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ORGANOMETALLIC PRECURSOR ROUTES TO Si-C-Al-O-N CERAMICS

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This report describes the results of a research program directed at the development of improved methods for the preparation of Si-C-Al-O-N ceramics using organometallic precursors. Two main approaches were employed in these studies, (1) co-pyrolysis of homogeneous mixtures of organosilicon and organoaluminum precursors and (2) pyrolysis of specially designed, single-component precursors containing both Si and Al.

Depending on the choice of precursors and the pyrolysis atmosphere employed, nanocrystalline -SiC/2H-AlN and Si_3N_4/AlN composites, 2H-SiC/AlN solid solutions, and various crystalline SiAlON phases were obtained as final ceramic products after annealing at 1400-1800 °C. In the course of this work, new precursors to both AlN and SiC were identified and their structures and pyrolysis reactions were investigated, providing useful information regarding structure/pyrolysis chemistry relationships for such precursor systems.

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In addition to establishing a general approach to nanocrystalline composites and solid solutions containing various nitride and carbide ceramics, this effort has led to new processible precursors that could find use in the application of protective coatings on metals, ceramic fibers, etc. and in the fabrication of ceramic matrices or fibers for high temperature structural composites.

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SUMMARY

This report describes the results of a research program directed at the development of improved methods for the preparation of Si-C-Al-O-N ceramics using organometallic precursors. Two main approaches were employed in these studies, (1) co-pyrolysis of homogeneous mixtures of organosilicon and organoaluminum precursors and (2) pyrolysis of specially designed, single-component precursors containing both Si and Al.

Depending on the choice of precursors and the pyrolysis atmosphere employed, nanocrystalline *β*-SiC/2*H*-AlN and Si_3N_4/AlN composites, 2*H*-SiC/AlN solid solutions, and various crystalline SiAlON phases were obtained as final ceramic products after annealing at 1400-1800 ^oC the initially amorphous pre-ceramic phases obtained on pyrolysis to 1000 ^oC. In the course of this work, new precursors to both AlN and SiC were identified and their structures and pyrolysis reactions were investigated, providing useful information regarding structure/pyrolysis chemistry relationships for such precursor systems.

Finally, preliminary studies were carried on single-component precursors which contained B and Ti in addition to Si and Al. These precursors yielded homogeneous nanocrystalline composites of BN and TiN with Si_3N_4 and AlN on pyrolysis in NH_3 to 1000 ^oC, followed by annealing at 1600-1800 ^oC.

In addition to establishing a general approach to nanocrystalline composites and solid solutions containing various nitride and carbide ceramics, this effort has led to new processible precursors that could find use in the application of protective coatings on metals, ceramic fibers, etc. and in the fabrication of ceramic matrices or fibers for high temperature structural composites.

INTRODUCTION

This program was originally funded for a 18 month period as a successor to a three-year research effort which was directed specifically at the preparation of SiC/AlN solid solutions (AFOSR Contract No. F49620-85-0019; 1985-8). A three-month, no-cost extension was subsequently granted, extending the duration of the program to a total of 21 months.

The chief objective of the new program was to develop organometallic precursor routes to specific compositions and phases in the Si-C-Al-O-N system and to demonstrate the potential utility of these precursors as a source of ultrastructures and nanocomposites in the Si-C-Al-O-N system. These nanocomposites are expected to exhibit unusual mechanical properties (from high strength and toughness to superplasticity) and improved improved microstructural stability at high temperatures relative to the individual component phases alone[1]. This combination of properties, coupled with the processing advantages afforded by their polymeric precursors, offers excellent opportunities for use of these materials as protective coatings on metals, carbon, etc. and as components (fibers, matrices and coatings) of structural composites with improved high temperature strength and toughness.

SUMMARY OF RESEARCH ACCOMPLISHMENTS

During the first year of the program, particular emphasis was placed on the synthesis and evaluation of precursors to SiC and AlN that could be used as alternatives to the commercial organosilicon polymers and the organoaluminum amides that we had employed previously for the preparation of SiC/AlN solid solutions. This was neccessitated by problems experienced in our earlier work with precursor immiscibility, premature pyrolysis of the organoaluminum amides, and control of carbon content in the final ceramic. During the remainder of the program, these precursors were employed, along with new single-component precursors, to obtain nanocomposites and solid solutions in the Si-C-Al-O-N system. In addition, preliminary work was carried out employing precursors which contained B and Ti in addition to Si and Al, to determine the generality of this polymer pyrolysis route to nanocrystalline composites of refractory nitride and carbide ceramics.

Investigation of AlN Precursors

Our prior studies of organoaluminum amides as precursors to AlN were extended to include an examination by NMR spectroscopy of the structures and reactions of the dialkylaluminum amides of the type $[R_2AlNH_2]_n$ in solution. The results, which indicate the existence of equilibria involving the dimeric (and presumably monomeric forms, i.e., n = 1 and 2) as well as rapid exchange reactions in the presence of ammonia and organic amines[2], provide an explanation for the effectiveness of ammonia in eliminating organic groups at low temperatures during the conversion of these amides to AlN.

In a separate investigation of the trialkylaluminum/ethylenediamine system as a potential source of polymer precursors to AlN suitable for the solution deposition of thin films, thermolysis of the initially formed R_3Al/en Lewis acid base adducts was found to lead, via a series of novel oligimeric species, to polymeric products showing different degrees of cross-linking depending on the initial R_3Al:en ratio.[3,4] Using a 2:1 R_3Al:en initial composition, soluble polymeric amides derivatives were obtained on heating which were used to deposit thin films of AlN on various substrates by solution deposition followed by pyrolysis under ammonia.[3]

Synthesis of New Polycarbosilane Precursors

Our efforts to synthesize new SiC polymer precursors were motivated by problems encountered in controlling the carbon content and microstructure of the product SiC employing commercial precursor sources. This work has focused on the preparation of near-stoichiometric, "SiH_2CH_2" polycarbosilanes by two different reaction pathways: (1) ring opening polymerization (ROP) of disilacyclobutanes, and (2) Grignard coupling of chlorocarbosilanes. In the former case, 1,3-dimethyl-1,3-dichloro- and 1,3-tetramethyl-disilacyclobutane were converted to high molecular weight polycarbosilanes by ROP with the aid of a platinum catalyst[5]. As was expected on the basis of prior studies, the fully methylated polycarbosilane gave a negligible char yield on pyrolysis under nitrogen; however, the $[SiMe(H)CH_2]_n$ polymer derived from the dimethyldichlorodisilacyclobutane, after reduction with $LiAlH_4$, gave a low yield of amorphous SiC on pyrolysis to 1000 °C which could be increased by increasing the molecular weight of the polymer or by holding at 400 °C to allow crosslinking by hydrogen elimination and Si-Si bond formation. We have recently extended this study to include ROP of the corresponding 1,1',3,3'-tetrachlorodisilacyclobutane. The linear $[SiH_2CH_2]_n$ polymer obtained in this case after reduction was found to have a surprisingly high ceramic yield (78%) on pyrolysis to 1000 °C in N_2, suggesting that crosslinking by Si-Si bond formation here competes effectively with the loss of volatile fragments by homolytic Si-C bond breaking.

