains one broad main peak, although the spectra from Blends B-F show evidence of a smaller shoulder on the upfield side (more negative ppm values) of the main peak. The position of the peak maximum for the major peak gradually shifts upfield from -9.1 ppm in the spectrum of Blend A (PMVS only) to nearly -50 ppm for Blend H (PHPS only). The shift of the peak position can be directly correlated with a change in the composition of the blend; from an amorphous SiC environment in PMVS [4,9,10,12,13] to amorphous Si_3N_4 in PHPS [15,16]. PHPS/PMVS Blends B-F show intermediate peak positions which are consistent with the presence of silicon in a mixed Si_3N_4/SiC environment.

PHPS/PMVS blend residues from the DTA experiments to 1600 °C were also examined by solid state ^{29}Si MAS NMR spectroscopy. Figure 9 shows a series of spectra for these samples. In general, these spectra contain significantly sharper peaks than those obtained from the corresponding 1000 °C samples (Figure 8), an indication of the increased crystallinity in the samples heated to 1600 °C. The presence of multiple peaks in the spectra of Blends D, E, and F suggests that phase separation into SiC (-17 ppm) and Si_3N_4 (-48 ppm) environments occurred. The intensity of the peak at -48 ppm increases with an increase in the amount of PHPS in the original blend (i.e. as the Si/C ratio increases in Table I). The spectrum of Blend H (PHPS only, not shown) has an additional sharp peak near -80 ppm, due to the presence of elemental Si.

Differential thermal analysis was used to examine the high temperature behavior of the PHPS/PMVS blend samples in argon. Figure 10 shows the resulting series of DTA curves for Blends A-H with the ratio of added Si to excess C increasing from 0 (PMVS only) to ∞ (PHPS only). The curve for PMVS shows a broad peak from 1000-1200 °C, indicating a sluggish exothermic event. This exotherm is attributed to the crystallization of the PMVS and associated reconstruction of the matrix following loss of residual hydrogen and carbon during the pyrolytic conversion of the polymer. The curve for the PHPS sample, on the other hand, shows a very

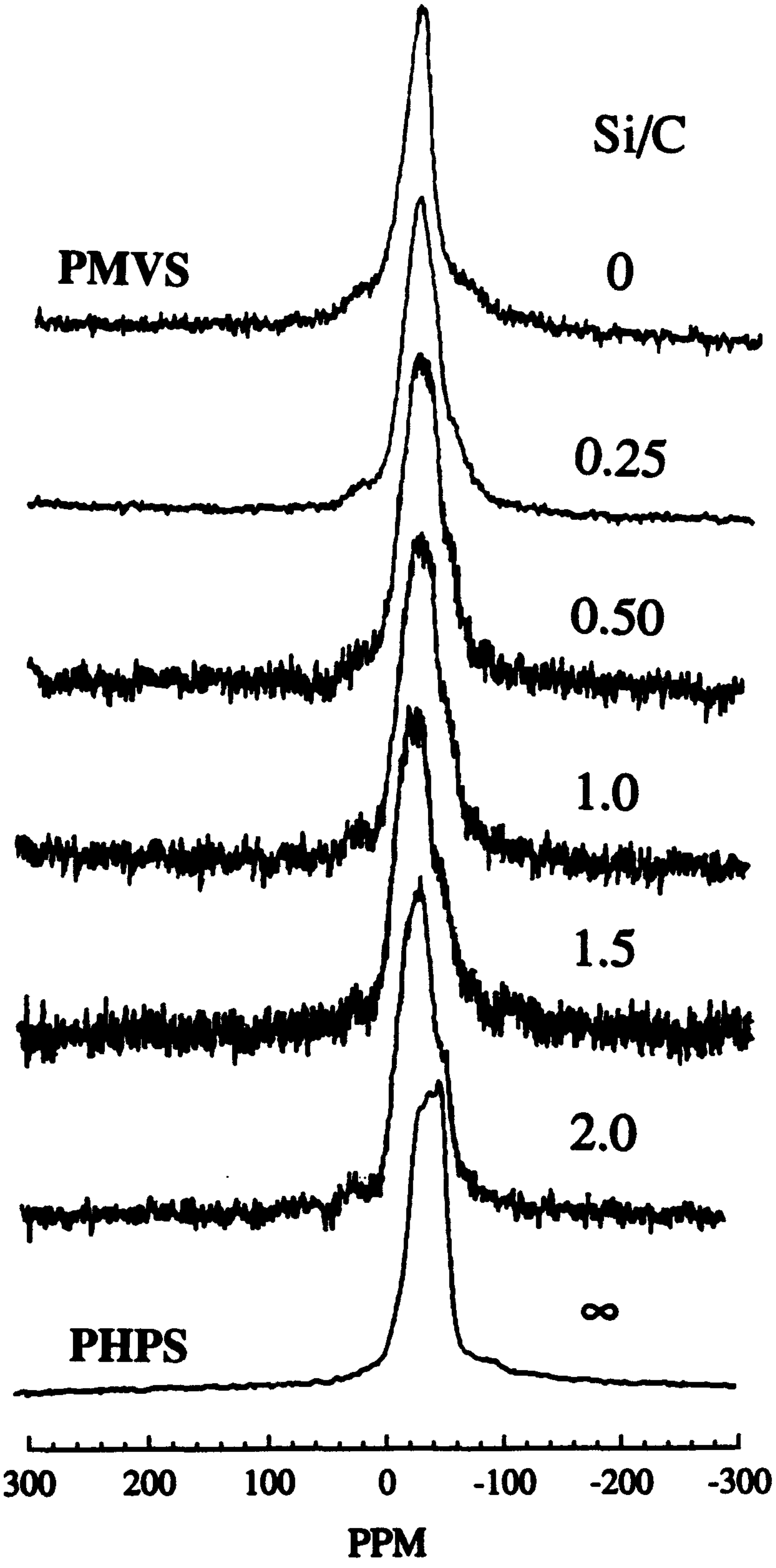


Figure 8. **Solid-state ^{29}Si MAS NMR Spectra of PHPS/PMVS Blends (Table I) Heated to 1000 °C in Argon for 1 Hour.**

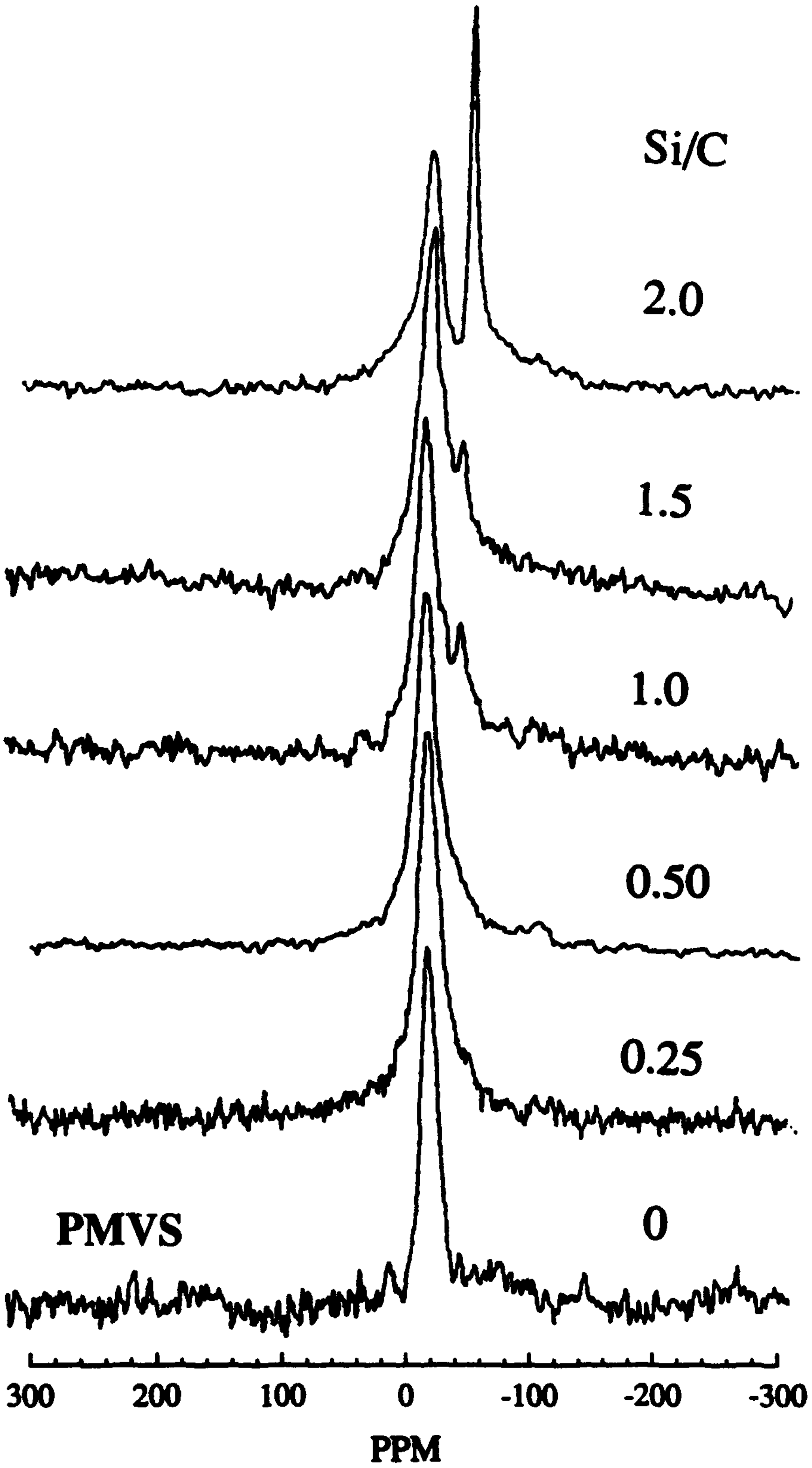


Figure 9. Solid-state ^{29}Si MAS NMR Spectra of PHPS/PMVS Blends (Table I) Heated to 1600 °C in Argon in the DTA Experiments.

sharp exothermic event near 1350 °C, followed by a minor endothermic event centered near 1450 °C. The former is consistent with the crystallization of the Si_3N_4 ceramic, while the latter is due to the melting of the excess Si remaining in the sample following conversion of the polymer precursor. As the relative amount of PHPS is increased in the blend the thermal profile of the samples changes. An increase in the ratio of added Si to excess C from 0 to 0.25, causes two broad exothermic peaks to appear. For ratios ranging from 0.5 to 1.5, one small exothermic peak is evident in each curve, which decreases in area with an increase in the Si/C ratio, and the peak maximum shifts to nearly 1400 °C. A further increase in the Si/C ratio to 2.0 causes a significant increase in the intensity and a broadening of the exothermic peak. This peak is similar to that seen for the crystallization of Si_3N_4 for PHPS only, but the endotherm due to Si melting is not apparent.

The X-ray powder diffraction patterns of the PHPS/PMVS blend samples, heated to 1000 °C in argon for 1 hour, indicate that these materials are poorly crystalline (Figure 11). As the relative weight percent of added PHPS in the blend increases from 0% (PMVS only) to 100% (PHPS only), the ratio of added Si (from PHPS) to excess C (from PMVS) increases from 0 to ∞, and the major peak in the diffraction pattern shifts from a 2Θ value of 35° to a broad hump covering the range of 20°-40°. The sharp, relatively small peaks in some of the diffraction patterns are due to contamination by the grinding media.

PHPS/PMVS blend samples that were heated in the simultaneous TGA/DTA experiments to 1600 °C in argon are significantly more crystalline than the samples heated to only 1000 °C. The X-ray powder diffraction patterns of the 1600 °C samples are shown in Figure 12. The diffraction pattern for PMVS shows the three major diffraction peaks expected for β-SiC as reported in Section III-A. As the relative amount of added PHPS increases (i.e. the Si/C ratio increases from 0 to 1.5; Blends A-E), the extent of crystallinity appears to decrease, as suggested by reduced diffraction peak intensity and peak broadening. At Si/C ratios of 1.0 and 1.5 (Blends D and E, respectively), small peaks are present near 30° and 38°, which continue to sharpen and increase in intensity as the Si/C ratio increases. When the Si/C ratio has reached 2.0 (Blend F), a diffraction pattern suggestive of a mixture of β-SiC, α-Si_3N_4 (major phase), and perhaps some β-Si_3N_4 is obtained. No peaks suggestive of elemental silicon are present in this pattern. Conversely, when PHPS only (Si/C ratio is ∞) is heated to 1600 °C, the resulting X-ray pattern shows sharp peaks for the three major expected diffractions of elemental Si near 2Θ values of 28°, 47.5° and 56° and an additional peak pattern that is consistent with crystalline α-Si_3N_4 [17].

