Aluminum-27 and Silicon-29 Solid-State Nuclear Magnetic Resonance Study of Silicon Carbide/Aluminum Nitride Systems: Effect of Silicon/Aluminum Ratio and Pyrolysis Temperature

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Three series of SiC/AlN samples were prepared by pyrolysis of "poly(aluminosilazane)", the product of the reaction between hexamethylcyclotrisilazane and triethylaluminum. The Si/Al ratio was varied for one series (with constant pyrolysis temperature) and the pyrolysis temperature was varied for the other two series, with Si/Al = 1 and 3. ^{27}Al and ^{29}Si magic angle spinning NMR were used to analyze these samples in terms of coordination number, nearest neighbor atoms, and crystallinity. NMR results indicate that higher crystallinity and phase separation into discrete SiC and AlN crystallites accompany an increase in pyrolysis temperature. Disorder and increased heterogeneity in connectivity are observed with increasing Si/Al ratio of the initial reactants.

Introduction

There is substantial interest in advanced ceramic materials that can be employed at temperatures where superalloys are no longer useful. In addition to having high-temperature applications, these ceramics are lightweight, have excellent wear, oxidation, and corrosion resistance, are potentially energy-saving, and may be used in electronic devices.[1] SiC has been studied extensively for these applications but there have been problems with its low fracture toughness.[2] One demonstrated method to improve its mechanical and physical properties is to alloy it with other ceramic materials.[3] However, the alloyed component must have similar atomic or ionic sizes, properties, and electronegativities in order to form solid solutions.[1,4] AlN is similar in atomic size to SiC and has itself been investigated as a potential material for heat engine and ballistic armor applications.[5] Solid solutions of SiC and AlN have received a great deal of attention since the 1970s.[6,7] Hot pressing and sintering are the conventional methods of choice for preparation of these solutions in the form of simple ceramic shapes. Characterization of the microstructure and phase relationships of these materials has included traditional techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM).[2,5,8]

Conventional methods to form solid solutions suffer from unacceptable levels of impurities and the inability to easily shape the final ceramic into workable parts.[1] The use of polymer precursors provides the potential for more control of composition, decreased impurity levels, and the ability to shape or mold the final ceramic, as well as a reduction in manufacturing costs.[9] SiC and Si$_3$N$_4$ have been prepared from polysilanes, polycarbosilanes, and polysilazanes, as well as other precursors.[9–13] SiC/AlN solid solutions have been prepared by copyrolysis of two separate precursors. Czekaj et al.[14] pyrolyzed dialkyl aluminum amide compounds with either polycarbosilane or vinylic polysilane. Schmidt et al.[15] have prepared SiC/AlN from a single-source polymer made from the reaction of alkylaluminum compounds and 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilazane. Paine and co-workers have investigated the preparation of [(Me$_3$Si)$_2$AlNH$_2$]$_2$ and its pyrolysis to form SiC/AlN mixtures.[16,17]

To properly characterize these materials, the chemical environments, coordination numbers, and order in the

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Scheme 1

Single-source polymer

"poly(aluminosilazane)"
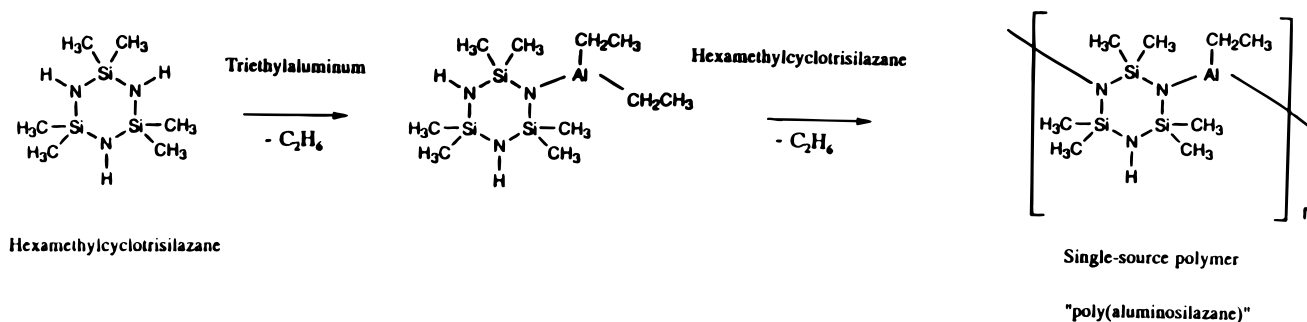
system must be known. Solid-state NMR has proven to be a useful analytical tool in the study of both polymer precursors and ceramic products. It has been applied to the characterization of materials such as SiC, SiC/Si_3N_4, Si_3N_4, AlN, Al_2O_3, SiC/AlN, and the sialons (ceramics containing Si, Al, O, and N).[9–11,15,18–25] Here we report ^{27}Al and ^{29}Si solid-state NMR data of SiC/AlN solid solutions prepared by the pyrolysis of "poly-(aluminosilazanes)"[15,26] with varied Si/Al ratios and varied pyrolysis temperatures. The results are discussed in relation to NMR data available for SiC, AlN, SiC/Si_3N_4, and the sialons, as well as the dependence of the ^{27}Al shifts on coordination number, the ^{27}Al signal intensity and line width on order, and the ^{29}Si shifts on connectivity to nearest neighbor atoms.