The second approach to polycarbosilane precusors to SiC has focused on the preparation of a highly branched polymer of the composition "$SiH_{1.85}Et_{0.15}CH_2$" (hitherto referred as "HPCS", or hydridopolycarbosilane) by Grignard coupling of chloromethyltrichlorosilane [Cl_3SiCH_2Cl] followed by reduction with $LiAlH_4$. This work was initiated during our prior AFOSR Contract (F49620-85-K-0019); however, substantial improvements in the synthesis method and the characterization of the polycarbosilane product were accomplished since the conclusion of that Contract and two full papers describing the results of this study and the synthesis and separate study of various "model" organosilanes used in the characterization of the polymer by NMR methods have been prepared and submitted for publication.[6,7] The resultant polycarbosilane was found to have a highly branched structure, analogous to the so-called "arborols"[8] or "starburst dendrimers"[9], in which the $-SiCH_2-$ units are joined "head-to-tail" in such a manner that there is extensive branching at the Si but little or no cross-linking. Thus the polymers are soluble in aliphatic hydrocarbon solvents and range from low-viscosity liquids to viscous syrups depending on the molecular weight. These polymers convert to essentially stoichiometric SiC in up to 67% ceramic yield on pyrolysis at 10 °C/min under nitrogen to 1000 °C in a TGA apparatus. The resultant solid is amorphous to x-rays but crystallizes to β-SiC on annealing at 1400-1600 °C. Moreover, the initial liquid polycarbosilanes undergo facile crosslinking on heating at 200-300 °C to produce glassy solids with little resultant weight loss. These glasses show very high char yields with an overall weight losses from initial polymer to SiC ceramic of less than 20%. Recently, we have found that this polymer can be used to solution coat carbon and other substrates with uniform, amorphous SiC films which appear to inhibit oxidation of the substrate in air at 600 °C. A patent application on the polycarbosilane compositions and method of preparation was submitted in July 1990 on behalf of RPI by the AKZO Corporation in exchange for a licence agreement.

A detailed study of the pyrolysis of this polycarbosilane under nitrogen was carried out which included the characterization of the intermediate solid products as a function of temperature during the pyrolysis to 1000 °C by solid state NMR (^{29}Si, ^{13}C and ^{1}H) and IR spectroscopy[10]. A key result is the finding that the concentration of the Si-H groups in the polymer decrease relative to the C-H groups during solidification, suggesting strongly that the elimination of H_2 from the Si-H functionalities, with resultant cross-linking via Si-Si bond formation, is responsible for the thermosetting observed on heating. We also see (by solid state ^{13}C NMR spectroscopy) very little excess carbon in the SiC ceramic obtained at 1000 °C. Consistent with this low free carbon content, the amorphous powder obtained at 1000 °C shows no apparent weight loss on heating in air to 1000 °C, whereas the corresponding powder obtained from a commercial vinylic polysilane commonly used as a SiC precursor (Y-12044, Union Carbide Corp.) shows a rapid ca. 7% weight loss above 650 °C under these same conditions. Clearly, this polymer shows considerable promise for use as a SiC precursor, both for coating applications and for preparation of SiC matrices by liquid phase infiltration. These applications are currently being pursued in the context of other programs in progress in our laboratory.

Preparation of SiC/AlN Solid Solutions Using the HPCS Polymer

Following the same general "copyrolysis" approach that we employed in our earlier work[11], the HPCS polymer was mixed with $[Et_2AlNH_2]_3$ to form a homogeneous liquid mixture which was subsequently pyrolyzed under different conditions to yield SiC/AlN ceramics[12]. In this case, the near-stoichiometric Si/C ratio and relative simplicity of the functional groups in the HPCS polymer afford an opportunity to control the carbon content of the final ceramics and to examine the precursor-to-ceramic conversion chemistry in more detail. As is suggested by the substantially enhanced TGA yield for the mixture, as compared to that of the two precursors alone, these precursors apparently undergo a reaction during pyrolysis which effectively inhibits the loss of volatile organosilane and aluminum species. The amorphous black solid obtained after pyrolysis to 1000 °C crystallizes directly to a *2H*-SiC/AlN solid solution on annealing to 1800 °C. A complete solid state NMR study of this system is currently in progress; however, preliminary ^{27}Al and ^{13}C NMR spectra obtained on the 1000 °C and 1800 °C samples suggests that phase separation occurs on crystallization to form AlN- and SiC-rich 2H solid solution phases, as expected from the preliminary phase diagram published by Ruh and Zangvil[13].

Single-component Precursors to SiC/AlN, Si_3N_4/AlN and SiCAlON Ceramics

The reaction of 1,3,5-trivinyl-1,3,5-trimethyltricyclosilazane, $[(CH_2{=}CH)(CH_3)SiNH]_3$, with Et_3Al or $[Et_2AlOEt]_2$ was employed to obtain single-component precursors to SiC(or Si_3N_4)/AlN and mixed phase SiCAlON ceramics, respectively[14,15]. This reaction appears to involve both the elimination of ethane, with Si-N-Al bond formation, and vinyl polymerization, as is suggested by the analysis of the gaseous products by g.c. and the IR and NMR spectra of the resultant polymeric products. Different ratios of the silazane to the two Al compounds yield materials ranging from syrupy liquids to glassy solids. From some of the mixtures polymeric fibers could be hand pulled and pyrolyzed to yield thin ceramic fibers. Pyrolysis of the Et_3Al-derived polymers was conducted under N_2 or NH_3 to yield SiC/AlN and Si_3N_4/AlN ceramics, respectively. Again, the initial products of pyrolysis to 1000 °C were amorphous by XRD, but crystallization could be induced by heating to 1600-1800 °C. The SiC/AlN ceramic products were *2H* solid solutions, whereas under NH_3 a nanocrystalline composite of β-Si_3N_4 and *2H*-AlN was obtained, as determined by XRD and TEM/SAD measurements.

The use of $[Et_2AlOEt]_2$ as the Al source led to O-containing ceramic products which included β-SiAlON phases; however, detailed examination of the final crystalline products obtained after annealing at 1600-1800 °C by XRD, TEM/SAD and solid state ^{27}Al NMR indicated that a mixture of phases invariably resulted, in which part of the Al had phase-separated as Al_2O_3 or AlN.

Preparation of BN and TiN-containing Nanocrystalline Composites

In a preliminary study of the polymer pyrolysis route to other nitride and carbide mixtures, several experiments were conducted in which B and Ti compounds were combined with organosilicon and aluminum derivatives to yield single-component precursors to Si_3N_4/BN, AlN/BN and TiN/BN[13]. The same compound employed in our work on single-component SiC(N)/AlN precursors, $[(CH_2{=}CH)(CH_3)SiNH]_3$, was refluxed in toluene with $BH_3{:}NEt_3$ to yield polymers which contained both B and Si. Hydroboration was evidenced by IR and NMR spectroscopy leading, presumably, to $SiCH_2CH_2B(X)CH_2CH_2Si$-bridged species. Pyrolysis of the resultant polymers under NH_3 led to amorphous solids at 1000 °C, which were still not very crystalline after annealing to 1600 °C. Crystallization to a homogeneous mixture of a turbostratic BN phase and mainly β-Si_3N_4 finally occurred at 1800 °C.

In the case of the BN composites with AlN and TiN, $B(HNEt)_3$ was employed as the B source in reactions with $[Et_2AlNH_2]_3$ and $Ti(NMe_2)_4$, respectively. These reactions resulted in viscous liquids or solids which were apparently polymerized through B-NR-M (M = Al or Ti) bridge bond formation. Pyrolysis under NH_3 again yielded the corresponding mixed-phase ceramic nitrides, which were found to be homogeneous and nanocrystalline after annealing to 1600 °C by XRD and TEM studies. A solid state NMR study was carried out by using high field magic angle spinning ^{11}B NMR spectroscopy of the BN in the AlN/BN system that also included the first high field NMR study of the various forms of crystalline BN[16]. This study revealed that the BN in this system is present as a separate phase with a hexagonal (or turbstratic) structure.

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PREPARATION OF NANOCRYSTALLINE COMPOSITES BY PYROLYSIS OF ORGANOMETALLIC PRECURSORS

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ABSTRACT

Nanocrystalline composite ceramic powders were obtained by the pyrolysis of organometallic precursors to AlN, BN, SiC, Si_3N_4, and TiN. Both mixtures of known precursors to the individual ceramic components and specially prepared single-component precursors were employed to obtain binary composites of the type, SiC/AlN, Si_3N_4/AlN, Si_3N_4/BN, AlN/BN, and TiN/BN.