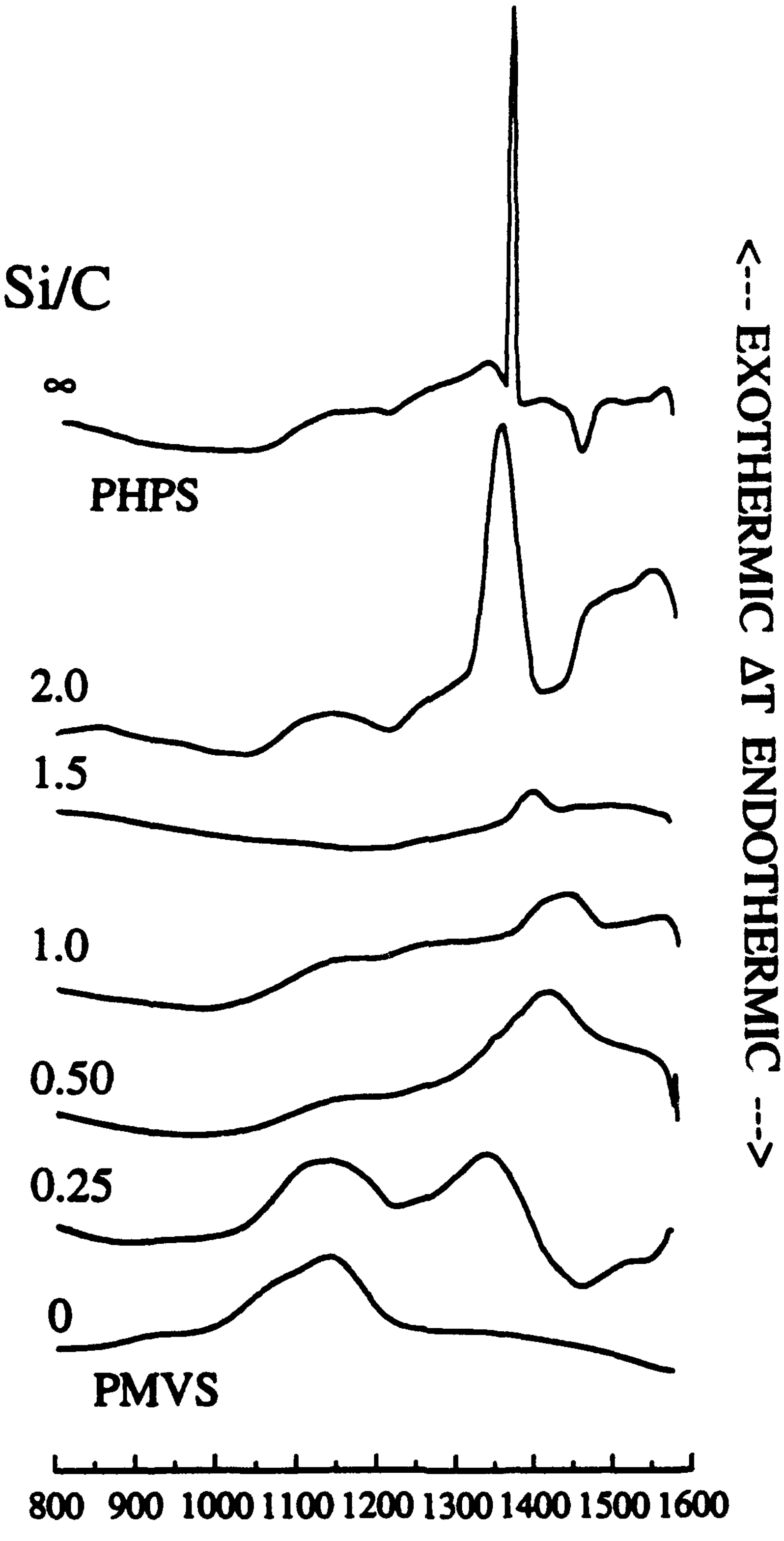


Figure 10. Differential Thermal Analysis Curves for PHPS/PMVS Blends (Table I) Initially Heated to 1000 °C in Argon for 1 Hour.

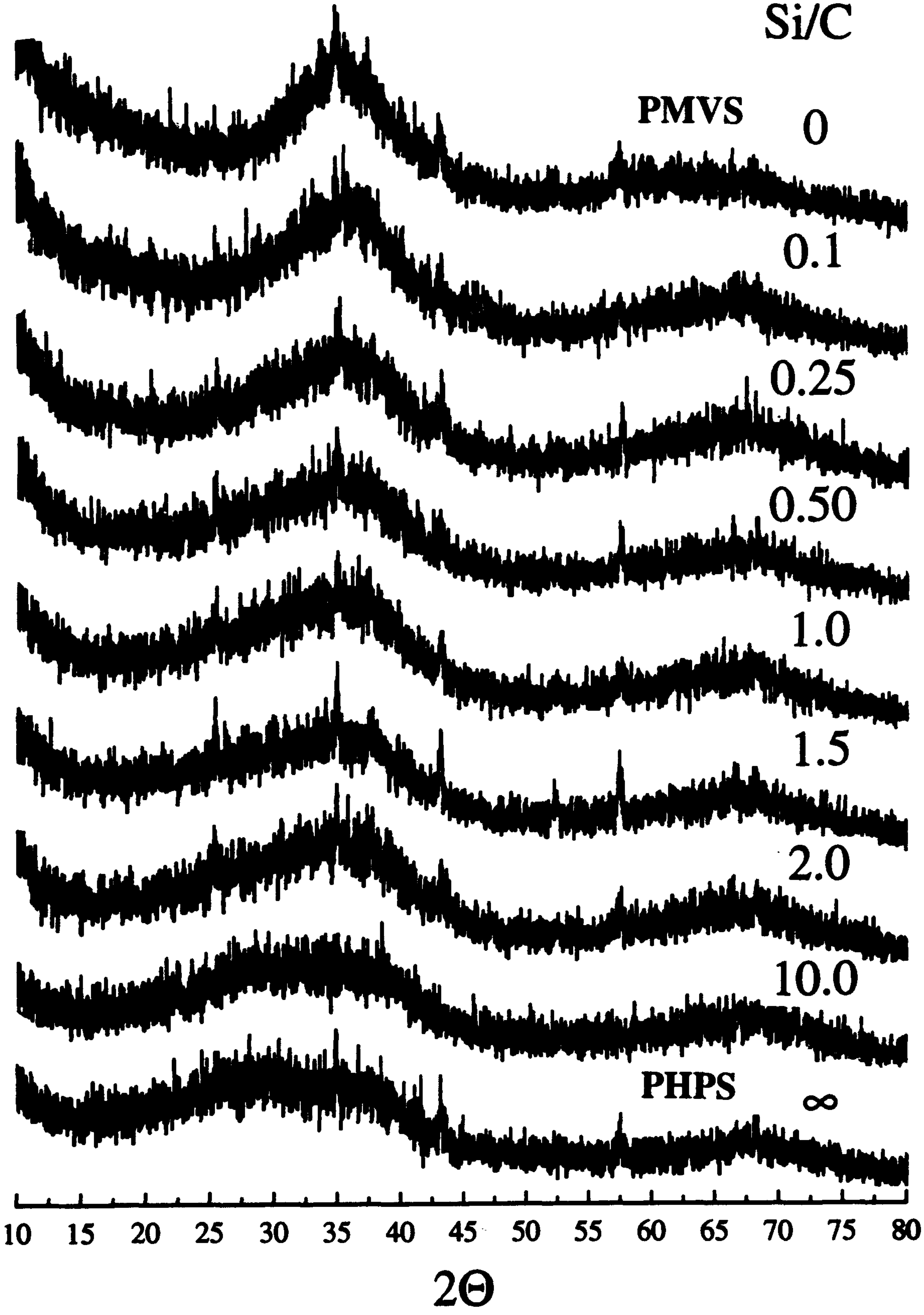


Figure 11. X-ray Diffraction Patterns of PHPS/PMVS Blends (Table I) Heated in Argon to 1000 °C for 1 Hour.

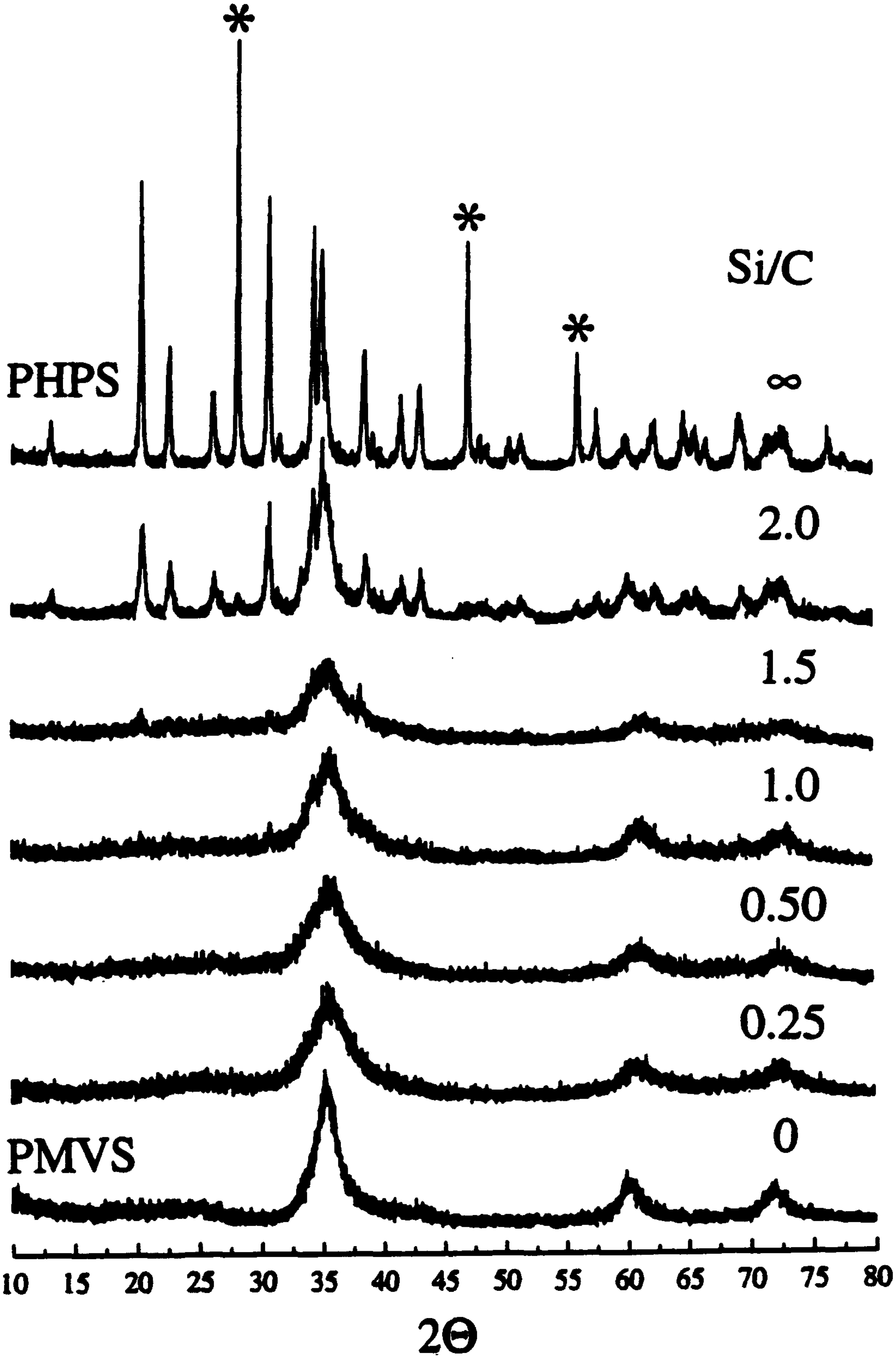


Figure 12. X-ray Diffraction Patterns of PHPS/PMVS Blends (Table I) Heated in Argon to 1600 °C in the DTA Experiments.

TEM analysis of the PHPS/PMVS blends that were heated to 1000 °C showed a homogeneous distribution of equiaxed 2-4 nm crystals. A similar analysis of the blends heated to 1600 °C showed an increase in the average crystal size. Figure 13 shows a dark field image of PHPS/PMVS Blend D, heated to 1600 °C, with a corresponding SAED pattern which was indexed to both SiC and Si_3N_4. A comparison of Figure 13 and the dark field image of PMVS heated to 1600 °C (the equivalent sample to Blend A) in Figure 6 shows that the crystals in Blend D are significantly smaller. These crystals are also smaller than those found in the PHPS (Blend H) sample heated to 1600 °C, which contained a distribution of relatively large, blocky 20-100 nm crystals. EDS confirmed the presence of nitrogen in samples which contained PHPS (i.e. Blend D at 1000 °C and 1600 °C), and showed no carbon in the sample of Blend H that was heated to 1600 °C. Blend A, which contained only PMVS-derived ceramic, did not contain nitrogen.

C. Blending Studies of Submicron Silicon Powder with PMVS

The submicron Si powder was characterized by both SEM and TEM analytical techniques. SEM examination confirmed that the powder consisted of a distribution of mostly submicron, agglomerated spheres with a smooth surface. TEM/SAED examination of the Si powder produced an electron diffraction pattern which indicated highly crystalline material (Figure 14). The corresponding elemental analysis by EDS (not shown) showed predominantly elemental silicon, with a trace of oxygen, which was most likely due to surface oxidation. Bright and dark field TEM analysis confirmed that the Si existed as dense spheres which contained one or more individual crystal grains (Figure 15).

The submicron Si was analyzed by DTA in argon and shows only a sharp melting endotherm centered near 1450 °C. The series of DTA curves for the submicron Si/PMVS blends (Table I), initially pyrolyzed to 1000 °C in argon, are shown in Figure 16. The curve for PMVS only (Blend Si-0) shows a single, broad exothermic peak. With added submicron Si, this exothermic peak sharpens slightly and shifts to higher temperatures. A new, relatively small exothermic peak is seen near 1500 °C in the curves for Si/C ratios of 0.05 and 0.1 (Blends Si-2 and Si-4). This exothermic peak is attributed to the reaction between the added Si and the excess C in the ceramic char to produce new SiC. When the Si/C ratio is 0.5 (Blend Si-6) or 1.0 (Blend Si-3), the second exothermic peak increases in intensity and shifts to somewhat lower temperatures. A slight endotherm is observed in the curve for the Si/C ratio of 1.0, which is an indication that slightly more Si is present than necessary to effectively scavenge the excess C in the ceramic char. When the level of added Si is much greater than the stoichiometric level, as for Blend Si-1 (Si/C

Figure 13. Dark Field Transmission Electron Micrograph of PHPS/PMVS Blend D Heated in Argon to 1600 °C in the DTA Experiment.