Experimental Section

Poly(aluminosilazane) (PAS) precursors were obtained by reacting hexamethylcyclotrisilazane (HMTS) and triethylaluminum (TEA) either neat or with both components dissolved in dry hexane at room temperature (see Scheme 1). Polymerization was monitored by IR spectroscopy and the N–H functionality was seen to decrease with time as the N–Al linkages were formed. Ethane formation was verified by mass spectroscopy. Network polymer formation was dependent on the ratios of the starting reactants. The polymers were pyrolyzed in nitrogen to obtain SiC/AlN ceramics. All chemicals and isolated products were handled in either a nitrogen-filled glovebox (H_2O, O_2 < 2 ppm) or using Schlenk techniques. Inert atmospheres were needed because of the pyrophoric nature of alkylaluminum compounds and the moisture sensi-

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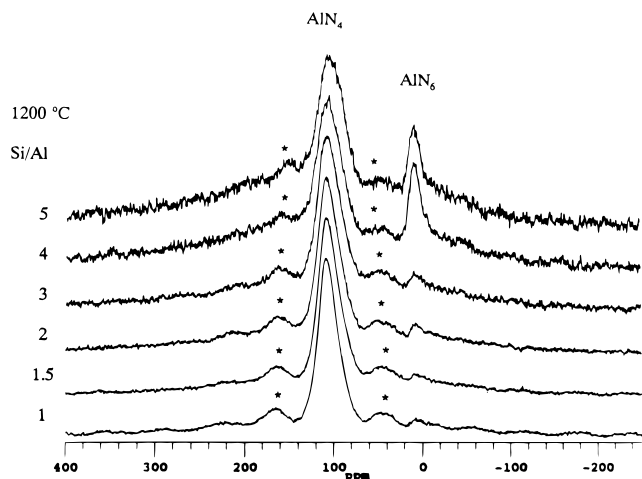
Table 1. Sample Series Studied, Including Sample Codes, Si/Al Ratios, and Pyrolysis Temperatures

series 1			series 2			series 3		
code	Si/Al ratio	temp[a]	code	Si/Al ratio	temp[a]	code	Si/Al ratio	temp[a]
A	1	1200	A300	1	300	C200	3	200
A′	1.5	1200	A400	1	400	C400	3	400
B	2	1200	A600	1	600	C600	3	600
C	3	1200	A800	1	800	C800	3	800
D	4	1200	A1000	1	1000	C1000	3	1000
E	5	1200	A1200	1	1200	C1200	3	1200
			A1400	1	1400	C1400	3	1400
			A1600	1	1600	C1600	3	1600
			A1800	1	1800	C1800	3	1800
			A1900	1	1900	C1900	3	1900

[a] Pyrolysis temperature in °C.

Table 2. Elemental Analysis of Sample C

element	wt %	mole ratio	pyrolysis temp, °C
C	18.34	2.81	1000
H	<0.5	0	1000
N	23.27	3.04	1000
Al	14.65	1.00	1000
Si	45.60	2.99	1000
C	17.54	2.64	1600
H	<0.5	0	1600
N	22.35	2.89	1600
Al	14.89	1.00	1600
Si	46.06	2.97	1600
C	19.48	2.41	1800
H	<0.5	0	1800
N	10.55	1.12	1800
Al	18.15	1.00	1800
Si	51.68	2.73	1800

tivity of high surface area ceramic powders. Polymer samples were pyrolyzed in nitrogen in a sealed quartz reactor from 200 to 1000 °C for 1 h, using 2 °C/min heating and cooling rates, and retrieved and ground in a glovebox for subsequent analysis. Samples heated from 1200 to 1900 °C were first pyrolyzed in nitrogen to 1000 °C, cooled, and subsequently transferred to an alternate furnace. Pyrolysis at the higher temperatures was also carried out under nitrogen.

Three series of samples were prepared, as summarized in Table 1. For series **1**, the ratio of HMTS and TEA was varied to achieve Si/Al ratios from 1 to 5 (samples **A** through **E** in Table 1) and pyrolysis was carried out at 1200 °C. It should be noted that the Si/Al ratio equals the N/Al, as shown in Scheme 1. Series **2** and **3** contained samples with Si/Al =1 and Si/Al = 3, respectively. These series were pyrolyzed to various temperatures from 200 to 1900 °C. Elemental analysis was performed on the samples having an initial Si/Al ratio = 3 by Galbraith Laboratories (Table 2). Compositions within a few percent of the starting materials for Si, N, and Al were found when the pyrolysis temperature was below 1600 °C. Above this temperature a loss of nitrogen is observed. The Si/C ratio was about 1.1 for all pyrolysis temperatures. No oxygen is apparent from the elemental analysis results,

Figure 1. ^{27}Al MAS NMR spectra of series **1**, with varied Si/Al ratios. (Asterisks denote spinning sideband.)