The powders obtained by heating the precursors to 1000°C all appeared to be amorphous based on XRD patterns, although some nm-size crystallites were observed by TEM. Annealing in N_2 at 1600°C produced a homogeneous distribution of nanocrystallites of the respective components.

This paper details the preparation of the precursor systems, the methodology employed for their pyrolysis, and the results of microstructural studies of the ceramic powders. The potential benefits of this approach to homogeneous, nanocrystalline, ceramic composites are discussed.

INTRODUCTION

Organometallic precursors to ceramics are receiving increasing attention in the context of high temperature structural composites [1]. Key reasons for the interest in these systems include the potential for 1) improved control over composition, phase distribution and homogeneity; 2) lower processing temperatures; 3) finer-grained materials; and 4) the generation of continuous fiber, films and other useful forms through solution or melt processing.

Following the successful development of Nicalon "SiC" fiber in Japan over 10 years ago [2], a variety of other covalent ceramic fibers have been obtained by using polymeric precursors [3]. In addition, such precursors have been employed to obtain fiber-reinforced ceramic matrix composites by liquid phase infiltration [4] and thin films on fibers and other substrates by solution deposition followed by pyrolysis [5]. In the course of this work, several examples of precursors to mixed ceramic phases have been identified [6 - 8]. Detailed studies of the mixed-phase ceramic products derived from these precursors have been limited and, in general, the use of organometallic precursors as a source of nanocrystalline composites has not received particular attention.

The high temperature stability, strength, and hardness of Si_3N_4, SiC, BN, TiN and AlN have made these materials of much interest as components of cutting tools, bearings and rotors, turbine engines, and high temperature composites. Various mixtures of these ceramics have been found to exhibit properties that are superior to those of the separate component ceramics. For example, the addition of AlN to SiC was reported to reduce grain size, improve microstructural uniformity, and vary thermal conductivity and expansion in hot-pressed samples [9]. In this case, the formation of a solid solution with the 2*H* structure over a broad range of AlN/SiC compositions was evidenced by TEM/SAD studies of samples obtained by hot-pressing AlN/SiC mixtures. Recently, such solid solutions were obtained by pyrolysis of organometallic precursors [6]. Similarly, the additions of AlN to BN [10], BN to Si_3N_4 [11], and TiN to BN [12] have been found to result in improved toughness, sinterability, and other specific property improvements. Our work on the Si_3N_4/BN system has evidenced a marked decrease in the activation energy for surface area reduction of precursor-derived amorphous Si_3N_4 powder in the presence of BN, while at the same time crystallization of the Si_3N_4 at 1600^0C was inhibited [13].

The recent discovery of ductility and even superplasticity for nanocrystalline ceramics and ceramic composites has generated considerable interest from both a theoretical and practical perspective [14 - 16]. The ready availability of such superplastic ceramic materials could permit the fabrication of complex parts via simple net shape forming processes, such as sinter forging or extrusion [14,15]. In addition, improvements in sinterability and resulting mechanical properties relative to conventionally prepared material have been observed [16].

The first observation of superplasticity in covalent ceramics is credited to Wakai and co-workers [17] who prepared a nanocrystalline Si_3N_4/SiC composite containing yttria and alumina, using a Si-C-N powder which was obtained from the vapor-phase reaction of $[Si(CH_3)_3]_2NH$ with NH_3. The resultant material exhibited superplastic elongation up to 150% in tension at 1600°C. An alternative approach to Si_3N_4-based superplastic ceramics was taken by Chen and co-workers [15] who used a nanocrystalline composite consisting mostly of a fine-grained, equiaxed, α'-sialon.

Based on this prior work, superplastic ceramics are apparently best realized with powders which have ultrafine (<500 nm), equiaxed grains, and a fairly uniform grain size distribution. This microstructure must also be stable under the conditions of the superplastic deformation. A second phase may be needed to inhibit crystal growth and enhance grain boundary diffusion.

Fabrication of nanocrystalline composites of covalent ceramic materials is problematic using conventional powders and processing techniques because: 1) the grain sizes and grain size distributions typically obtained by most powder production methods are too large; 2) the ability to control the purity and crystalline form of the product is limited; and 3) mixing two or more ceramic powders to form a composite which is homogeneous at the nanoscale level is often difficult if not impossible. Moreover, nanocrystalline, high-surface area powders, prepared typically by vapor phase and laser-initiated gas reactions, are expensive and difficult to handle, pack, and process without introducing impurities [18].

In the case of oxide ceramics, sol-gel processing of mixed metal alkoxides has provided an effective alternative to these other methods of preparing homogeneous, nanocrystalline composites [19]. In much the same way, the pyrolysis of appropriately designed organometallic precursors may provide a better general route to nanocrystalline covalent ceramic composites, while also enabling the preparation of new types of mixed-phase, ceramic fibers and matrices. We report here preliminary results of our efforts to develop organometallic precursor routes to nanocrystalline composite materials containing Si_3N_4, SiC, AlN, BN and TiN.

EXPERIMENTAL PROCEDURE

General

All precursor handling and preparation was done in a N_2-filled glovebox or with Schlenk techniques. The procedures used for precursor synthesis, handling, and characterization follow standard practice in organometallic chemistry [20] and have been described in detail in our earlier publications [6].

All ceramic products were handled in the glovebox due to their high surface area and affinity for moisture, except when preparing samples for X-ray diffraction, microscopy, and surface area determination. In the latter cases, the exposure to air was minimized as much as possible.

Electron microscopy[$] samples of finely ground ceramic materials were prepared by passing Cu grids through a suspension of the powder in nitrocellulose/1 % amyl acetate, which was sonicated to break apart agglomerates. The grids were then lightly coated with C and/or Au to prevent charging in the electron beam. X-Ray diffraction measurements were made between $2\theta = 15 - 80^{0}$[@]. TGA experiments were carried out in flowing, prepurified N_2 or NH_3 with a heating rate of $10^{0}C/min$[@@].

Precursors

Diethylaluminum amide, $[Et_2AlNH_2]_3$, was used as the precursor to AlN and prepared from the reaction of triethylaluminum with NH_3 [6]. A vinylic polysilane (VPS) (Union Carbide Corp. Y-12044) of approximate composition, $\{[(SiMe_3)]_{0.32}[Si(CH{=}CH_2)Me]_{0.35}$-$[Si(H)Me]_{0.18}[SiMe_2]_{0.07}[CH_2SiMe]_{0.08}\}_n$, with n *ca*. 50, and a branched methylhydridopolycarbosilane (MPCS), $[MeHSiCH_2]_n$, were used as the polymeric precursors to SiC [6]. VPS was also used as a source of Si_3N_4 [21].

Single-component precursors to AlN/BN, TiN/BN, and Si_3N_4/BN composite powders were employed. The precursor to AlN/BN was prepared by refluxing a 1:1 (B:Al) molar ratio of tris-ethylaminoborane $(EtNH)_3B$ with diethylaluminum amide at 100°C for 2 h and cooling to room temperature [22]. This reaction yielded a viscous, turbid liquid which was used directly for the pyrolysis experiments described below. After pyrolysis the resulting white ceramic product was found to have a 1:2 ratio of B:Al, presumably due to loss of some of the $(EtNH)_3B$ reagent during pyrolysis. The TiN/BN precursor was prepared by the reaction of a 3:1 molar ratio of $(MeNH)_3B$ and tetrakis-dimethylaminotitanium, $(Me_2N)_4Ti$, at room temperature. After several hours, the initially liquid reaction mixture converted to a dark red solid with little overall loss in weight. The Si_3N_4/BN precursor was prepared by refluxing 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilazane with trimethylamine borane adduct, $BH_3{:}N(CH_3)_3$, in toluene for up to

12 hours and removing the solvent under vacuum. Reactions were performed using Si/B ratios of 9, 3, and 1.