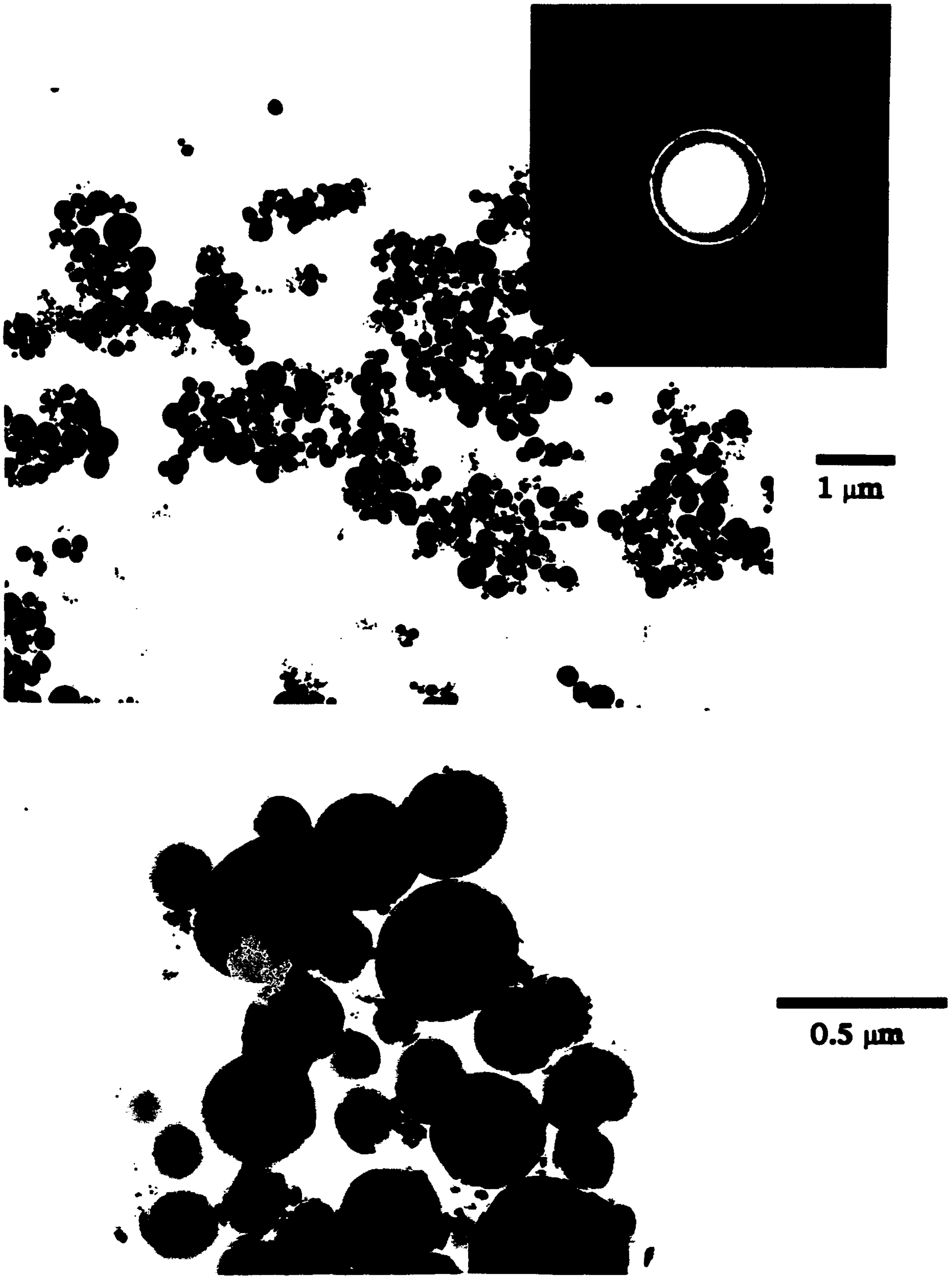


Figure 14. Bright Field Transmission Electron Micrographs of Submicron Silicon Powder with the Corresponding Electron Diffraction Pattern.

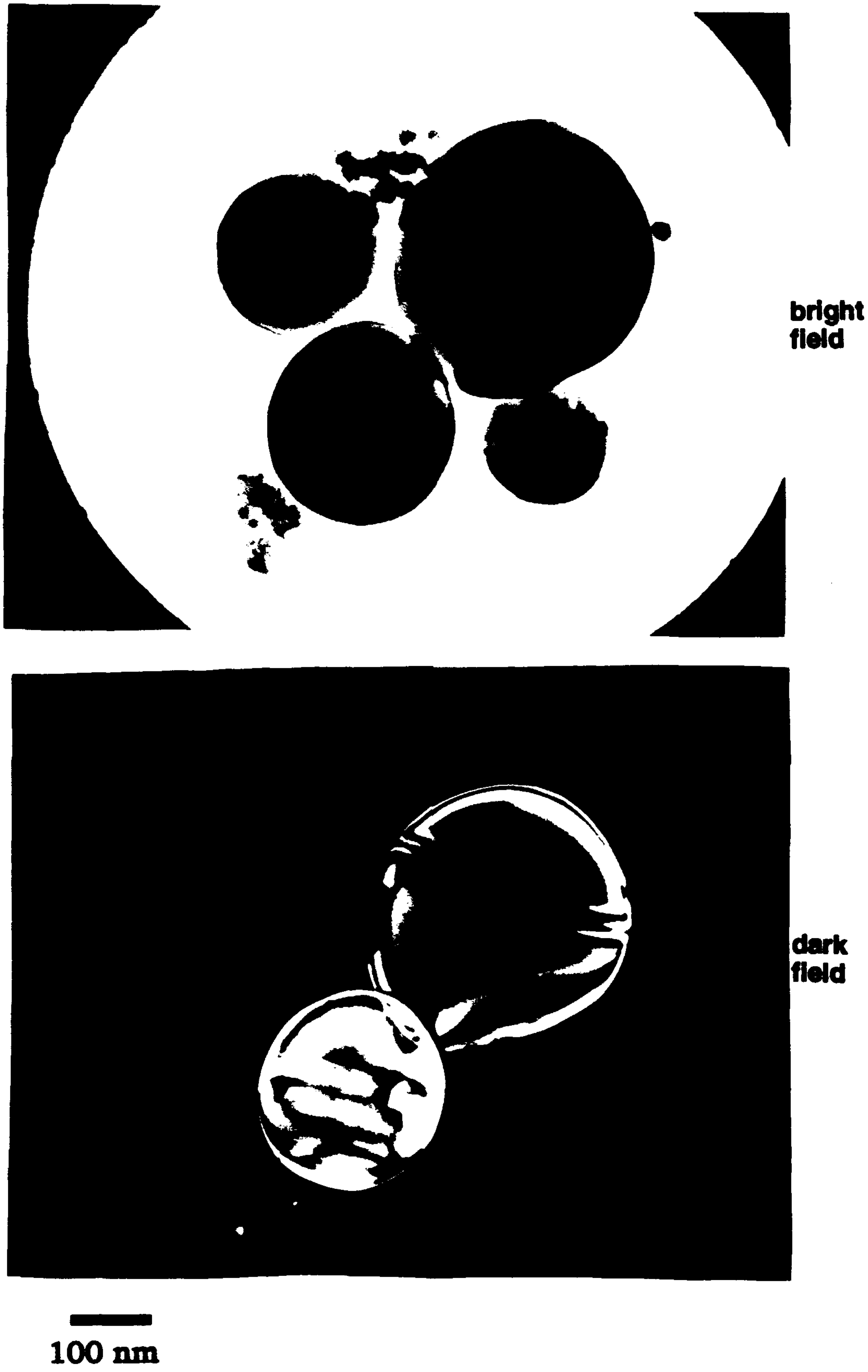


Figure 15. Bright and Dark Field Transmission Electron Micrographs of Submicron Silicon Powder.

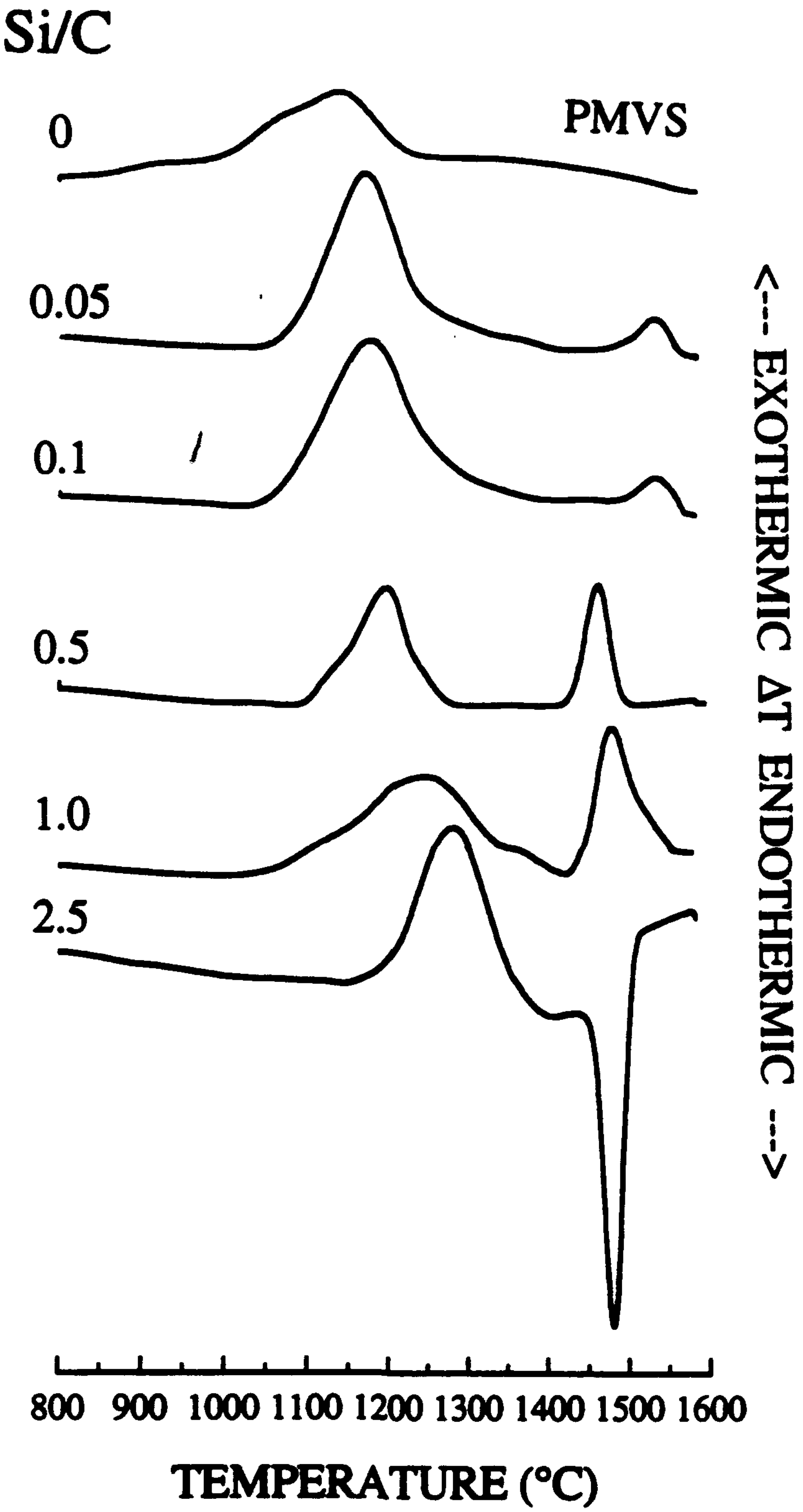


Figure 16. Differential Thermal Analysis Curves of Submicron Si/PMVS Blends (Table I) Initially Heated in Argon to 1000 °C for 1 Hour.

ratio of 2.5), only the main exotherm is evident, along with a sharp endotherm produced by the melting of the excess Si.

Solid-state ^{29}Si MAS NMR spectra were obtained for the submicron Si/PMVS blends that were heated in argon to 1000 °C in the pyrolysis experiments and to 1600 °C in the DTA experiments. At 1000 °C, the relatively broad peak centered near -10 ppm confirms the presence of SiC. With increasing amounts of added submicron Si powder, the intensity of a new peak near -80 ppm increases (Figure 17), indicating that elemental Si exists as a separate phase in the sample. At 1600 °C, the peak for silicon in SiC sharpens, which is expected from the increased crystallinity, and the peak for elemental Si has decreases in intensity. Figure 18 shows three spectra for submicron Si/PMVS Blends Si-1, Si-3, and Si-2. The spectrum for Blend Si-1 shows both SiC (-16.4 ppm) and elemental Si (-82.0 ppm) phases. The spectrum for Blend Si-3 shows three peaks at -15.8 ppm, -19.7 ppm and -25.2 ppm, which may be due to the presence of both β-SiC and α-SiC phases [4,9,10,12,13]. The spectrum for Blend Si-2 shows only the peak indicative of SiC.