Figure 2. ^{29}Si MAS NMR spectra of series **1**, with varied Si/Al ratios.

consistent with the NMR results (vide infra) and the oxygen-free environments in which the samples were prepared. The sample with a Si/Al ratio of 3:1 gave $Si_{3.0}C_{2.8}AlN_{3.0}$ following 1000 °C pyrolysis, $Si_{3.0}C_{2.6}AlN_{2.9}$ following pyrolysis at 1600 °C, and $Si_{2.7}C_{2.4}AlN_{1.1}$ after 1800 °C pyrolysis. For the last two series, references to samples will be made by their Si/Al ratio (**A** for Si/Al = 1, **C** for Si/Al = 3) and pyrolysis temperature. For example, the sample from series **3** with Si/Al = 3 and pyrolyzed at 1600 °C is listed as **C1600** in Table 1.

^{29}Si and ^{27}Al solid-state magic angle spinning (MAS) NMR spectra were recorded on a Chemagnetics CMX-360 spectrometer, operating at 71.52 MHz for Si and 93.79 MHz for Al. Zirconia PENCIL rotors were used, and samples were packed in an argon atmosphere. Magic angle spinning speeds of 4.7–5.0 kHz and single-pulse excitation with phase cycling were employed. ^{27}Al spectra were acquired with a pulse width of 1.1 μs (π/15 flip angle) and a 5 s recycle delay. These spectra were referenced to aqueous $Al(NO_3)_3$ (0 ppm). The rotors contain no background ^{27}Al signals. For ^{29}Si, a pulse width of 2.7 μs (π/6 flip angle) and a 60 s recycle delay were used. ^{29}Si spectra were referenced to tetrakis(trimethylsilyl)silane, which was itself referenced to tetramethylsilane (TMS) at 0 ppm.

XRD specimens were prepared by finely grinding the samples with either an alumina or boron carbide mortar and pestle. Ground samples were examined using a low-background specimen holder. 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 10–80°, with a count time of 1.5 s at each step. A 0.05° receiving slit and a 1° divergence slit were used for all data.

Results: Variation of the Si/Al Ratio

All of these samples were pyrolyzed at 1200 °C. At this low pyrolysis temperature, the samples were not sufficiently crystalline for X-ray diffraction structure determination. Therefore only NMR results are reported. Figure 1 shows the ^{27}Al spectra for the samples pyrolyzed to 1200 °C with varied starting composition (series **1**). For **A**, a relatively sharp peak near 109 ppm is observed. There is no major change in the spectrum for **A′**, with a Si/Al ratio of 1.5. As the Si/Al ratio is increased in **B**–**E** a new resonance at 8 ppm becomes more pronounced. The major peak near 100 ppm moves gradually upfield and the signal-to-noise ratio decreases.

Figure 2 shows the ^{29}Si NMR results for series **1**. For **A**, a broad, symmetric peak at −18 ppm is seen. For **A′**, the same broad peak is observed, with the hint of
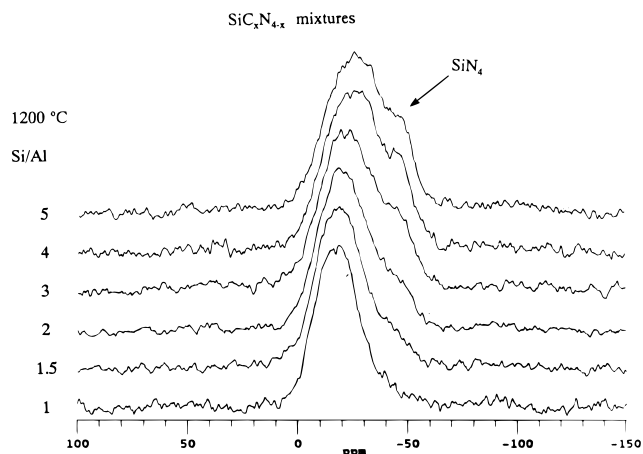
an upfield shoulder. In **B**, a definite shoulder in the main peak appears at −47 ppm. The spectrum of **C** looks similar to **B**. In samples **D** and **E**, the main resonance has moved slightly upfield, with a definite shoulder near −45 ppm still visible.

Discussion: Variation of the Si/Al Ratio

^{27}Al NMR. 27Al chemical shifts are very dependent on coordination number. This has been well established in studies of zeolites where both AlO_4 and AlO_6 units have been identified.[27] The tetrahedral unit appears between +50 and +80 ppm and the octahedral unit between −10 and +20 ppm. For alkylaluminum compounds, the peak position in solution-state NMR moves upfield with increasing coordination number.[28] Three-coordinate alkylaluminum compounds show resonances in the 270−210 ppm range, four-coordinate appear in the 210−140 ppm range, and five-coordinate are in the 140−110 ppm range. For Al−N coordination compounds,[29] solution NMR has shown that the chemical shift for tetrahedrally coordinated Al appears near 108 ppm. As the coordination increases to octahedral, the shift moves upfield to 6 ppm. Five-coordinate Al and distorted octahedra have shifts between these two values. Solid-state NMR studies of AlN (which has a wurtzite structure with tetrahedrally coordinated Al) have shown that Al exhibits a resonance near 110 ppm.[20−22,24] The exact resonance position depends on the magnetic field strength used, due to contributions from second-order quadrupolar interactions.[20]

In the ^{27}Al spectra of varying compositions (Figure 1), all of the samples exhibit a peak near 108 ppm. At the higher Si/Al ratios, a peak near 6 ppm appears, and the signal-to-noise ratio of the major peak decreases. The downfield peak is assigned to tetrahedral AlN_4 units and the upfield peak is assigned to octahedral AlN_6 units, based on peak positions of coordination complexes in solution and compounds in the solid state. The formation of octahedral Al at higher Si/Al ratios is

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expected as the system attempts to accommodate the increasing number of N atoms (Si/Al = N/Al, see Scheme 1).