Preparation of Precursor Mixtures

Homogeneous liquids consisting of various ratios of VPS/$[Et_2AlNH_2]_3$ and MPCS/$[Et_2AlNH_2]_3$ were prepared by thoroughly mixing the respective liquid precursors. Precursors to Si_3N_4/BN composites were also obtained by mixing VPS with poly(borazinylamine) (PBZA), a known precursor to BN [23], in 1:1 and 10:1 weight ratios, as detailed elsewhere [7]. Except in the case of VPS/$[Et_2AlNH_2]_3$ where a small amount of a gas, identified as mainly ethane, was evolved, no obvious reaction of these precursor mixtures was observed prior to their use in the pyrolysis experiments.

For the preparation of the Si_3N_4/AlN composites, a large batch of the VPS/$[Et_2AlNH_2]_3$ mixture was initially prepared by mixing 34.3 g of VPS with 2.83 g of the aluminum amide. This was calculated to give a 95% Si_3N_4/ 5% AlN by weight composite after pyrolysis, based on the known ceramic yield of the separate precursors [6].

Pyrolysis of Precursors

Direct Pyrolysis (Procedure A)

Except as noted below, precursors mixtures were typically heated at 1-5^{0}C/min in molybdenum foil boats to 1000^{0}C in NH_3. Samples were held at the desired temperature for 6-14 h and annealed at 1600^{0}C in N_2 for 4 h.

Hot Drop Si_3N_4/AlN (Procedure B)

A quartz reaction vessel [6a] was maintained at 500°C while flowing (0.05 SCFH) NH_3 gas through it. Roughly 1/3 of the VPS/$[Et_2AlNH_2]_3$ mixture, prepared as described above, was loaded into a gas-tight, plastic syringe, equipped with a needle, which then was transferred from the glovebox and pierced through the septum on the reaction vessel. The viscous liquid mixture was "dropped" onto the heated surface at a rate of 1 drop every 5-10 sec. After complete addition of the mixture, the highly porous, white solid product was allowed to cool and collected in the glove box. Subsequent conversion to ceramic was carried out by direct pyrolysis as noted above.

Preheating Followed by Pyrolysis Si_3N_4/AlN(Procedure C)

Approximately 1/3 of the VPS/$[Et_2AlNH_2]_3$ mixture was first heated at 140-150°C for 1 h in the glovebox and allowed to cool to room temperature. The resulting material was a tacky, gum-like solid. Subsequent heating to 1000°C was carried out in a tube furnace in flowing NH_3 (0.3-0.4 SCFH) employing the following schedule: heating to 140°C in 1 h, holding at 140°C for 1 h, heating to 1000°C in 6 h with a 14 h hold at 1000°C. The sample was then furnace cooled in N_2.

RESULTS

SiC/AlN

The results of our studies of the VPS/$[R_2AlNH_2]_3$ and MCPS/$[R_2AlNH_2]_3$ (where R = i-Bu or Et) precursor systems to SiC/AlN solid solutions and composites have been detailed elsewhere [6]. Based on the XRD data and TEM/SAD studies, both nanocrystalline composites of *2H* AlN and β-SiC and *2H* solid solutions of SiC/AlN were identified as products of the pyrolyses depending on the specific pyrolysis procedure and precursor combinations employed. In either case, after annealing the powders at 1600°C, the crystallite sizes were less than 500 nm and typically on the order of 10-50 nm.

Si_3N_4/AlN

Application of the three different pyrolysis procedures in NH_3 (see Experimental Procedures A, B, and C) to the VPS/$[Et_2AlNH_2]_3$ mixture yielded, after the 1000°C heating stage, tan powders which were apparently amorphous by XRD. However, TEM/SAD studies of these samples indicated small regions of nanosized crystallites in a matrix of predominantly amorphous material. After annealing to 1600°C, the powders were still white and consisted mainly of nanocrystalline α- and β-Si_3N_4 based on TEM/SAD and XRD results.

The major difference in these powders was that the relative distribution of α/β-Si_3N_4 significantly varied among the three samples. The sample pyrolyzed in the "hot drop" apparatus (Procedure B) exhibited the most α, the one pyrolyzed in the furnace by using a linear temperature ramp (Procedure A) contained a mixture of α and β, whereas the sample held at 140-150^{0}C prior to pyrolysis (Procedure C) exhibited essentially all β-Si_3N_4.

The crystallites exhibited two distinct shapes; blocky, equiaxed and rod-like, elongated shapes. The rod-like crystals exhibited a β-Si_3N_4-like electron diffraction pattern. The typical grain size in these materials was 40-80 nm.

Solid state ^{27}Al NMR showed that the Al environments are different in the three samples (Figure 1). The "hot drop" sample (Procedure B) gave a sharp resonance at 114.3 ppm, indicative of AlN_4 tetrahedra found in h-AlN, a broad peak between 100-40 ppm, which may be $Al(O, N)_{4-6}$ type species and a weaker feature near 15 ppm, which may be indicative of AlO_6 octahedra such as those in Al_2O_3 [24]. The sample derived from Procedure A exhibits a lower intensity 114.3 resonance, a sharper peak of enhanced intensity near 70 ppm, and a more intense 15 ppm peak. Finally, the sample obtained by Procedure C exhibits virtually no AlN_4, a broad peak due to multicoordinated Al(O,N) environments, and a strong peak at 15 ppm which is close in appearance and position to that exhibited by Al_2O_3.

Si_3N_4/BN

Composites derived from VPS/PBZA mixed precursors have been described previously [7]. IR spectral data corroborate the presence of both BN and Si_3N_4 in all samples; however, the XRD data indicate that, in close analogy to the results obtained using added h-BN powder [13], crystallization of the Si_3N_4 was inhibited in the presence of the BN precursor. Thus for the 1:1 VPS:PBZA samples, even after heating to 1600^{0}C, only a very weak pattern indicative of α-Si_3N_4 was observed on a background of the broad peaks typical of turbostratic BN. On the other hand, for the 10:1 wt. % VPS:PBZA mixture significant crystallization of the Si_3N_4 was evident after the 1600^{0}C anneal by XRD.

The products obtained from reactions of the methylvinylsilazane and the borane adduct ranged from a pale yellow liquid (Si/B = 9) to white, semi-solid pastes (Si/B = 3 and 1), and were soluble in aromatic hydrocarbon solvents. The char yields for the products pyrolyzed to 1100^{0}C in NH_3 were 40%, 20% and 20%, and were 52%, 40%, and 42% in N_2, for Si/B = 9, 3, and 1, respectively. The separate reactants gave 0% char yields when pyrolyzed under the same conditions. Analysis of the Si/B = 9 NH_3 pyrolysis product, after annealing at 1600^{0}C in N_2, gave$^{\$\$}$: Si 54.2%, N 32.6%, B 2.8%, C <0.5%.