The X-ray powder diffraction patterns of the submicron Si/PMVS blends heated to 1000 °C (Figure 19) contain sharp peaks from elemental Si at 2Θ values of 28°, 47.5°, 56°, 68° and 76°, which are noted with asterisks. The intensity of these peaks increases with the level of added Si in the sample. The diffraction curves for these samples also contain very broad peaks indicative of nanocrystalline SiC, as seen in Figure 5 for the pyrolyzed PMVS sample. No diffraction peaks for elemental Si are observed for the sample without added Si (Blend Si-0, not shown).

An increase in the processing temperature to 1600 °C causes significant changes in the X-ray diffraction patterns of these blends. With no added Si, the diffraction peaks for SiC have sharpened slightly, relative to the pattern obtained for the 1000 °C sample. However, as the amount of added Si in the blend increases, the sharpness and intensity of the SiC peaks also increase. Figure 20 shows a series of expanded X-ray diffraction patterns for the submicron Si/PMVS 1600 °C blends. The trend towards sharper diffraction peaks with an increase in the ratio of added Si to excess C is evident. Diffraction peaks for elemental Si (not shown) are present in the pattern for the sample with a stoichiometric ratio of Si/C (Blend Si-3), suggesting that there is a slight excess of added Si in this sample. In general, the intensities of the diffraction peaks for elemental Si increase with an increase in the Si/C ratio; no Si peaks are in the diffraction patterns samples with a Si/C ratio less than 0.5.

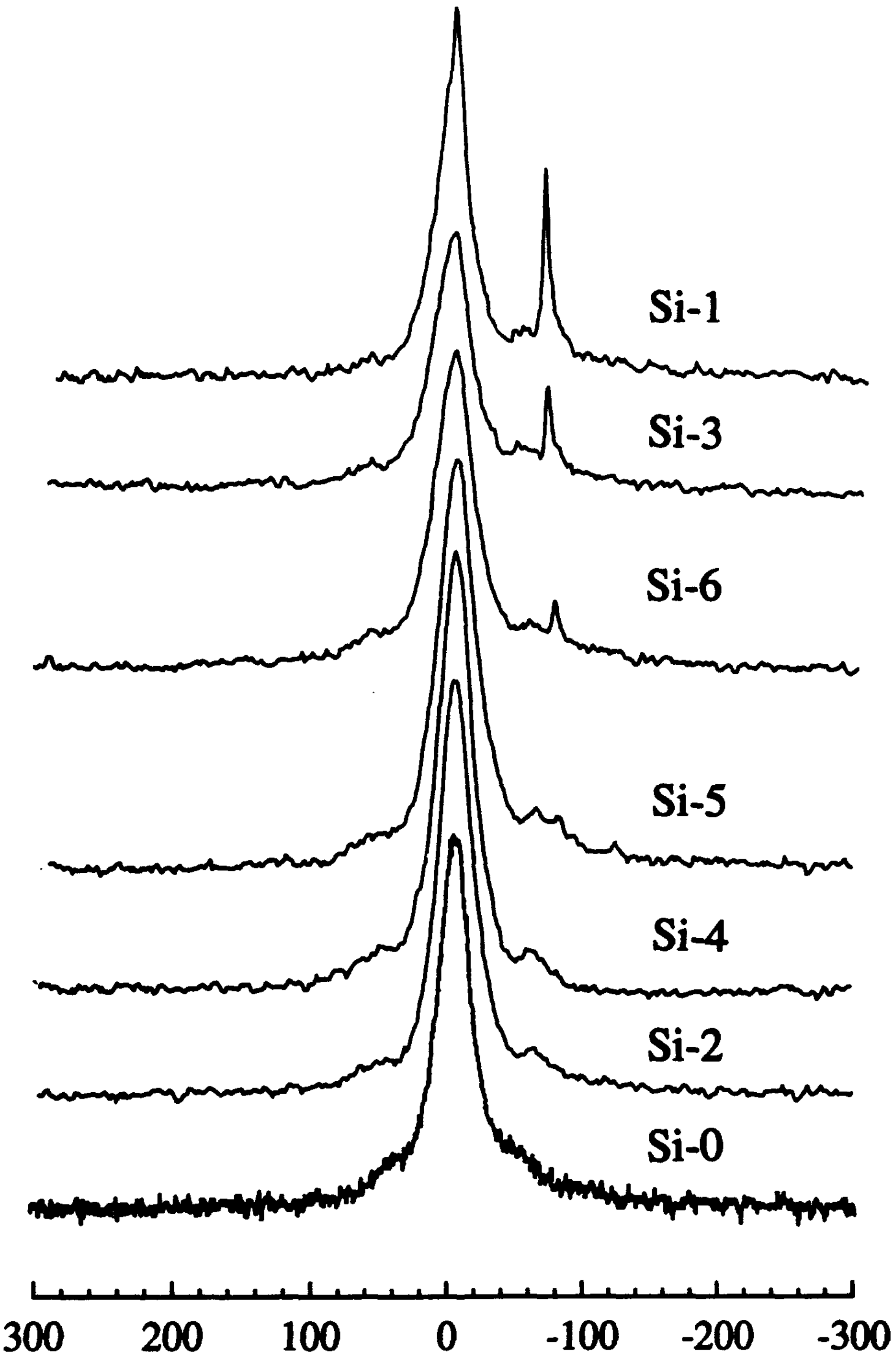


Figure 17. Solid-state ^{29}Si MAS NMR Spectra of Submicron Si/PMVS Blends (Table I) Heated in Argon to 1000 °C.

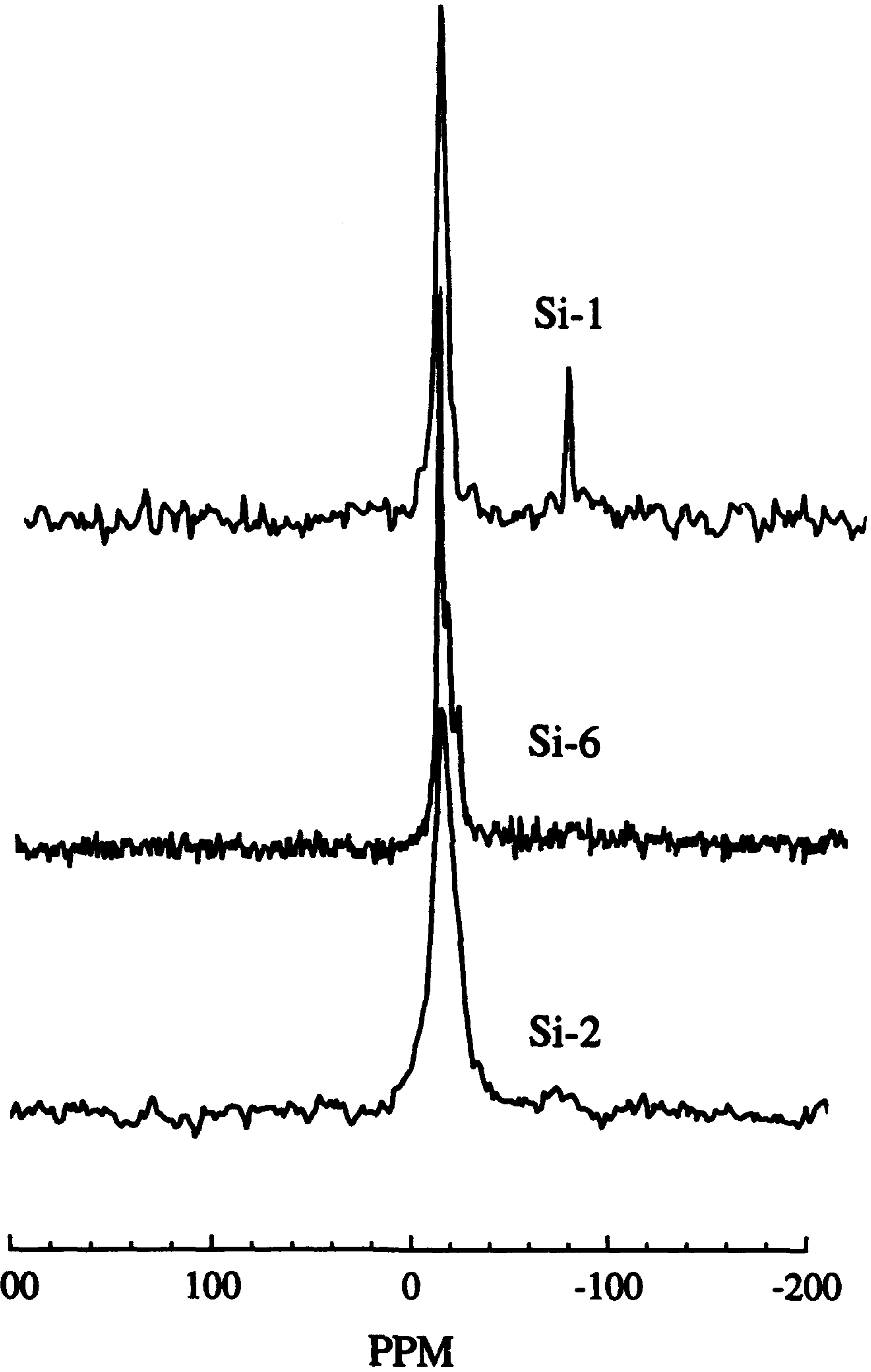


Figure 18. Solid-state ^{29}Si MAS NMR Spectra of Submicron Si/PMVS Blends (Table I) Heated in Argon to 1600 °C in the DTA Experiment.

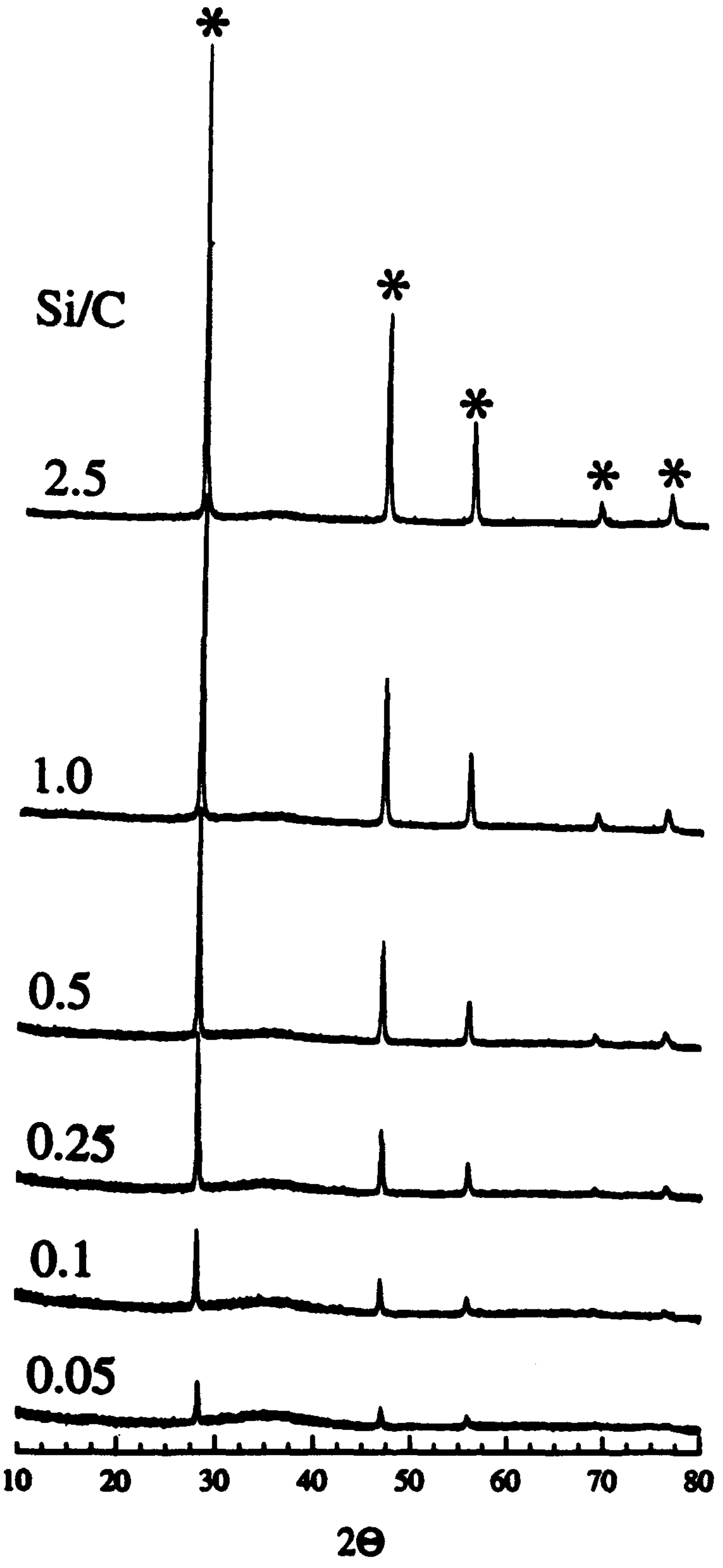


Figure 19. X-ray Diffraction Patterns of Submicron Si/PMVS Blends (Table I) Heated in Argon to 1000 °C.