The loss of ^{27}Al NMR intensity along with the slight broadening of the tetrahedral peak is consistent with the increase in the electric field gradients surrounding the Al center. This could be due to either a loss in crystallinity or the formation of AlC_xN_{4-x} units, both of which create an asymmetric environment about the Al nucleus. Formation of AlC_xN_{4-x} units has been discussed in other work on the synthesis of SiC/AlN ceramics from organometallic precursors;[30] however, limited NMR data is available. Severe distortion leads to "NMR-invisible" aluminum species and a decrease in signal intensity.[20]

^{29}Si NMR. [29]Si chemical shifts for SiC_xN_{4-x} units in ceramics have been calculated based on shifts for organosilicon compounds and on model calculations.[17,31] For SiC_4 units, the shift is expected at −20 ppm. SiC_3N units show a "sagging behavior" with a peak at −14 ppm. This same trend has been observed in the siliconoxycarbides, SiC_xO_{4-x}. SiC_2N_2, $SiCN_3$, and SiN_4 units have shifts at −22, −37, and −48 ppm, respectively, although the chemical shifts in a particular sample may vary significantly due to second nearest neighbors. In the ^{29}Si NMR spectrum (Figure 2) of **A** (Si/Al = 1), there is a broad peak centered at −18 ppm. This broad peak appears to arise from a mixture of SiC_4, SiC_3N, and SiC_2N_2 units. As the Si/Al ratio increases, a shoulder at −48 ppm becomes more prominent. This position is assigned to Si_3N_4 (SiN_4 units).[10,19,24,31] The peaks in the [29]Si spectra become broader as the Si/Al ratio increases. Under MAS this broadening is due to an increase in the distribution of isotropic shifts caused by an increase in sample heterogeneity. The observed resonances confirm a mixture of SiC_xN_{4-x} units.

Results: Variation of Pyrolysis Temperature (Si/Al = 1)

The [27]Al and [29]Si spectra for the series **2** samples (series with Si/Al = 1) are shown in Figures 3 and 4, respectively. The [27]Al spectrum of **A300** (the lowest temperature which gave a solid for this Si/Al ratio) shows a very broad peak centered at 30 ppm. For **A400**, three peaks are visible above the broad base, at 52, 33, and −1 ppm. In the spectrum of **A600**, there are also three peaks, at 102, 55, and −4 ppm, the middle resonance having the greatest intensity. As the pyrolysis temperature is increased to 800 °C (**A800**) only two peaks are visible, at 103 and 6 ppm, and these are approximately the same height. For **A1000**, a single peak at 103 ppm is seen. For **A1200**, **A1400**, **A1600**, **A1800**, and **A1900**, the resonance sharpens and remains near 109 ppm. There are drastic changes in signal/noise ratio as the pyrolysis temperature is varied.

In the [29]Si spectrum of **A300**, a large peak near 0 ppm is seen. A [29]Si−{[1]H} cross polarization experiment (CPMAS) produced an identical spectrum (not shown). For **A400**, there is a large peak at 3 ppm with a small shoulder at −22 ppm. For **A600**, a resonance at −13
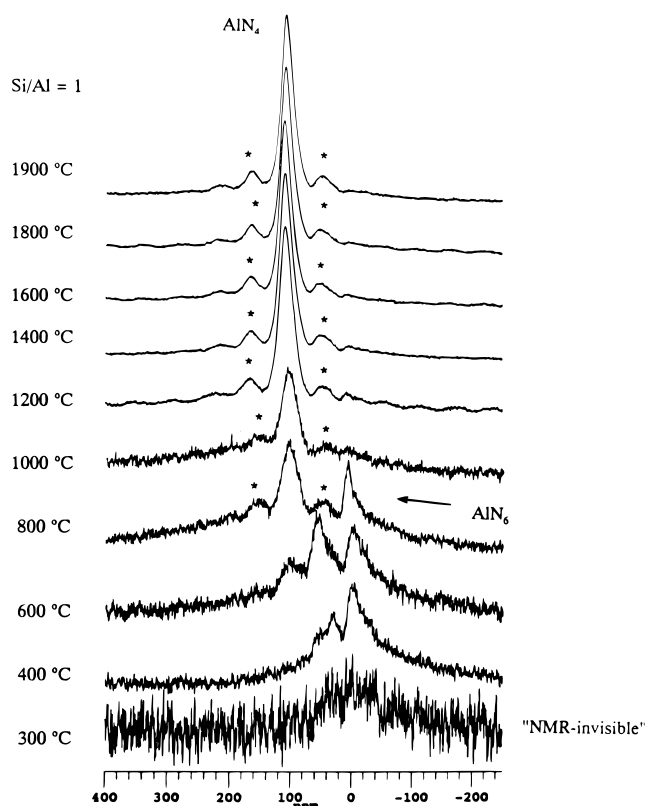
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(31) Gerardin, C.; Henry, M.; Taulelle, F. *Mater. Res. Soc. Symp. Proc.* **1992**, *271*, 777−782.