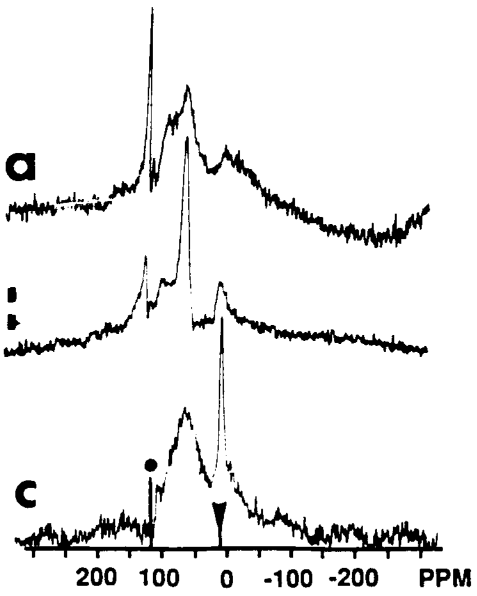

Figure 1. ^{27}Al solid state NMR spectra of Si_3N_4/AlN a) Hot drop (Procedure B), b) linear ramp (Procedure A), and c) preheated mixture (Procedure C); all heated to 1600^{0}C. ● - AlN, ▼ - Al_2O_3

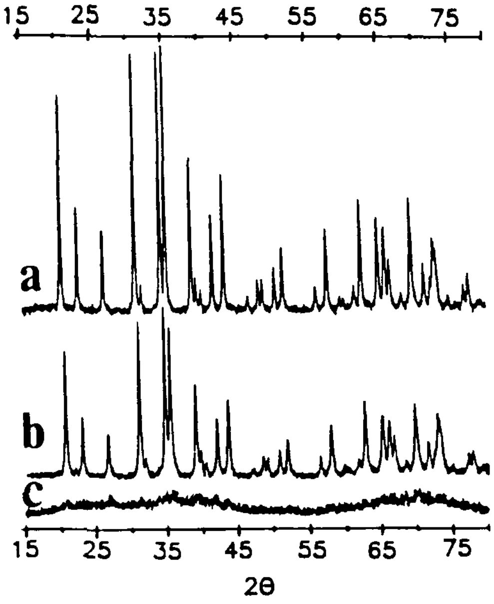

Figure 2. XRD patterns of a) VPS-derived Si_3N_4, b) VPS/-PBZA-Si_3N_4/BN, and c) single component precursor Si_3N_4/BN following NH_3 pyrolysis and 1600^{0}C anneal.

The IR spectrum of the liquid polymer (Si/B = 9) showed a decreased intensity of the vinyl stretch at 3050 cm^{-1} relative to the N-H stretch at 3390 cm^{-1} compared to the spectra of the starting silazane and a new band at 1300-1360 cm^{-1} assigned to B-N and/or B-C. The ^{1}H, ^{13}C, and ^{11}B NMR spectra also showed a reduction in relative intensity of the peaks due to the vinyl groups and new peaks attributed to the CH_2CH_2B group.

The Si_3N_4/BN composites derived from the single-component precursor had IR spectra that were similar to those obtained from the mixed-precursors. However, in this case the XRD patterns of samples heated to 1000°C and 1600°C show only broad features which are typical of nanocrystalline or amorphous materials. Distinguishable XRD patterns were only observed after heating the samples to 1750-1800°C for at least 2 hours. These indicated that a mixture of α-Si_3N_4 (minor), β-Si_3N_4 (major), and t-BN (minor) was present.

Figure 2 compares the XRD patterns of Si_3N_4 from VPS alone [21], Si_3N_4/BN from 10/1 wt. % VPS/PBZA [7], and Si_3N_4/BN from the 9:1 Si:B single-component precursor, after heating to 1600°C for 4 hr. Crystal sizes were calculated from the XRD peak widths to be ca. 40 nm for the VPS-Si_3N_4 and 30 nm for the VPS/PBZA-Si_3N_4, which are in agreement with TEM measurements. TEM examination of the 1600°C composite powder derived from the single-component precursor showed mainly featureless particles with a few nm-sized crystals of Si_3N_4. The Si_3N_4 grain size in this sample was substantially smaller than either the VPS-derived Si_3N_4 or that obtained by pyrolysis of VPS/PBZA.

AlN/BN

The single component precursor to this composite yields a white solid in 40% char yield after pyrolysis in NH_3 to 1000°C. The IR spectrum of the 1000°C sample shows features characteristic of both the B-N and Al-N bonding in the respective ceramic materials [22,24]. The XRD pattern of the 1000°C sample confirms the presence of partially crystalline AlN. Further heating of the composite to 1600°C improves the crystallinity of the AlN and reveals two broad peaks indicative of t-BN at $2\theta=25^\circ$ (002) and 42° (100, 101) [25]. TEM of the 1000°C material shows AlN grains which are uniformly sized (5-10 nm) and homogeneously dispersed in a matrix of t-BN (Figure 3).

TiN/BN

Following pyrolysis in NH_3 to 1000°C, this composite was obtained in 30% char yield as a dark brown solid. The XRD pattern exhibits broad characteristic peaks for TiN at $2\theta=37^\circ$ (111), 43° (200), and 62° (220) and t-BN at $2\theta=25^\circ$ and 42° (buried under TiN peak). The TiN peak width was used to calculate a particle size of ca. 3 nm, which is in good agreement with the 3-6 nm particle size observed by TEM (Figure 4).

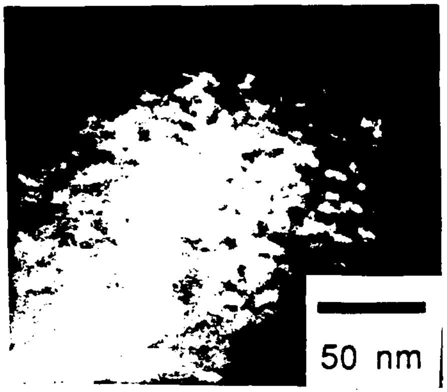

Figure 3. Dark field transmission micrograph of of AlN/BN composite.

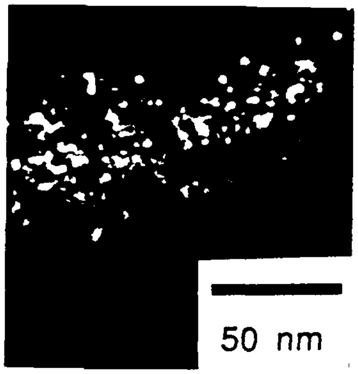

Figure 4. Dark field transmission micrograph of TiN/BN composite.

DISCUSSION

Preliminary results of this investigation have shown that both mixtures of precursors to the separate ceramics and single-component precursors in which the metals (or metalloids) of interest are precombined in a common structure can be used to obtain homogeneous, nanocrystalline composites containing SiC, Si_3N_4, AlN, BN, and TiN. However, it is also clear from these studies that the choice of precursor systems and also the pyrolysis procedure can have a profound effect on the composition and microstructure of the ceramic end product. For example, we have found that a sequence of NH_3 and N_2 treatments yields SiC/AlN materials from mixed organosilicon and organoaluminum precursors, whereas heating the same precursor mixtures in NH_3 alone gives Si_3N_4/AlN mixtures [6c]. For the SiC/AlN system, variations in the pyrolysis procedure (i.e., using a rapid pyrolysis vs. a slow temperature ramp) and in the precursor source were employed to obtain either a nanoscale mixture of β-SiC and 2*H*-AlN or a 2*H*-SiC/AlN solid solution [6]. The difference in the products appears to be related to the different rates of solidification of the two initially liquid precursors and the need to maintain an atomically mixed Si/Al precursor during conversion to the ceramic phases. Rapid pyrolysis apparently aids in maintaining such a mixture as does reaction between the precursors prior to their conversion to solids.

The utility of chemical interactions between the precursor sources, as a means of limiting the degree of phase separation in the product ceramic, is also suggested by the results of our studies of the two different precursor routes to Si_3N_4/BN composites. The use of a mixture of the poly(borazinylamine) and VPS was found to yield appreciably larger grain sizes for the Si_3N_4 crystallites in the t-BN matrix as compared to the single-component, boron and silicon-containing precursor. The limited miscibility and different decomposition temperatures of the PBZA and VPS precursors are clearly not conducive to obtaining a homogeneous ceramic mixture after pyrolysis. On the other hand, in the case of the single-component precursor, NMR and IR data indicate that the BH_3 reacts with the vinyl groups on the silazane during the toluene reflux, presumably leading to an ethylene-bridged borosilazane polymer containing a homogeneous distribution of B and Si atoms [27]. This atomic-level distribution of B and Si is apparently maintained to an appreciable extent during the subsequent pyrolysis of this polymer to the ceramic composite.