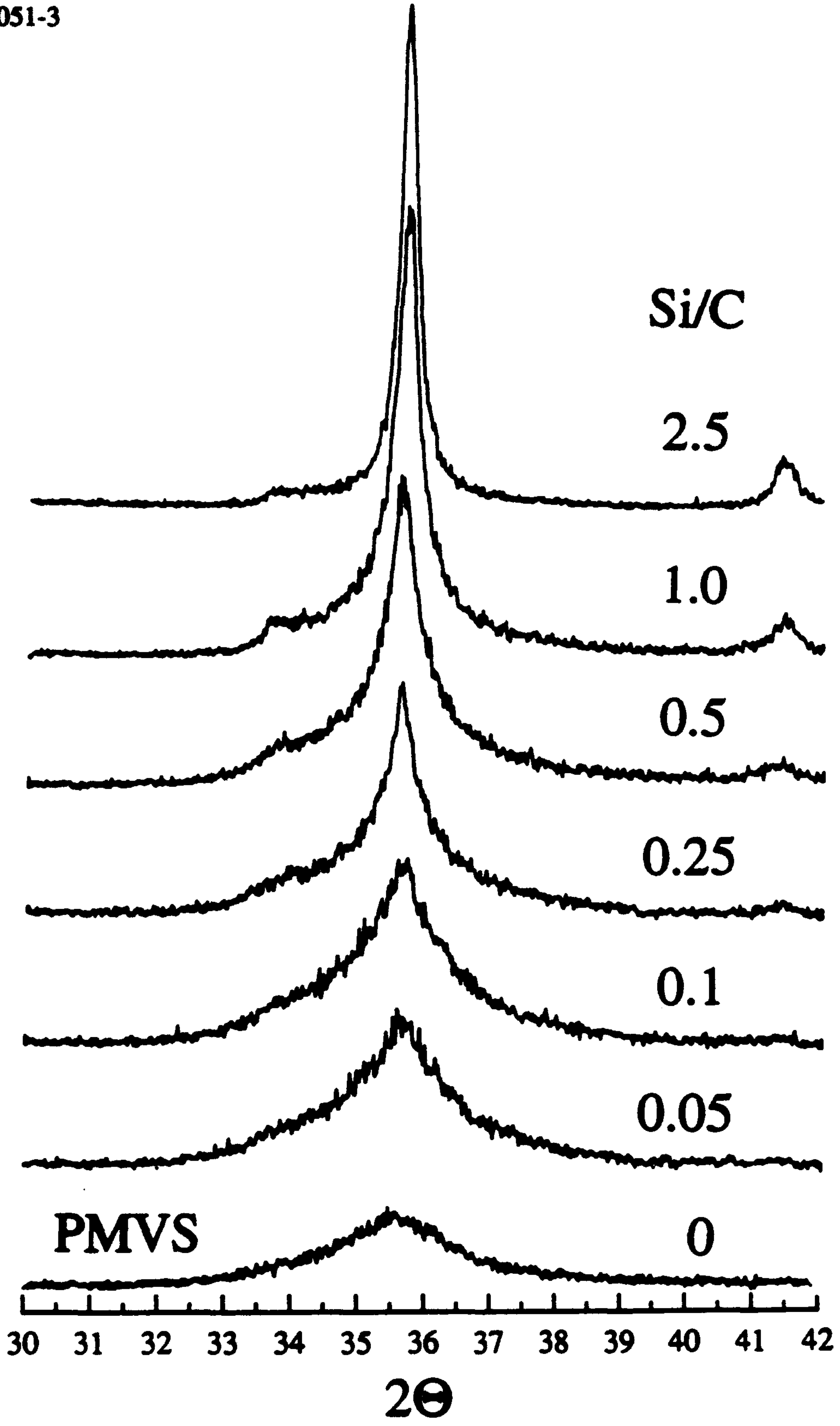


Figure 20. X-ray Diffraction Patterns of Submicron Si/PMVS Blends (Table I) Heated in Argon to 1600 °C in the DTA Experiments.

Typical TEM micrographs for submicron Si/PMVS blends (Blends Si-1 and Si-6), heated to only 1000 °C, are shown in Figure 21. The micrographs show a distribution of intact Si spheres within a nanocrystalline SiC matrix. The corresponding electron diffraction pattern for Blend Si-1 was indexed as crystalline elemental Si plus finely crystalline SiC. Blends that were heated to 1600 °C show a significant increase in the average crystal size (Figure 22), which is consistent with the X-ray diffraction experimental results shown in Figure 20. Although the electron diffraction patterns show more ordering of the SiC phase, elemental Si is also present when the level of added Si is greater than the stoichiometric ratio needed, as in Blend Si-1 (Figures 21 and 22). The micrograph for Blend Si-6 (Si/C equal to 0.5) in Figure 22 shows that a void remains where a Si sphere previously existed, and a ring of relatively large SiC crystals is surrounding the void. Closer examination of the image shows that in general, the crystal size is larger nearer the void. It appears that the added Si initially melts prior to reaction with the excess C in the matrix.

D. Characterization of CMCs Fabricated by Polymer Impregnation-Pyrolysis

During the fabrication of the CMCs, the changes in density were monitored as a function of increasing processing cycle. Figure 23 shows that the initial density of the cured "green" composites ranges from about 1.55 g/cc for the CMC with a PHPS/PMVS matrix, to about 1.65 g/cc for CMCs with the two other matrices. Following the first processing cycle, the density of each composite decreases, due to the loss of volatile species from the polymer(s) during the pyrolysis. Subsequent impregnation and pyrolysis cycles produce a gradual increase in the bulk density of the composites. An increase in the density of the CMC with an increase in the number of processing cycles is typical of CMCs derived by polymer pyrolysis techniques.

Table III summarizes the Archimedes liquid displacement density measurements, obtained using isopropanol as the medium, for the three completed composite panels. Each composite has extensive porosity, which is primarily attributed to the relatively few (5) impregnation-pyrolysis cycles used for CMC fabrication. Although optical microscopy of polished cross-sections of CMC samples shows good infiltration of the matrix material(s) within and between fiber tows, there are large regions between fiber tows that are void of any matrix material. The open architecture (1.14 mm^2 voids) of the Nicalon™ Si-C-O plain weave in the CMC could contribute to matrix pull-out during polishing, however, the major source of porosity can likely be attributed to the loss of volatile species during pyrolysis.

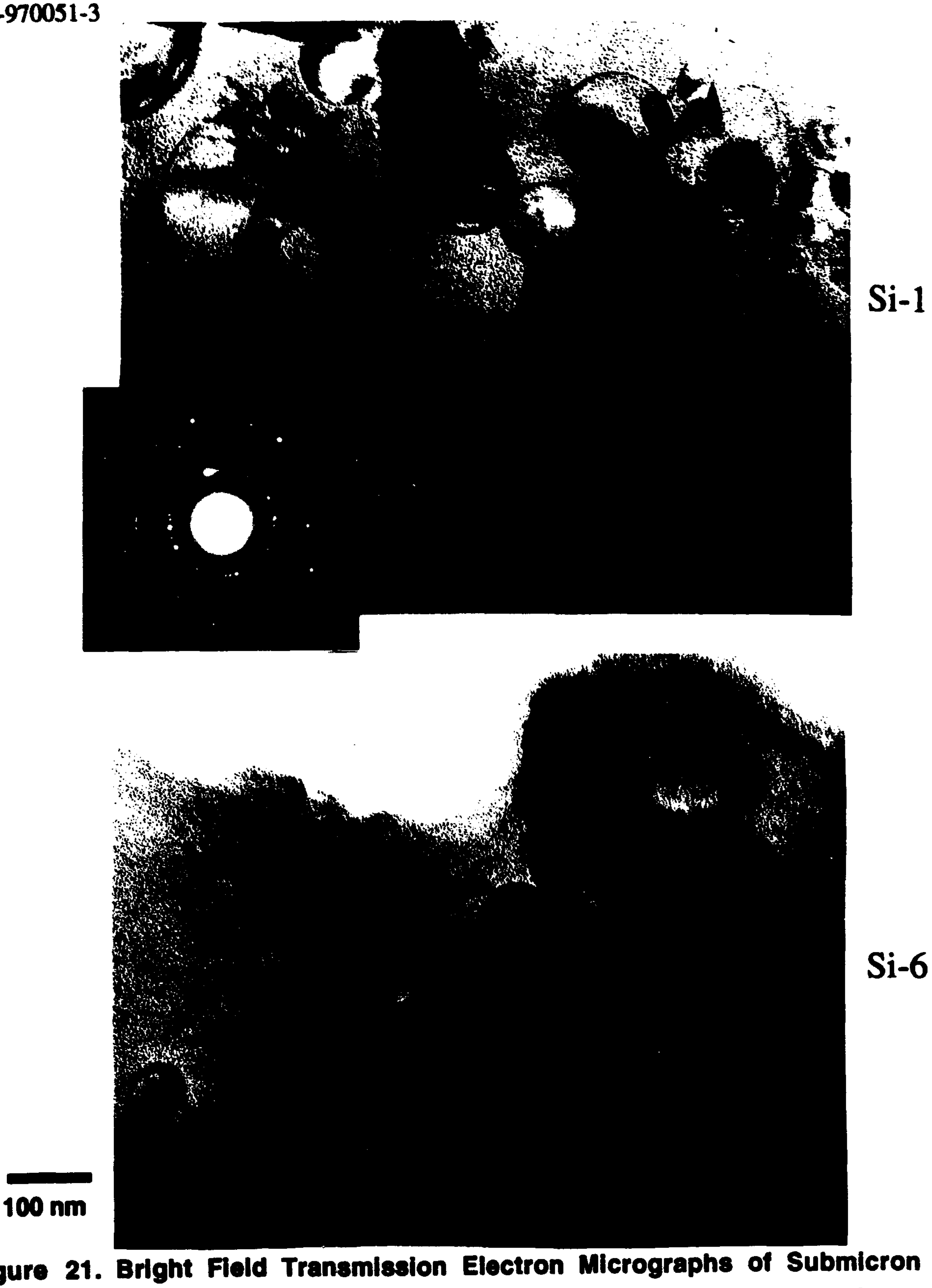


Figure 21. Bright Field Transmission Electron Micrographs of Submicron Si/PMVS Blends Si-1 and Si-6 Heated in Argon to 1000 °C. The Corresponding Electron Diffraction Pattern is Shown for Blend Si-1.

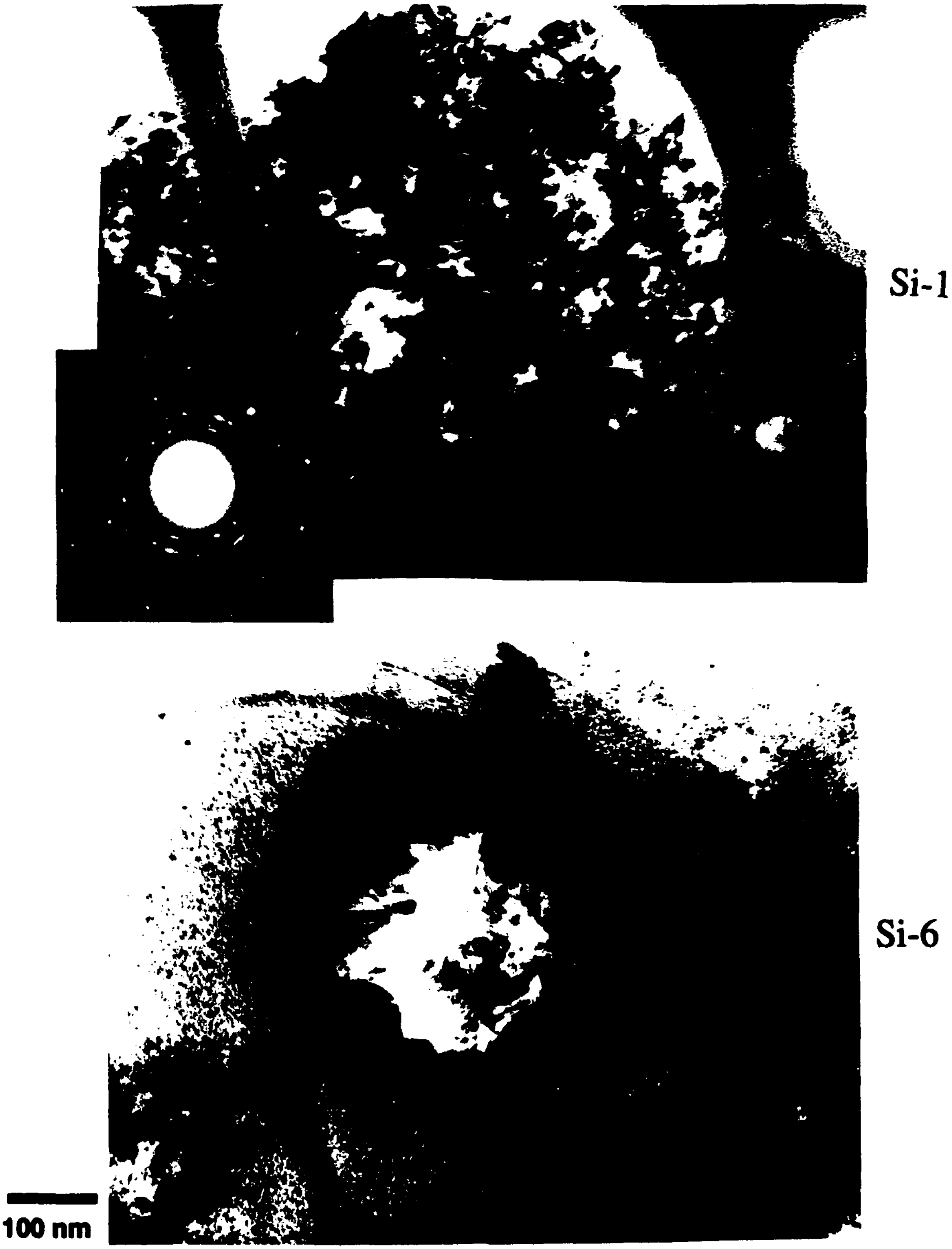


Figure 22. Bright Field Transmission Electron Micrographs of Submicron Si/PMVS Blends Si-1 and Si-6 Heated in Argon to 1600 °C in the DTA Experiments. The Corresponding Electron Diffraction Pattern is Shown for Blend Si-1.