Figure 3. ^{27}Al MAS NMR spectra of series **2**, with Si/Al = 1 and varied pyrolysis temperatures. (Asterisks denote spinning sidebands.)

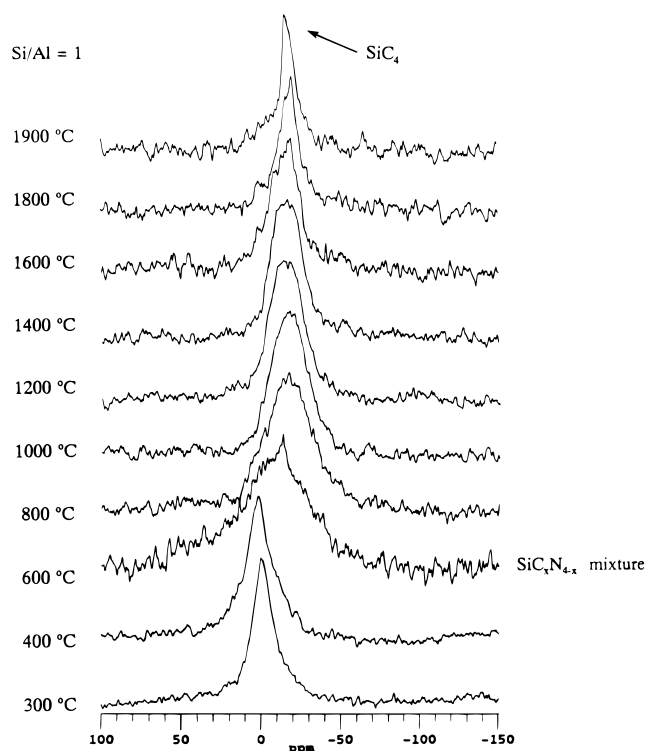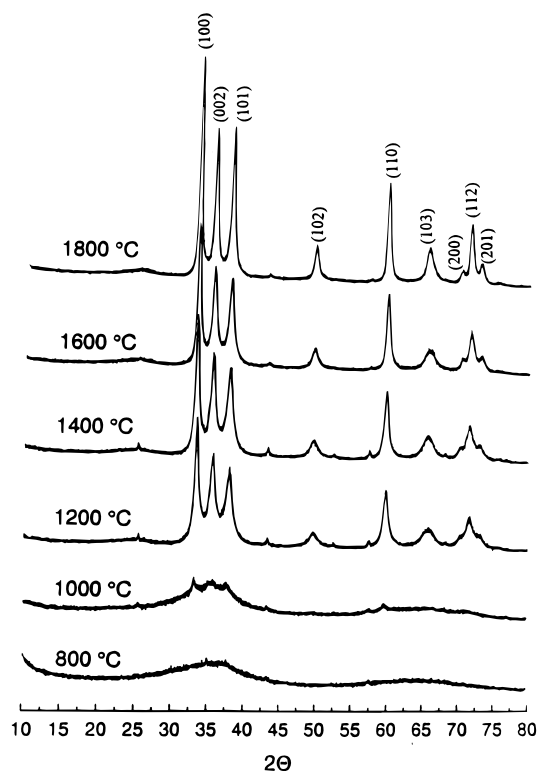**Figure 4.** ^{29}Si MAS NMR spectra of series **2**, with Si/Al = 1 and varied pyrolysis temperatures.

ppm with a broad downfield shoulder is seen. For **A800**, there is a very broad peak at −17 ppm. As the pyrolysis temperature is increased from 1000 to 1900 °C, a peak near −16 ppm becomes visible and sharpens with increasing temperature.

Figure 5. XRD patterns for series **2** samples, from 80 to 1800 °C.

Figure 5 shows the XRD patterns for series **2**, with Si/Al = 1 and pyrolysis temperatures from 800 to 1800 °C. Sample crystallinity does not appear to any significant extent until 1200 °C. As the temperature is further increased, crystallinity increases, as evidenced by sharper lines.

Discussion: Variation of Pyrolysis Temperature (Si/Al) = 1

^{27}Al NMR. Figure 3 shows the effect of pyrolysis temperature on the ^{27}Al spectra of samples with Si/Al = 1. The spectrum at 300 °C shows a very broad resonance, indicating that the environment around the Al atoms is very distorted. The starting coordination of Al in the polymer is trigonal, which is not a high-symmetry cubic environment. Al remaining in this coordination upon solidification is expected to be broad or invisible. At 400 °C, broad peaks appear near 52, 33, and −1 ppm. For Al−N complexes in solution, distorted octahedra and five-coordinate Al have peaks at 25−41 ppm and ∼84 ppm, respectively. We tentatively assign the intermediate resonances at 33 and 52 ppm to AlN_5 units. At 600 °C, a peak near that of tetrahedral AlN appears (100 ppm) with the peaks near 33 and 52 ppm still visible. At 800 °C there are peaks at 103 and 6 ppm, indicating slightly distorted AlN_4 units and some AlN_6 units. At 1000 °C only the tetrahedral peak is visible. At 1200 °C there is a drastic increase in intensity, indicating a great increase in symmetry around the Al atoms in the material. As the pyrolysis temperature increases through 1900 °C, only the tetrahedral resonance associated with AlN is seen, becoming narrower and moving downfield. This behavior indicates higher symmetry and crystallinity at the higher temperatures.