The ability to control the composition and phase distribution of the ceramic products through variations in the pyrolysis procedure is also illustrated by the results of the study of the 95% Si_3N_4/5% AlN system. In this case, the proportion of α- to β-Si_3N_4, obtained on annealing the initially obtained amorphous powder at 1400-1600°C, appears to depend on the heating rate used for pyrolysis of the precursor mixture. As the precursor mixture is held for a longer time period between ca. 100°C and 200°C, the proportion of β-Si_3N_4 seems to increase, whereas rapid pyrolysis by dropping the precursor mixture onto a very hot surface yields almost entirely the α-phase. Based on solid state ^{27}Al NMR results (Figure 1), the proportion of β-Si_3N_4 correlates with the amount of Al that has been converted to AlO_x species, presumably by reaction of the organoaluminum amide with adventitious sources of oxygen in the initial polymer or in the environment prior to its conversion to AlN. Alumina is known to catalyze the α to β transition in Si_3N_4 [28] and the presence of these AlO_x species in the mixture may be effective in promoting the crystallization of the β-form from the initial amorphous phase.

This work has provided ample evidence for the potential utility of the "precursor pyrolysis" approach as a means of generating nanophase composites of a wide range of covalent ceramic materials. However, it is also clear that much remains to be learned about the detailed nature of these materials and the role of precursor structure and chemistry in determining their microstructure. Moreover, the conversion of these nanocrystalline (or amorphous) ceramic powder mixtures to monolithic ceramic objects, or the direct use of the precursors to prepare fibers, matrices or coatings, represent major steps to be surmounted before the full potential of this approach can be adequately assessed. Efforts to resolve these and other key issues relating to the application of organometallic precursors to the fabrication of composite materials are currently in progress in our laboratories.

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[$] Joel 100CXII
[@] Phillips 1710W Automated Powder Diffractometer, equipped with a monochrometer
[@@] Perkin Elmer Series 7 Thermal Analysis System
[$$] Galbraith Laboratories, Inc.

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SYNTHESIS AND PYROLYSIS CHEMISTRY OF POLYMERIC PRECURSORS TO SiC AND Si_3N_4

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ABSTRACT

A commercial vinylic polysilane has been used to obtain both SiC and Si_3N_4 by pyrolysis in N_2 and NH_3, respectively. The polymer-to-ceramic conversion process was studied by GPC, TGA/DTA, elemental analyses, FTIR, solid state NMR (^1H, ^{13}C and ^{29}Si), XRD, BET surface area measurements, and analysis of the gaseous decomposition products, providing a detailed picture of the cross-linking process and the evolution of the ceramic products.

In pursuit of alternative precursors to SiC and Si_3N_4, a novel branched polycarbosilane of the approximate composition $[SiH_{2-x}Et_xCH_2]$ (where $x = 0.15$) was obtained by the Grignard coupling of chloromethyltrichlorosilane followed by reduction with $LiAlH_4$; cleavage of diethylether by the chlorosilane was identified as the source of the ethyl groups in the final hydridopolycarbosilane. This polycarbosilane yields partially crystalline SiC ceramic on pyrolysis to 1000 °C in N_2. Annealing of this product at 1400-1600 °C results in further crystallization of β-SiC. Preliminary studies of the polymer-to-ceramic conversion process in N_2 by GPC, TGA, FTIR and NMR methods indicate that cross-linking occurs by H_2 elimination and Si-Si bond formation and that the 1000 °C product has a much lower proportion of free carbon than the corresponding ceramic derived from the vinylic polysilane.

1. INTRODUCTION

A wide range of organosilicon polymers have been studied over the last 15 years as potential precursors to SiC [1]. Several of these systems have found commercial use as sources of SiC fibers and as ceramic binders. A common feature of these precursors is that they generally contain a higher proportion of carbon to silicon than is demanded by the 1:1 stoichiometry of SiC, requiring the elimination of the excess organic functionality during pyrolysis and thereby lowering the potential char yield of SiC. Moreoever, the pyrolytic conversion of such precursors to SiC is rarely accomplished cleanly, which leads to the incorporation of substantial quantities of excess carbon in the ceramic product. It has recently been shown that some of these same organosilicon polymers can be used as sources of Si_3N_4 by carrying out the pyrolytic conversion in NH_3 [2].

Most of the available precursors are obtained as highly crosslinked polymers of uncertain and often variable structure and composition, which causes difficulties in controlling physical properties that are appropriate for processing as well as for maintaining a uniform and consistent ceramic composition and microstructure. Furthermore, pyrolytic conversions in an inert atmosphere or in ammonia were followed by complete analysis of the intermediate and final products in only a few cases [3]. A detailed understanding of the relevant chemical processes involved in either case is still lacking.

Work in our laboratory has been directed towards three main goals: (1) the elucidation of the polymer-to-ceramic conversion process for selected organosilicon polymers in sufficient detail to enable the intelligent selection of both precursors and functionalities appropriate to particular processing objectives; (2) the synthesis and characterization of new precursors to SiC and Si_3N_4; (3) the application of polymeric precursors to the preparation of ceramic nanocomposites and ultrastructures containing two or more components (e.g., SiC and AlN).

In this paper we will summarize the key results of our investigation of the polymer-to-ceramic conversion process for a commercial vinylic polysilane and then describe the synthesis of a new polycarbosilane and the preliminary results of the study of its pyrolysis in N_2.

2. RESULTS AND DISCUSSION

2.1. STUDIES OF THE PRECURSOR TO CERAMIC CONVERSION OF VINYLIC POLYSILANE.

Our initial efforts to characterize the conversion process for polymeric organosilanes have focused on a detailed study of a vinylic polysilane (VPS) [Union Carbide, Y-12044] [4]. Based on our solution and solid state NMR studies of VPS, an approximate composition, $[[(SiMe_3)]_{0.32}[Si(CH{=}CH_2)Me]_{0.35}[Si(H)Me]_{0.18}[SiMe_2]_{0.07}[CH_2SiMe]_{0.08}]_n$ was derived for the sample that we obtained from Union Carbide. This polymer has been widely employed as a precursor to silicon carbide [1d-e, 4] and has been used recently as the matrix source in SiC/SiC ceramic composites [5]. VPS is obtained by sodium-induced coupling of a mixture of chloromethyl-, chloromethylhydrido- and chloromethylvinylsilanes [4] and is known to give a carbon-rich silicon carbide ceramic on pyrolysis [4b,6]. Preliminary studies of the thermosetting process known to occur at around 225 °C have been carried out by Lee and Hench [7] while Bowen and coworkers monitored the increasing crystallinity of the resulting ceramic with increasing temperature from 1000 °C to 2100 °C [6]. Solid solutions and composites of SiC and Si_3N_4 with AlN or BN have been prepared by copyrolysis of VPS with organoaluminum amides [8a] or a polymeric precursor to boron nitride [8b].