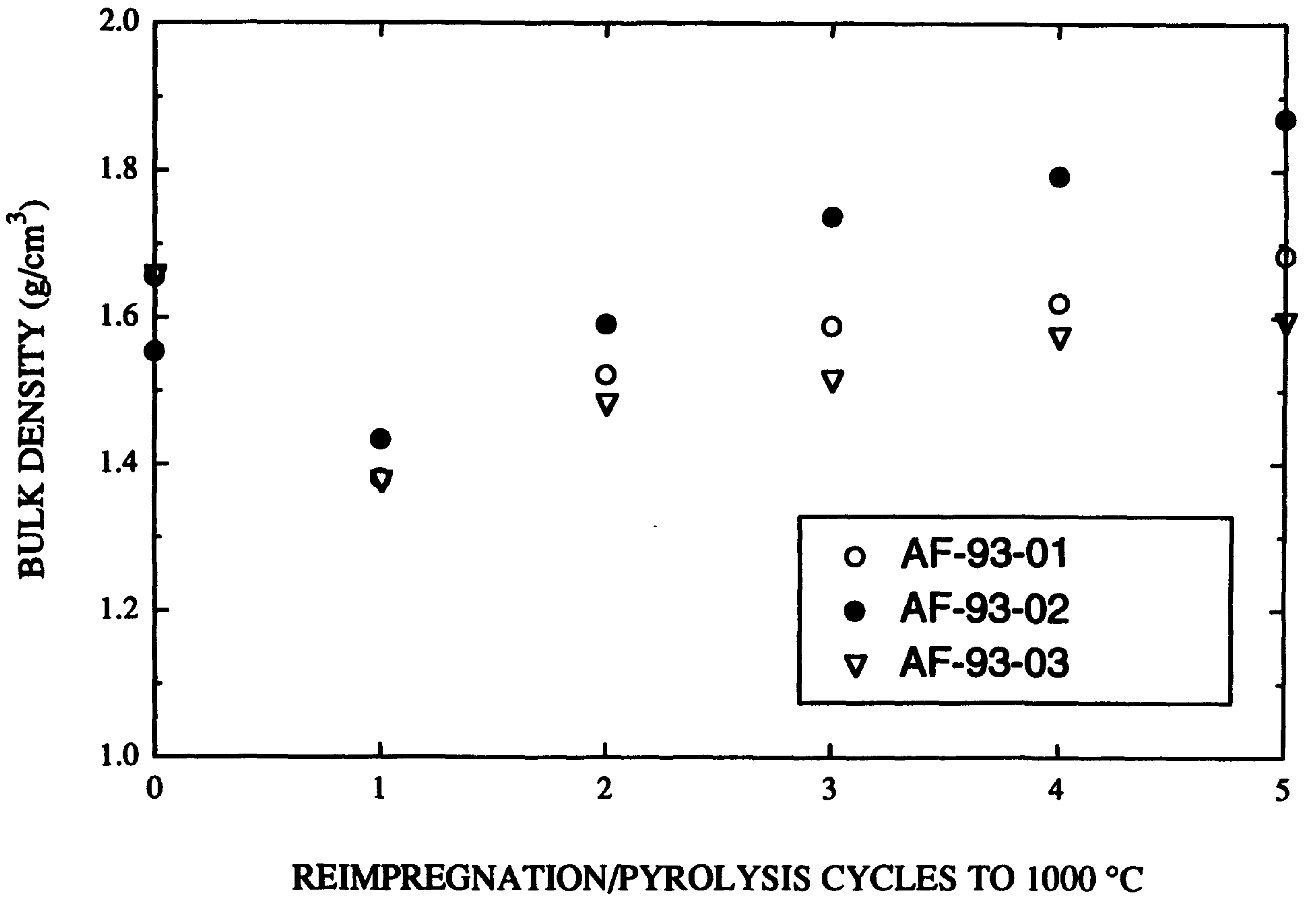


Figure 23. The Dependence of the CMC Bulk Densities on the Number of Polymer Impregnation-Pyrolysis Processing Cycles.

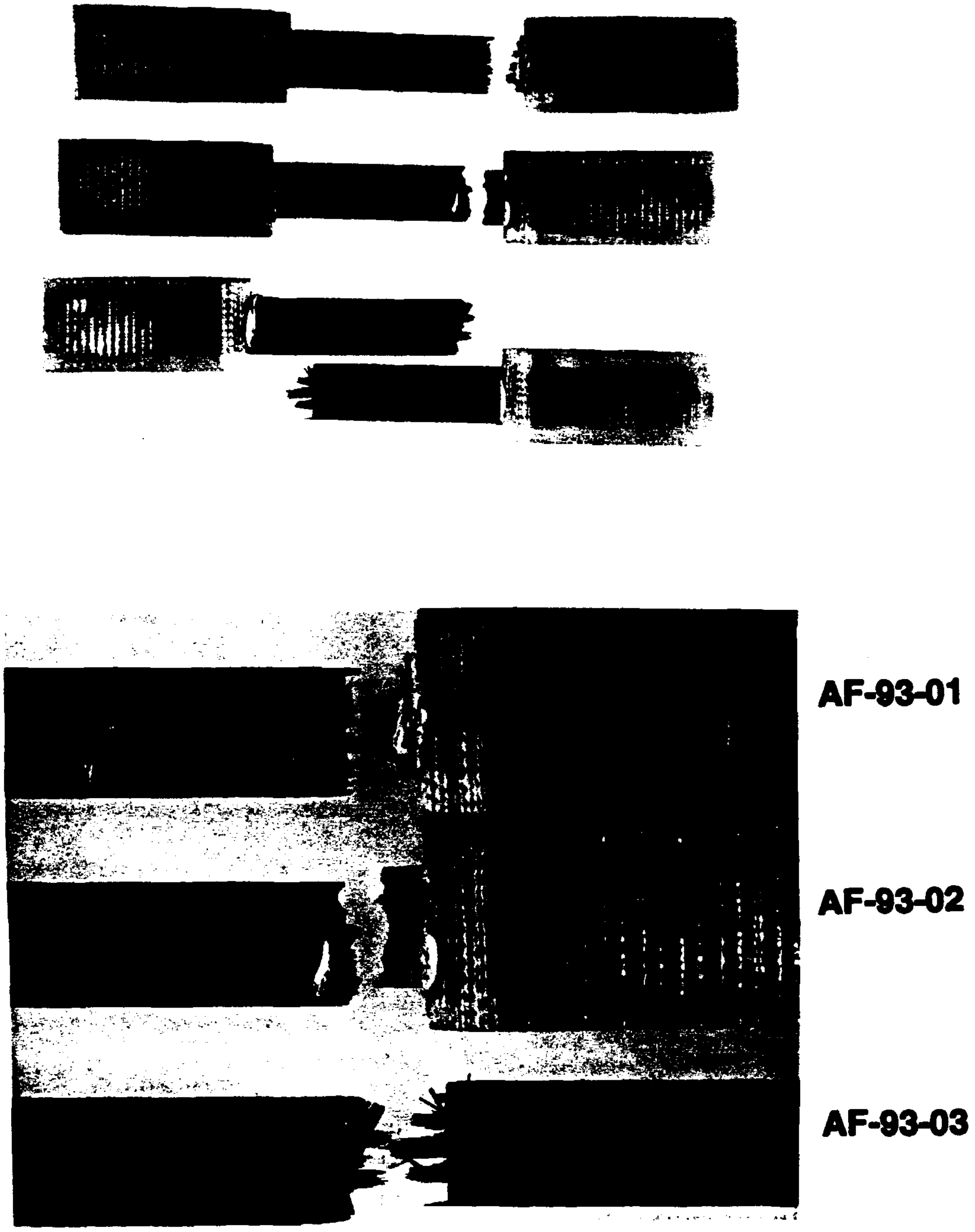


Figure 24. Optical Micrograph of Representative Tensile Fracture Specimens of PMVS Polymer-Derived CMCs.

TABLE III.

LIQUID* DISPLACEMENT DENSITIES OF CMCs DERIVED FROM PMVS AND PMVS BLENDED WITH SILICON SOURCES

		Density (g/cc)		
Composite	*Matrix Composition*	*True*	*Bulk*	*Apparent Porosity (%)*
AF-93-01	PMVS only	2.23	1.75	21.5
AF-93-02	PHPS/PMVS (Blend D)	2.37	2.06	13.1
AF-93-03	subμm Si/PMVS (Blend Si-3)	2.11	1.77	15.9

*isopropanol was used as the liquid

Table IV summarizes the three-point flexural data that were obtained from mechanical testing of the polymer-derived composite samples in air. In general, the samples showed load versus deflection curves typical of non-brittle failure and good mechanical strength. Room temperature flexural strengths ranged from 18 to 23 ksi, and the moduli ranged from 8 to 11 Msi. Composites made with PMVS only or with a PHPS/PMVS polymer blend retained their strength during the test at 1000 °C, although the modulus decreased slightly. The composite made with the submicron Si/PMVS blend matrix showed significantly reduced flexural strength and modulus at 1000 °C, which may be associated with oxidation of the elemental Si in the matrix.

Optical and scanning electron microscopy were used to examine the fracture surfaces of composite samples following tensile testing in air at 22 °C. An optical micrograph of representative tested specimens is shown in Figure 24 for the three matrix compositions. The scanning electron micrographs of the tensile fracture surfaces, shown in Figures 25-27, indicate that the tensile specimens generally exhibited fibrous fracture.

TABLE IV.

THREE-POINT FLEXURAL DATA FOR BN-COATED, NICALON™ REINFORCED CMCs FABRICATED WITH MATRIX DERIVED FROM PMVS AND PMVS BLENDED WITH SILICON SOURCES

Composite	*Matrix Composition*	*Test Temperature in Air (°C)*	*Flex Strength (ksi)*	*Modulus (Msi)*	*Comments*
AF-93-01	PMVS only	22	23.2	10.2	Tough Fracture
		1000	21.5, 19.2	6.6, 6.4	Strength Maintained
AF-93-02	PHPS/PMVS	22	21.7	11.1	Tough Fracture
	(Blend D)	1000	30.6, 25.8	7.7, 8.2	Strength Maintained
AF-93-03	subμm Si/PMVS	22	18.1	8.4	Tough Fracture
	(Blend Si-3)	1000	6.7, 6.2	3.6, 3.0	Oxidation of Si filler

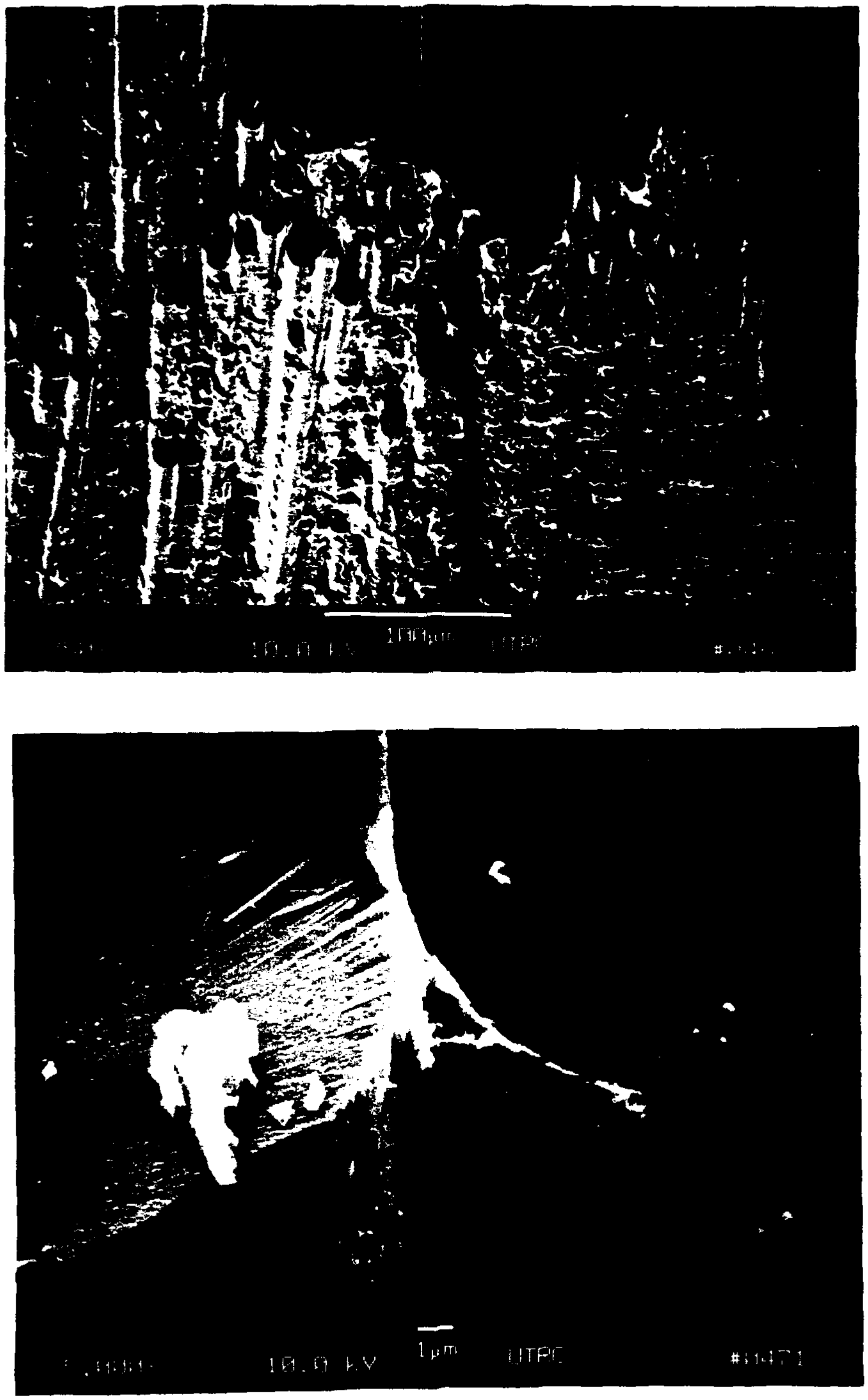


Figure 25. Scanning Electron Micrographs of Fracture Surface of CMC Containing PMVS-Only Matrix.