^{29}Si NMR. In the ^{29}Si spectra of the same series (Figure 4), a peak near 0 ppm is seen at 300 °C. The position of the peak and the fact that a CPMAS spectrum was obtainable indicates that there are Si centers with the starting methyl groups still present. The initial Si structure is SiC_2N_2, with hydrogen as the second-nearest neighbor on C. At 400 °C, other $SiC_xN_{4−x}$ units begin to form. Between 600 and 1000 °C, there appears to be a mixture of $SiC_xN_{4−x}$ units, yielding a broad peak. Spectra of the samples pyrolyzed above 1000 °C exhibit even narrower resonances, indicating higher crystallinity and less Si−N bonding. This behavior is indicative of SiC formation.

XRD. XRD patterns (Figure 5) show an increase in crystallinity with increased temperature. There is an especially prominent increase at 1200 °C. This is consistent with both the ^{27}Al and ^{29}Si spectra which show increases in signal-to-noise ratio and narrower peaks that are close to AlN and SiC values as the temperature is increased. It should be noted that the highest temperature used in this study was below the temperature for solid solution formation according to the SiC/AlN phase diagram proposed by Zangvil and Ruh.[8] AlN- and SiC-rich phases are expected below 1950 °C (δ_{AlN} and δ_{SiC}). XRD results indicate solid solution formation, having intermediate 2Θ values. The NMR results, while showing that both bonding environments exist, do not yield information on the scale of mixing.

Results: Variation of Pyrolysis Temperature (Si/Al = 3)

Figures 6 and 7 show the ^{27}Al and ^{29}Si NMR results for series **3** (sample **C** with Si/Al = 3). The ^{27}Al spectrum of **C200** shows two peaks, one at 55 ppm and the other near 0 ppm. The **C400** spectrum looks similar to that of **A300**, with a very broad, almost undetectable resonance. For **C600**, the spectrum shows a large peak at 95 ppm and the indication of some signal buried upfield in the broad base. The spectra of **C800** and **C1000** each have a resonance at 95 ppm and one at 8 ppm. For **C1200**, the major signal is at 108 ppm with a small peak at 6 ppm. A major increase in signal-to-noise ratio accompanies heating to 1400 °C with this Si/Al ratio. In **C1400** and **C1600** the major resonance is still at 108 ppm, with a definite peak at 8 ppm. The spectra of **C1800** and **C1900** show a peak at 110 ppm with a small but very sharp peak at 141 ppm.

For the ^{29}Si spectra of sample **C**, very broad resonances are seen from 200 to 1600 °C, with the peak center moving upfield with increasing temperature. **C200** and **C400** show peaks centered downfield (compared to the low pyrolysis temperature ^{29}Si spectra of series **2**) with shoulders on the upfield side, close to −20 ppm. **C600** to **C1200** contain one broad peak moving upfield with higher temperature. **C1400** and **C1600** show resonances centered at −20 ppm with shoulders at −50 ppm. **C1800** and **C1900** each contain a much narrower peak near −20 ppm, with a small signal on the downfield side.

Figure 8 shows the XRD patterns for series **3**, with Si/Al = 3 and pyrolysis temperatures from 800 to 1800
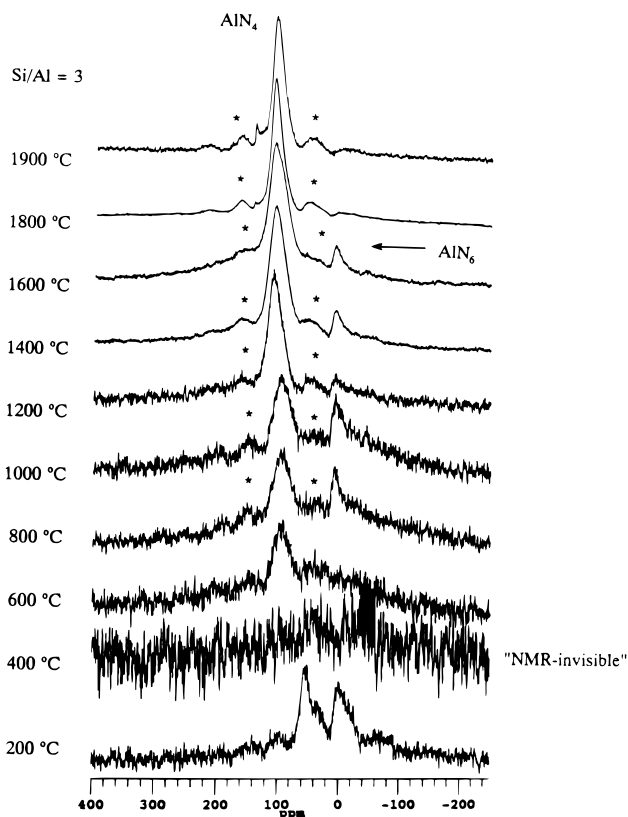
Figure 6. ^{27}Al MAS NMR spectra of series **3**, with Si/Al = 3 and varied pyrolysis temperatures. (Asterisks denote spinning sidebands.)
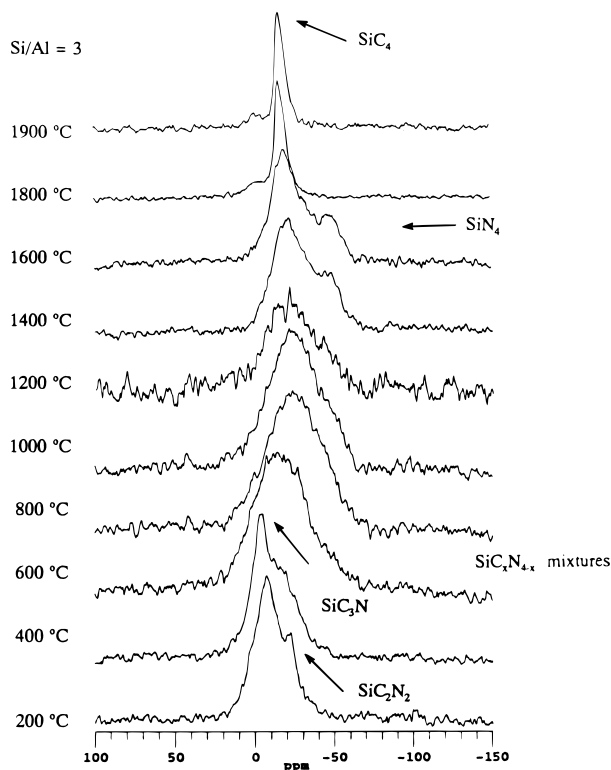