We have carried out studies on the pyrolysis of VPS under both N_2 [9] and NH_3 [2d,10] with TGA/DTA, and have examined the intermediate and final solid products by elemental analyses, FTIR, solid state NMR (^1H, ^{13}C and ^{29}Si), and XRD, as well as the gaseous products by gas chromatography, mass spectrometry and FTIR. The main chemical differences between the conversion of VPS under N_2 and NH_3 begin to appear only above ca. 250 °C, where substantial changes in the nature of the solid products are seen by solid state NMR, IR and other methods. The detected gaseous decomposition products appear to be basically the same for the two atmospheres, consisting of trimethysilane and lesser amounts of hydrocarbons and other methylsilanes. Moreover, the general shape of the TGA curves for the pyrolysis in N_2 and NH_3 are quite similar (Figure 1), although pyrolysis in NH_3 causes larger weight losses from 50-150 °C and 300-600 °C, which results in a 15% lower char yield than in N_2. The ceramic products obtained at 1000 °C are

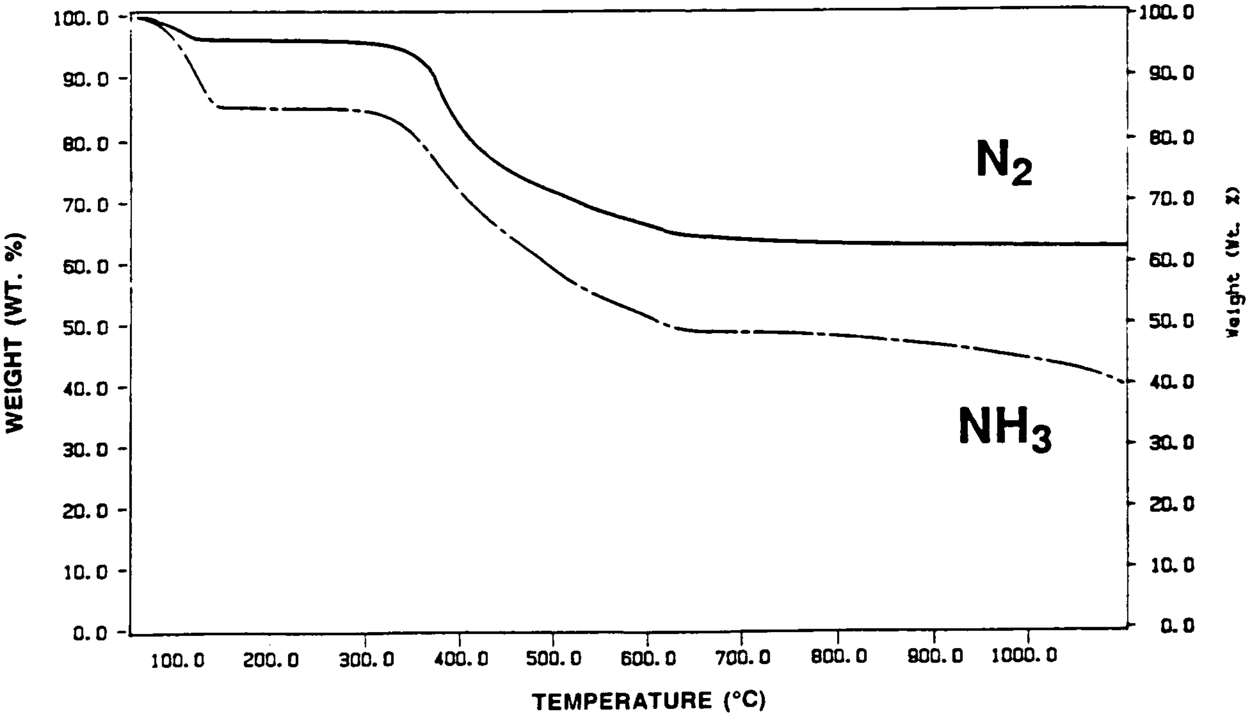

Figure 1. TGA curves for VPS heated in N_2 and NH_3 at a rate of 5 °C/min.

substantially different, consisting of C-rich, partially crystalline β-SiC in the case of N_2 and essentially pure, partially crystalline α-Si_3N_4 when NH_3 is used. In both cases the polymer undergoes extensive crosslinking between ca. 100 and 250 °C, resulting in the formation of a translucent glassy solid. The chemistry occuring in this temperature regime appears to be essentially independent of the atmosphere and to consist of both direct vinyl coupling (presumably radical initiated) and hydrosilation, with a greater proportion of direct vinyl coupling relative to hydrosilation. This conclusion was reached on the basis of solid state ^{13}C and ^1H NMR measurements utilizing the CRAMPS technique, and FTIR, where a plot of the ratio of the vinyl C-H to the Si-H stretching frequency intensities vs temperature shows a sharp drop in the same temperature region as the observed solidification of the polymer (120-200 °C).

On heating above 300 °C in N_2, the yellowish glassy solid was transformed into a black solid by 600 °C, resulting in a major fraction of the overall 35-40 % weight loss observed by TGA to 1000 °C. As suggested by the results of the IR, NMR studies and the gas product analysis, the chemistry occurring in this region appears to be quite complex, involving extensive homolytic bond cleavage and, presumably, radical chain reactions. Both the IR and NMR data suggest that extensive methylene insertion into the Si-Si bonds occurs above 300 °C, adding substantially to the small amount of $Si-CH_2-Si$ units initially present in the polymer. A similar reaction has been proposed in the case of the conversion of poly(dimethylsilanes) to Yajima's polycarbosilane [11]. The major gaseous product (ca. 90% of the total amount) in the region of maximal weight loss (300-750 °C) is trimethylsilane, suggesting that extensive chain scission, presumably by homolytic Si-Si bond cleavage, occurs during decomposition of the polymer. Significant amounts of C_1 to C_4 hydrocarbons and Me_xSiH_{4-x} ($x = 1 - 4$) were also observed among the gaseous products, indicating that rearrangement of H and alkyl groups on Si probably occurs as well as radical cleavage and coupling reactions.

The IR and NMR spectra of the solids isolated at various temperatures during the decomposition show the gradual conversion of the polymer to a preceramic SiC. Thus the IR and ^1H CRAMPS spectra confirm the decreasing concentration of hydrogen with increasing pyrolysis temperature. The ^{13}C NMR demonstrate the coalescence of the various Si_x-C_y units to a single peak representing the SiC_4 units in SiC and the development, above 400 °C, of a separate peak at lower field due to excess carbon. ^1H -> ^{13}C cross polarization NMR experiments indicate that even after heating to 1000 °C, a significant hydrogen concentration remains in the ceramic, which may serve to complete bonding saturation around carbon and Si centers. Preliminary ESR studies of the 1000 °C sample suggests that there is also a significant concentration of free radicals which are probably associated with incompletely bonded C or Si sites. Elemental analysis indicates that the H concentration is ca. 0.5 % and that there is a 17 % excess carbon than in stoichiometric SiC.

As was observed previously [6], further heating to 1600-1900 °C is required to fully crystallize the SiC. An XRD pattern consistent with that of partially crystalline β-SiC was obtained for the 1000 °C N_2 pyrolysis product of VPS. Further crystallization occurred after annealing this powder to 1600 °C.

The main differences in chemistry that occur during pyrolysis in NH_3 start to appear above 250 °C. The graph of the elemental compositions of the solids isolated after pyrolysis in NH_3 for 10 h at the indicated temperature (Figure 2), shows that nitrogen begins to appear in significant amounts in the solids at 400 °C, and by 650 °C it has virtually replaced the carbon that was present in the original polymer. The 1000 °C product was found to contain only 1.8 % carbon; after annealing this solid at 1600 °C under N_2 the analysis corresponds reasonably well to stoichiometric Si_3N_4. Both the IR and NMR spectra

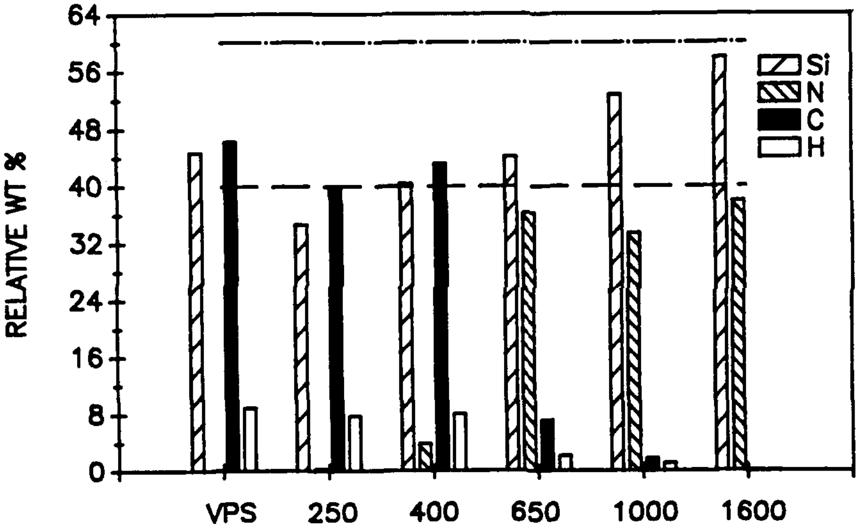

Figure 2. Elemental Analyses for solids isolated during pyrolysis of VPS in NH_3 to 1000 °C and annealed in N_2 at 1600 °C. Lines indicate theoretical levels of Si and N in stoichiometric Si_3N_4.