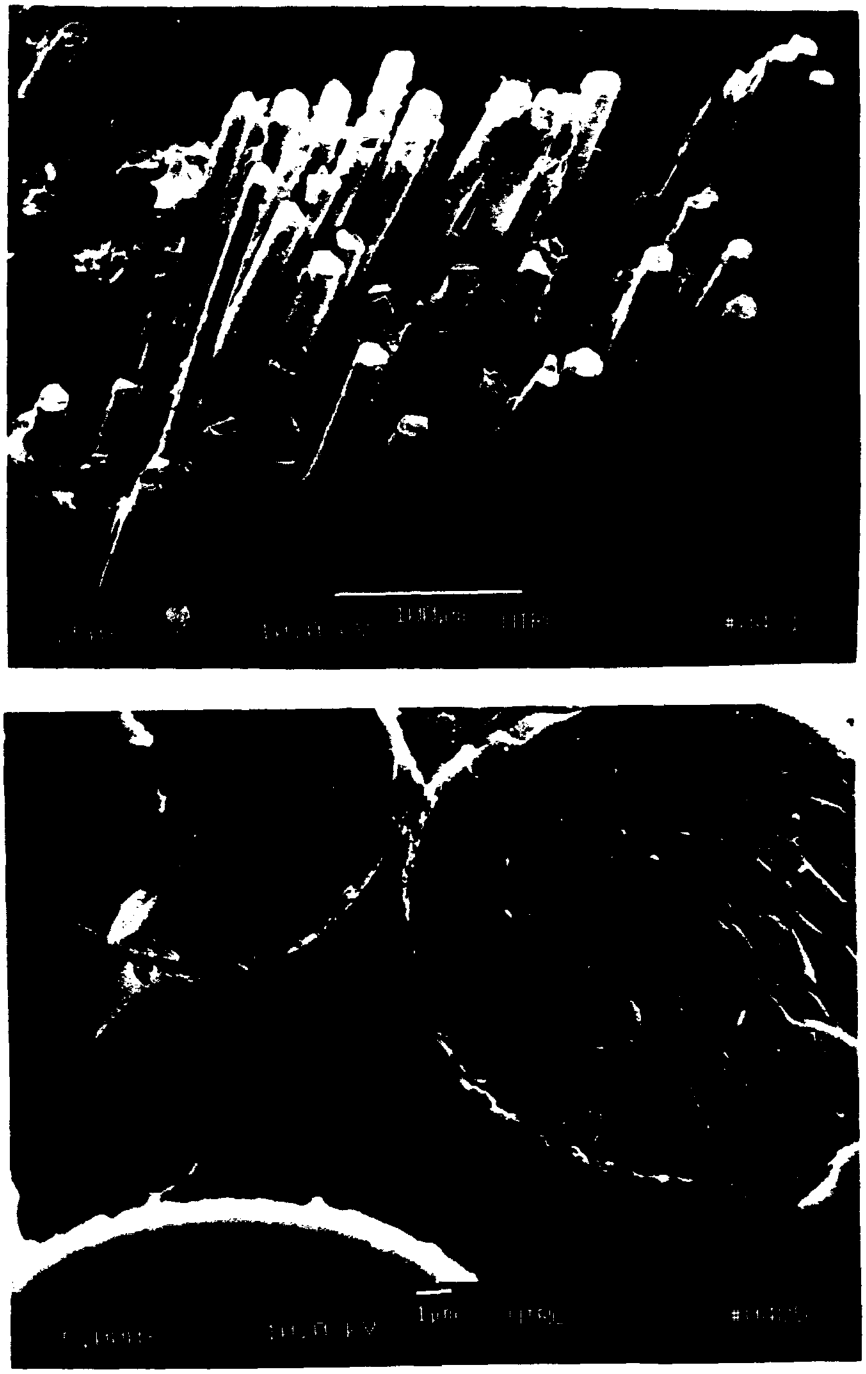


Figure 26. Scanning Electron Micrographs of Fracture Surface of CMC Containing PHPS/PMVS Blend D Matrix.

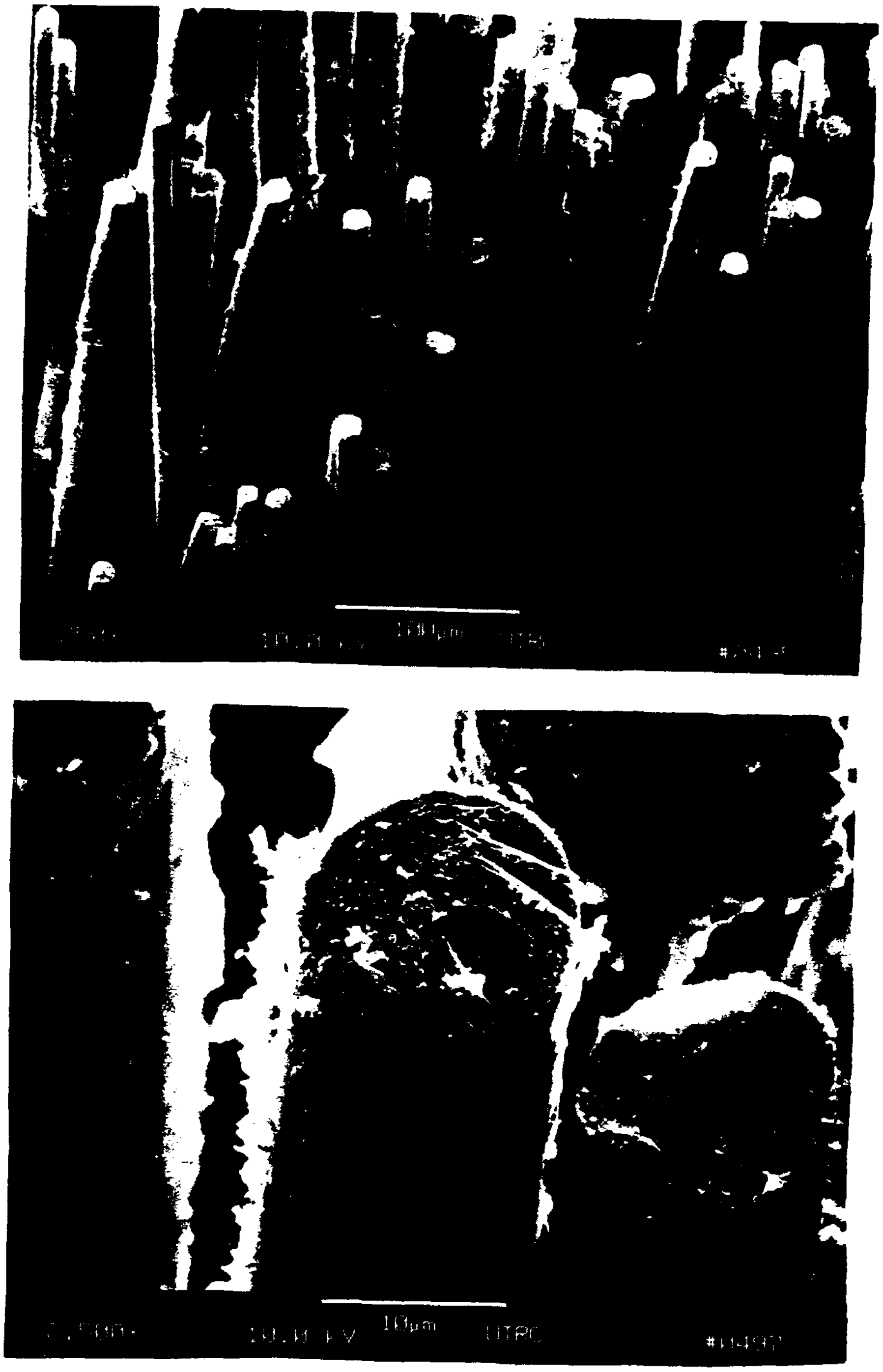
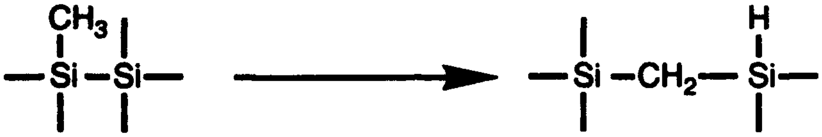


Figure 27. Scanning Electron Micrographs of Fracture Surface of CMC Containing Submicron Si/PMVS Blend Si-3 Matrix.

IV. DISCUSSION

Poly(methylvinylsilane), PMVS, converts to C-rich SiC ceramic material during pyrolysis of the polymer in an inert atmosphere, such as argon, through a series of integrated stages: crosslinking (curing), decomposition, and crystallization. The resulting ceramic microstructure can be ultimately controlled if there is an understanding of the effects that the pyrolysis atmosphere, heating rate, final pyrolysis temperature, and initial polymer chemistry have on these stages during the polymer-to-ceramic conversion. With relatively slow heating to temperatures near 300 °C, PMVS loses a small fraction of its initial weight through volatilization of low molecular weight oligomeric material, as seen in the TGA curve (Figure 1). During such heating, the structure of PMVS is changing due to crosslinking reactions, predominantly between the vinyl groups, which act to increase the molecular weight of the polymer. An obvious indication of the increase in the molecular weight of PMVS during crosslinking is the solidification of the initially liquid polymer (Table II). Additional evidence for crosslinking reactions is provided by the reduction in the relative concentration of vinyl groups as detected by both infrared (Figure 2) and ^{13}C NMR (Figure 3) spectroscopic techniques.

Pyrolysis of PMVS to 1000 °C produces an additional large weight loss (by TGA), which is caused by the decomposition of the polymer chain, as well as extensive cleavage of the polymer side groups and loss of volatile species containing Si, C and H. Spectroscopic analysis was used to confirm these structural changes during decomposition and conversion of PMVS to the ceramic phase. Infrared spectra (Figure 2) revealed the loss of methyl side groups (3000-2800 cm^{-1}) upon heating the polymer from 25 °C to 800 °C. Within this temperature range the polymer also undergoes an insertion reaction of some of the remaining methyl groups into the original poly(silane) backbone to produce a poly(carbosilane) structure according to Reaction 3. This type of reaction is supported by the observed increase in the infrared intensity near 1050 cm^{-1} from additional $Si\text{-}CH_2\text{-}Si$ vibrations, as well as the development of new Si-H bonding near 2100 cm^{-1} in the infrared spectra of PMVS samples heated from 400-600 °C. Spectral changes in the type and number of bonding environments, as observed by both solid state ^{29}Si and ^{13}C NMR spectroscopy, corroborate this type of decomposition reaction. Yajima utilized this insertion reaction in his original work with the Nicalon™ poly(carbosilane) precursor [18], and evidence for the reaction has been observed for the conversion of a similar poly(silane) [4]. The combined analytical techniques also show that with further heating to 1000 °C, most organic functionality in PMVS decomposed, and the remaining bonding environments correspond to ceramic SiC.



$$-\overset{CH_3}{\underset{|}{\overset{|}{Si}}}-\underset{|}{\overset{|}{Si}}- \longrightarrow -\underset{|}{\overset{|}{Si}}-CH_2-\underset{|}{\overset{H}{\overset{|}{Si}}}-$$

REACTION 3

Following pyrolysis to 1000 °C, infrared and solid state NMR spectroscopy indicate that the PMVS char is a complicated network structure containing bonded Si and C atoms. X-ray diffraction and transmission electron microscopy show that the char contains nanocrystalline β-SiC. Additional heating to higher temperatures causes both structural ordering, as noted by the increased sharpness of the solid state NMR peaks, and grain growth of the SiC crystals, as seen by TEM and by the sharpened X-ray diffraction peaks. Peak broadening measurements (Figure 5) show that crystal growth in PMVS is slow between 1000-1400 °C, but increases significantly at temperatures near 1600 °C. The presence of excess C in the SiC char may inhibit crystal grain growth at the lower temperatures.