Figure 7. ^{29}Si MAS NMR spectra of series **3**, with Si/Al = 3 and varied pyrolysis temperatures.

°C. The samples remain amorphous up to 1600 °C, with some crystallinity below this temperature. There is an unmistakable increase in crystallinity between 1600 and 1800 °C.
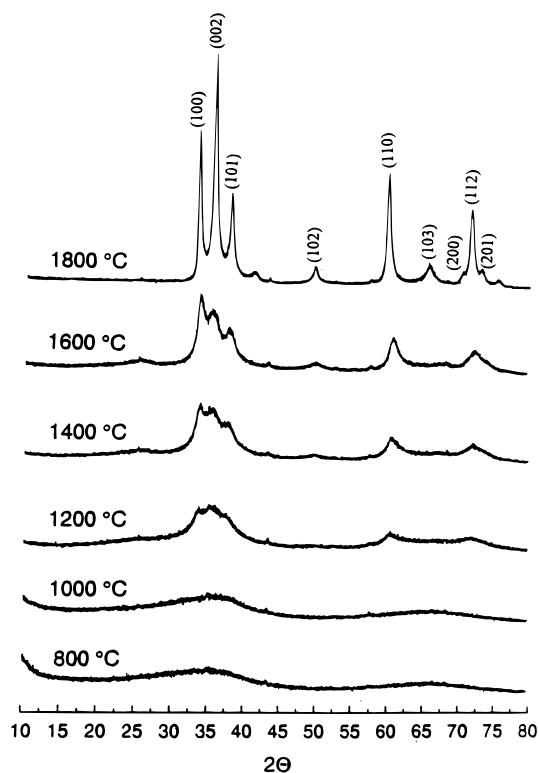

Figure 8. XRD patterns for series **3** samples, from 800 to 1800 °C.

Discussion: Variation of Pyrolysis Temperature (Si/Al = 3)

^{27}Al NMR. In the [27]Al spectra following pyrolysis at 200 °C, signals at 55 and 0 ppm are seen. While the position of the resonance at 55 ppm is coincidentally near that expected for oxygenated Al,[27] we are certain it does not correspond to AlO_4 units. The [29]Si spectrum shows no evidence of oxidation (i.e. resonances for SiO_4 and SiO_3X units, X = C or N). Careful procedures for eliminating oxygen exposure were used throughout sample preparation and analysis. In addition, those samples tested via elemental analysis showed no oxygen present. We therefore assign this resonance to five-coordinate Al. At 400 °C no peaks are visible, indicating a very distorted Al environment. At 600 °C, a broad peak at the position of AlN_4 units appears. At 800 and 1000 °C a resonance associated with octahedral coordination reappears. At higher pyrolysis temperatures, the intensity of the octahedral peak decreases and eventually vanishes while the tetrahedral resonance narrows and the signal-to-noise ratio improves. Again, this is attributed to higher crystallinity and higher symmetry about Al. The origin of the small but sharp signal at 141 ppm is not clear at this time.

^{29}Si NMR. Figure 7 shows the [29]Si spectra of this same series. At 200 °C, a broad resonance from 0 to −15 ppm and a second major resonance at −22 ppm are observed. Again, SiC_2N_2 units are expected early in the pyrolysis because of the poly(aluminosilazane) structure, accounting for the peak at −22 ppm. The broad resonance to low field is probably due to formation of SiC_3N units. Thus, there is already a hint of the formation of a mixture of SiC_xN_{4-x} units, with x = 1 and 2. As the temperature increases, the variety of SiC_xN_{4-x} units increases, including SiN_4 (visible at 600

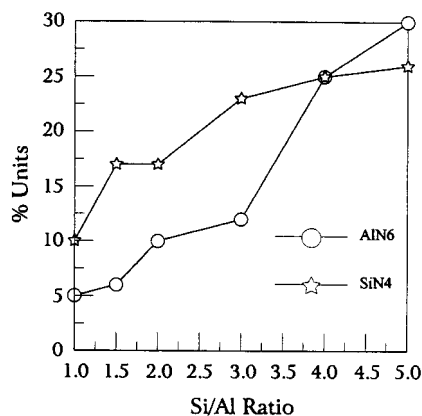**Figure 9.** Plot of integration results for percentage of AlN_6 and SiN_4 units in series **1** samples (varied Si/Al ratio).