Perhydropoly(silazane), PHPS, is a convenient polymeric source of both Si_3N_4 and excess Si. PHPS undergoes a polymer-to-ceramic conversion process that is similar to that of PMVS, with crosslinking, decomposition, and crystallization stages. As a homogeneous source of excess Si, PHPS was used in this investigation to scavenge the excess C formed by the pyrolytic conversion of PMVS, to form additional SiC. On a weight basis, however, PHPS generates relatively little Si, with respect to the excess C formed by PMVS, so that a stoichiometric ratio of added Si to excess C consists of only 20% by weight of PMVS. Nevertheless, polymer blends of PHPS and PMVS show significantly improved ceramic char yields compared to either polymer alone. This enhancement is presumably due to chemical reactions between the polymers during curing and subsequent pyrolysis. It is likely that the PHPS acts as a source of Si-H bonds which can react with the vinyl groups of the PMVS at relatively low temperature (below 400 °C) to enhance crosslinking [3,4]. This scenario is supported by the relatively small weight losses that are seen in the TGA curves of the PHPS/PMVS blends below 500 °C, where the major weight loss is seen for the sample containing 100% PMVS (Figure 7).

The DTA curves in Figure 10 show that the PMVS char crystallizes rather sluggishly over a broad temperature range (1000-1200 °C), with a resulting crystal size of approximately 2 nm (by XRD and TEM). Significant crystal growth is not obtained until samples are heated at 1600 °C. Conversely, the DTA curve for the PHPS char shows a rapid crystallization below 1400 °C, and subsequent analyses (XRD, TEM) confirms the formation of relatively large (50-200 nm) crystals of α-Si_3N_4 and regions of excess, crystalline Si. The corresponding DTA curves for the PHPS/PMVS blends exhibit features which are different than either component polymer, and confirm that the blends behave as distinct materials.

Prior to pyrolysis, blends of PHPS and PMVS produce homogeneous, single-phase liquid polymeric precursors. Proper control of the ratio of the two polymers in the blend allows the preparation of a range of unique, compositionally distinct solid materials with interesting properties. The chars of these pyrolyzed blends can be considered as "ceramic alloys", which are analogous to either metal alloys or organic (engineering) polymer blends. Polymer blending produces a more disordered network of Si and C environments in the chars than exhibited by either component polymer. As a result, crystallization of the blends is generally more difficult. DTA demonstrates that the crystallization behavior of the char depends on the blend composition. For example, PHPS/PMVS Blend D, which initially contains 80% by weight of the easily crystallized PHPS, exhibits a DTA trace which shows a very small exotherm, which indicates that the process is not highly energetic. XRD and TEM analysis show that the 1600 °C solid contains smaller crystals than those obtained from either component polymer.

Pyrolysis of PHPS/PMVS blends results in ceramic chars that contain an atomic distribution of SiC, Si_3N_4, and mixed Si-C-N environments. Solid state ^{29}Si spectroscopy of the 1000 °C chars (Figure 8) shows isolated, broad peaks which suggest a distribution of similar bonding environments. The position of the peak maximum, however, smoothly shifts from that of SiC to that expected for Si_3N_4 with an increase in the Si/C ratio. The X-ray diffraction patterns for the 1000 °C chars show a similar shift in the major diffraction peak for these poorly crystalline materials as the blend composition is varied (Figure 11). The individual ceramic components separate into chemically distinctive phases, upon additional heating to 1600 °C, as indicated by ^{29}Si NMR spectroscopy. TEM analysis, coupled with SAED and EDS, provides supportive evidence for the separation of the ceramic phases. The corresponding XRD patterns generally show that these chars are less crystalline than either component ceramic, and confirm that phase separation occurs readily in blends with a higher initial PHPS concentration. A more detailed examination of the crystallization kinetics of such polymer-derived nanocrystalline SiC/Si_3N_4 ceramics would be beneficial.

Elemental silicon powder provides a higher level of reactive Si per unit weight than the PHPS polymeric source (Table I). There are difficulties, however, in achieving a homogeneous distribution of the Si because of the large size of the powder, relative to the size of polymer molecules, and the lack of miscibility compared to the PHPS/PMVS blends. After pyrolysis to 1000 °C, the submicron Si/PMVS chars contain pockets of intact Si spheres. XRD, ^{29}Si NMR spectroscopy, and TEM analysis show that the submicron Si exists as a chemically distinct phase from the PMVS-derived nanocrystalline SiC.

Differential thermal analysis shows that temperatures above the melting point of Si (1410 °C) are required for the added Si to react with the excess C from PMVS. The magnitude of the exothermic reaction between the Si and the excess C clearly depends on the amount of excess Si that is in the blend; higher Si levels show more intense exothermic events. This effect may be due to an increased local concentration of Si, which essentially increases the probability that Si is available for scavenging the C in a specific area. The enhanced reaction caused by the increased level of Si is clearly seen in the XRD patterns of the 1600 °C chars. Significantly sharper peaks are seen at higher levels of added Si, which are indicative of crystal growth. This result demonstrates that excess Si is not a hindrance to crystallization. Solid state ^{29}Si NMR spectra also show a sharpening of the peak for SiC as the level of elemental Si increases, suggesting both an increase in the level of crystallization, and atomic-level interactions between SiC and Si.

In addition to the DTA evidence for the exothermic reaction between the added Si and the excess C, transmission electron microscopy provides photographic evidence of the reaction process. At 1000 °C, the chars contain submicron spheres of unreacted elemental Si. After heating to 1600 °C, TEM examination shows that the chars contain roughly spherical voids, which are surrounded by ring of highly crystalline SiC. This observation suggests that a reaction occurs between the C-containing SiC matrix and molten or softened elemental Si spheres. As the Si diffuses or "wicks" into the matrix material, a reaction zone moves outward from the original Si core, leaving behind a wake of crystalline SiC. The formation of larger SiC crystals nearer the void suggests that the concentration of elemental Si decreases as the reaction zone moves outward. These data support the conclusion that the added Si powder reacts more energetically and rapidly than the Si generated by the PHPS polymer source, and produces more highly crystalline SiC than that obtained by the crystallization of PMVS or the PHPS/PMVS blends.

The ceramic composites that were fabricated using PMVS, PHPS/PMVS, and submicron Si/PMVS precursors as the matrix source exhibited good mechanical properties. The polymer-only matrices resulted in composites that had similar values for strength and modulus. Densities of the resulting composites were relatively low (1.6-1.9 g/cc), however, compared to either the density of the fiber reinforcement (2.55 g/cc) or the desired SiC ceramic phase (3.2 g/cc). Processing with additional impregnation and pyrolysis cycles would likely have increased the densities, as well as reduced the open porosities of the composites. Pyrolysis at temperatures higher than 1000 °C also would have increased the densities of the composites by increasing the crystallinity of the matrix. After pyrolysis at 1000 °C, PMVS contains poorly crystalline SiC, which is expected to have a density between that of the original polymer (1 g/cc) and fully crystalline SiC (3.2 g/cc). Likewise, the PHPS/PMVS char contains poorly crystalline atomically distributed SiC/Si_3N_4, which is expected to have a lower density than either crystalline SiC or Si_3N_4. Microscopic analysis showed good infiltration of the polymers into the fiber tows of the resulting CMCs.

The submicron Si/PMVS matrix contains unreacted Si and poorly crystalline SiC from PMVS. Differential thermal analysis of the matrix showed that temperatures greater than 1000 °C were necessary to initiate a reaction between the added Si and the excess C, but these temperatures would severely degrade the properties of the Nicalon™ fiber and possibly the BN coating. Improved ceramic fibers and advanced fiber coatings are required to use this matrix system to its full potential. Mechanical testing in air at 1000 °C suggests that oxidation of the added Si may degrade the mechanical properties of this composite. While some Si may provide a beneficial source of an oxidation resistant scale, it would be more efficient to process the Si-containing phase at higher temperatures in an inert atmosphere to generate SiC by reaction with excess C, followed by a low temperature processing step in air to generate oxide scale.

V. SUMMARY AND CONCLUSIONS

UTRC has developed a family of reactive endblocked poly(methylvinylsilane), PMVS, precursors with desirable characteristics such as air stability and processability with low to modest applied pressures. Control of synthesis conditions was developed to the level where a baseline PMVS polymer could be prepared in multiple batches with reproducible properties. The baseline PMVS was prepared in sufficient quantity to examine modifications of the polymer chemistry during processing and pyrolysis. Monomer stoichiometry was varied to maximize the yield of processible polymer and to optimize the ceramic conversion of these reactive endblocked PMVS polymers. Branching was introduced into the PMVS polymer structure during a separate set of experiments, but had the effect of reducing the ceramic yield of all the derivative PMVS precursors. Studies of the rheological properties, curing characteristics, and pyrolysis kinetics indicated that these polymers exhibited appropriate characteristics for CMC processing [1-3].

A variety of complementary analytical techniques, including infrared and nuclear magnetic resonance spectroscopy, thermal analysis, X-ray diffraction, and electron microscopy were employed to examine the precursor-to-ceramic conversion process and the development of microstructure in the resulting ceramic phases. A detailed characterization of the pyrolysis of PMVS in argon shows that the polymer undergoes conversion to C-rich nanocrystalline SiC. Crystallization of the SiC from the matrix depends on both the processing time and temperature. Studies performed during the first two years of the program showed that the resulting ceramic composition could be modified by blending small quantities of SiH-containing materials into the PMVS polymer immediately prior to curing, or pyrolyzing in reactive gases.

The excess C in PMVS ceramic chars can be effectively scavenged with an added Si source. A variety of blends were prepared to cover a range of molar ratios of added Si to excess C from PMVS. Perhydropoly(silazane), PHPS, was used as a polymeric source of homogeneous Si_3N_4 and excess Si. The polymer produced a series of novel nanocrystalline ceramics when blended with the PMVS prior to pyrolysis. PHPS/PMVS polymer blends had higher char yields (70-85%) than either component polymer. Crystal growth was inhibited in the chars derived from PHPS/PMVS polymer blends, especially near stoichiometric ratios of added Si to excess C.

Elemental powder was a more effective source of Si than the PHPS polymer. The addition of submicron Si particles to the PMVS polymer was effectively employed to reactively scavenge the residual C from the PMVS char, but these particles were inhomogeneously distributed within the polymer matrix. Crystal growth of SiC was significantly enhanced above the melting point of Si in the submicron Si/PMVS blends.

Several representative ceramic matrix composites with good mechanical properties were fabricated with preceramic polymers and blends as the matrix source. The composites showed load versus deflection curves typical of non-brittle failure and tensile specimens shows fibrous failure. Microscopic analysis of the CMCs showed good infiltration of the polymer-derived matrix within and between fiber tows.

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VII. REFERENCES

1. "A Study of the Critical Factors Controlling the Synthesis of Ceramic Matrix Composites from Preceramic Polymers", J. R. Strife, J. P. Wesson and H. H. Streckert, AFOSR Contract F49620-87-C-0093, Final Technical Report (15 December 1990).

2. "Novel Precursor Approaches for CMC Derived by Polymer Pyrolysis", J. P. Wesson and J. R. Strife, AFOSR Contract F49620-91-C-0017, Annual Technical Report (15 December 1991).

3. "Novel Precursor Approaches for CMC Derived by Polymer Pyrolysis", J. P. Wesson and J. R. Strife, AFOSR Contract F49620-91-C-0017, Annual Technical Report (15 December 1992).

4. W. R. Schmidt, L. V. Interrante, R. H. Doremus, T. K. Trout, P. S. Marchetti, and G. E. Maciel, *Chem. Mater.* **3**[2] (1991) 257-267 and references therein.

5. C. L. Schilling, Jr., *Brit. Polym. J.* **18**[6] (1986) 355.

6. B. C. Mutsuddy, *Ceram. Int.* **13** (1987) 41-53.

7. G. Ramis, P. Quintard, M. Cauchetier, G. Busca, and V. Lorenzelli, *J. Am. Ceram. Soc.* **72**[9] (1989) 1692-1697.

8. (a) E. A. Williams in *The Chemistry of Organic Silicon Compounds*; eds. S. Patai and Z. Rappoport, Wiley: New York, 1989; Chapter 6. (b) E. A. Williams in *Annual Reports on NMR Spectroscopy*; Academic Press: London, 1983; Vol. 15.

9. K. R. Carduner, S. S. Shinozaki, M. J. Rokosz, C. R. Peters, and T. J. Whalen, *J. Am. Ceram. Soc.* **73**[8] (1990) 2281.

10. G. W. Wagner, B.-K. Na, and M. A. Vannice, *J. Phys. Chem.*, **93**[13] (1989) 5061.

11. D. T. Haworth and C. A. Wilkie, *J. Inorg. Nucl. Chem.* **40** (1978) 1689.

12. K. E. Inkrott, S. M. Wharry, and D. J. O'Donnell, *Mater. Res. Soc. Symp. Proc.* **73** (1986) 165.

13. G. R. Finlay, J. S. Hartman, M. F. Richardson, and B. L. Williams, *J. Chem. Soc., Chem. Commun.* (1985) 159.

14. B. D. Cullity, "Elements of X-Ray Diffraction", Addison-Wesley Publishing: London, 1978, p. 102.

15. K. R. Carduner, R. O. Carter, III, M. E. Milberg, and G. M. Crosbie, *Anal. Chem.* **59** (1987) 2794.

16. G. R. Hatfield and K. R. Carduner, *J. Mater. Sci.* **24** (1989) 4209.

17. based on a comparison with JCPDS-ICDD powder diffraction file card 41-360 (1993).

18. S. Yajima, *Philos. Trans. R. Soc. London, A* **294** (1980) 419.