°C). SiN_4 units appear in the spectrum up to 1600 °C. Above 1800 °C, only a SiC resonance is present.

XRD. XRD patterns for series **3** show the same trends as for series **2**. Increased temperature results in increased crystallinity. Specifically, a dramatic improvement in crystallinity is seen above 1600 °C. It is interesting to note that for all three series the appearance of an ^{27}Al resonance at 6 ppm (for six-coordinate Al) coincides with the appearance of the peak for SiN_4 units in the ^{29}Si spectra. In particular for this last series, the resonances for AlN_6 units and SiN_4 units both disappear above 1600 °C. A possible mechanism for the disappearance of SiN_4 units is the reaction of Si_3N_4 with excess C to form N_2: $Si_3N_4 + 3C \rightarrow 3SiC + 2N_2$. The disappearance of the NMR signals for AlN_6 and SiN_4 species coincides with the increase in crystallinity from the XRD results.

For series **1**, with increasing Si/Al ratio, the spectra were integrated in order to determine the percentages of AlN_6 and SiN_4 units in the material. Figure 9 shows the results for these samples. The percentages of Al as AlN_6 units track the percentages of Si as SiN_4 units. From the coexistence of SiN_4 and AlN_6 units in all three series and from the observation of increased crystallinity with their co-disappearance (from XRD and NMR results), a structure for an intermediate during the pyrolysis can be proposed. When both AlN_6 and SiN_4 units exist concurrently, the structure of part of the sample may take on the form of a coordination complex, with the silazane rings coordinated around the Al. Because of steric considerations, this "complex" would have varying bond angles and lack crystallinity. Also, several different AlC_xN_{4-x} and SiC_xN_{4-x} units would be present in the remainder of the sample. The purpose of the proposed structure in Figure 10 is to correlate the existence of both AlN_6 and SiN_4 and does not represent a repeat unit. These environments would cause broadening of the ^{27}Al and ^{29}Si NMR resonances as well as deviations from the resonance positions expected for each unit, which is observed in the NMR results. Paine et al.[17] have proposed a similar molecular structure for $Al[(Me_3Si)_2Al(NH_2)_2]_3$, which upon pyrolysis at 930 °C in vacuo produces a powder X-ray diffraction pattern that is similar to that shown in Figure 5 for the sample heated to 1200 °C. Prior studies have shown that the sharpness and relative intensity of the
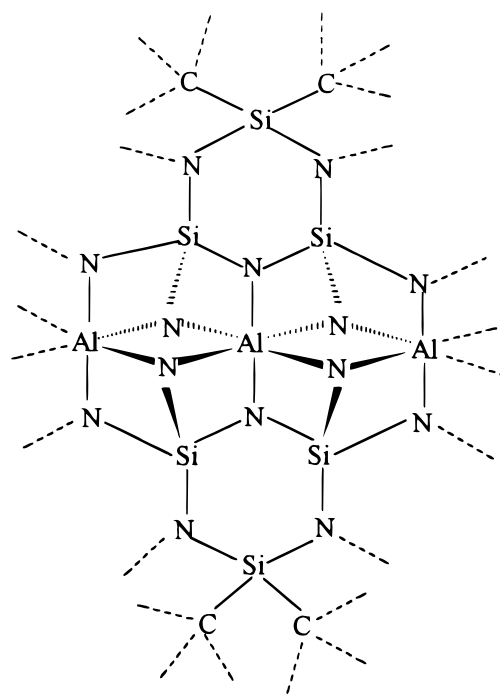

Figure 10. Proposed intermediate structure of SiC/AlN ceramic prepared from poly(aluminosilazane), showing coexistence of AlN_6 and SiN_4 units.

three primary peaks in the diffraction pattern depend on the Si/Al ratio used in the initial reaction.[32]

Conclusions

Solid-state NMR spectroscopy has been shown to be a useful tool in the characterization of SiC/AlN ceramics. For these series of SiC/AlN ceramics, the number of different SiC_xN_{4-x} and AlC_xN_{4-x} units increased with increasing Si/Al ratios. ^{27}Al and ^{29}Si spectra showed the formation of AlN_6 and SiN_4 units as the Si/Al (and N/Al) ratio was increased. Increasing the pyrolysis temperature increased the crystallinity of these samples, and NMR results indicated phase separation into SiC and AlN at the highest temperatures. SiC and Si_3N_4 were found upon pyrolysis at 1600 °C. A connectivity between the formation of six-coordinate Al and Si_3N_4 was established. The poly(aluminosilazane) used in this study was shown to be a promising single-source precursor to SiC/AlN materials. Change in pyrolysis temperature and starting ratio determined the composition of the final product, which proves that control of the final product can be achieved.

(32) W. R. Schmidt, unpublished work.