(^{13}C and ^{29}Si) show corresponding changes in this region that are consistent with the introduction of NH_x groups and loss of C-H functionality. The solid state ^{13}C MAS NMR spectrum of the 400 °C sample shows a broad peak centered near 5 ppm, whereas the spectra obtained for the 650 and 1000 °C samples show no peaks above background. In the ^{29}Si NMR spectra, very broad resonances are observed for the 250 and 400 °C samples, suggesting a large number of different Si environments. By 650 °C these peaks have coalesced into a single, relatively sharp peak near -45 ppm, indicative of a SiN_4 environment analogous to that in the amorphous and crystalline forms of Si_3N_4 [12].

The 1000 °C product is already partially crystalline by TEM/SAD and has an effective surface area of 250 m^2/gm based on BET measurements with N_2 adsorption. This solid crystallizes to high purity α-Si_3N_4 on heating above 1400 °C with a considerable (90%) reduction in the surface area [2d].

The detailed nature of the chemical reactions occuring in the presence of NH_3 in the 250-650 °C region remains to be fully determined; however, our TGA and gas analysis results suggest that one of the roles of NH_3 is to facilitate the elimination of silanes and hydrocarbons, possibly by acting as an efficient source of hydrogen and a radical trap. The introduction of N presumably occurs by nucleophilic attack of NH_x species on Si, allowing elimination of the C-containing substituents as simple hydrocarbons.

2.2. SYNTHESIS OF NEW POLYCARBOSILANE PRECURSORS

Our efforts to synthesize new SiC polymer precursors have focused on the preparation of polycarbosilane polymers by two main reaction pathways: (1) ring opening polymerization (ROP) of disilacyclobutanes, and (2) Grignard coupling of chlorocarbosilanes. In the former case, 1,3-dimethyl- and 1,3-tetramethyl-1,3-disilacyclobutane were converted to high molecular weight polycarbosilanes by ROP with the aid of a platinum catalyst [13]. As was previously known [14], the fully methylated polycarbosilane gave a negligible char yield on pyrolysis in N_2; however, the $[SiMe(H)CH_2]_n$ polymer derived from the dimethyldisilacyclobutane gave a low yield of amorphous SiC on pyrolysis to 1000 °C, which could be increased by increasing the molecular weight of the polymer or by holding at 400 °C to allow cross-linking by hydrogen elimination and Si-Si bond formation [13].

The second approach to polycarbosilane precursors to SiC has involved the preparation of a highly branched polymer of the approximate composition "SiH_2CH_2" by Grignard coupling of chloromethyltrichlorosilane [Cl_3SiCH_2Cl] followed by reduction with $LiAlH_4$ [15].

$$Cl_3SiCH_2Cl \xrightarrow[\text{reflux, 5d}]{\text{Mg, }Et_2O} \text{"}[SiCl_2CH_2]_n\text{"} \xrightarrow[\text{2] }H_2O/HCl]{\text{1] }LiAlH_4/Et_2O} \text{"}[SiH_2CH_2]_n\text{"} \quad (1)$$

This process was followed in detail by trapping intermediates with methanol, isolating low molecular weight reduced products, and by carrying out selected model reactions with monofunctional chlorosilanes. Reactions employing $LiAlD_4$ and D_{10}-ether were also performed in order to characterize the various functional groups on Si which were introduced during the Grignard coupling reaction and the subsequent reduction. The key features of the coupling reaction are an almost exclusive occurance of "head-to-tail" coupling (i.e., C to Si) and extensive branching at Si due to the trifuctional nature of the Si "tail". The result is a complex arrangement of $-SiCH_2-$, $=SiCH_2-$ and $\equiv SiCH_2-$ units, along with Cl_3Si- and $-CH_2Cl$ end groups. Due to the propensity for "head-to-tail" coupling and the 1:1 ratio of C to Si atoms, there is little or no crosslinking; thus, the polymers are viscous oils which are largely soluble in hydrocarbon solvents.

A further level of complexity is introduced by the chlorosilane-induced cleavage of the diethylether solvent during the course of the Grignard coupling reaction. This reaction is carried out under ether reflux for several days to build up the molecular weight of the polymer. Under these conditions the following ether-cleavage reaction occurs [16], leading to the substitution of -OEt groups onto the Si-Cl sites and the formation of EtCl.

$$\equiv SiCl + Et_2O \longrightarrow SiOEt + EtCl \qquad (2)$$

In the presence of Mg this EtCl forms a Grignard reagent which also reacts with the Si-Cl groups.

$$EtCl + Mg/Et_2O \longrightarrow EtMgCl/Et_2O \qquad (3)$$

$$EtMgCl/Et_2O + \equiv SiCl \longrightarrow \equiv SiEt + MgCl_2 + Et_2O \quad (4)$$

Conclusive evidence for these reactions has been obtained from ^2D-NMR measurements carried out on the product isolated from the Grignard reaction conducted in D_{10}-ether. Based on NMR integrations, the level of -OEt and -Et introduction into the initial chloropolycarbosilane was estimated to be on the order of one Et and one OEt group per 13.3 SiCl sites, resulting in the following average composition for this polymer, $[SiCl_{1.7}Et_{0.15}OEt_{0.15}CH_2]$.

Fortunately, after reduction with $LiAlH_4$ the -OEt groups are efficiently reduced along with the remaining Si-Cl functionalities, leading to a somewhat less complicated and apparently oxygen-free hydridopolycarbosilane with the average formula, $[SiH_{1.85}Et_{0.15}CH_2]$. Again, isotopic labeling along with a full characterization of the polycarbosilane product by ^1H, ^{13}C, and ^{29}Si NMR (including Si DEPT) and IR spectroscopy were used to assign the average formula and to characterize the various structural units in the polymer. The assignment of the broad peaks in the NMR spectra of this polycarbosilane was aided by the synthesis of a series of "model compounds" of the type, $[Me_3SiCH_2]_xSiH_{4-x}$ (x = 1 - 4), which simulated the local environment around Si in the polymer [17].

The molecular weight distribution of a sample of this polycarbosilane was determined by gel permeation chromatography using polystyrene standards. A very broad MW distribution was found, with most of the polymer falling between 450 and 3000 amu, but tailing off gradually to 80,000 amu to give a large polydispersity value of 6.95. The M_w for this polymer was 745, corresponding to about 15.4 repeat units as $SiH_{1.85}Et_{0.15}CH_2$.

At the intermediate "chloropolycarbosilane" stage the polymer is readily susceptible to structural modification through the reaction of the Si-Cl groups with Grignard or lithium reagents. A preliminary attempt to add vinyl groups at this stage led to the preparation of a 10 %-substituted vinylic hydridopolycarbosilane after reduction which was found to undergo facile crosslinking via Pt-catalyzed hydrosilation at 150 °C.

2.3. CROSSLINKING AND PYROLYSIS OF THE "SiH_2CH_2" POLYMER

The SiH_2CH_2 polymer was obtained from these reactions as a pale yellow, reasonably air-stable oil which gradually solidified on standing over several months with the generation of a gas (later identified as H_2). This solidification process is accelerated by heating the neat polymer and proceeds rapidly above about 150-200 °C (the rate of solidification appears to depend markedly on the molecular weight of the polymer, increasing with increasing molecular weight). Based on GPC, NMR and IR analysis of the polymer during solidification, a crosslinking reaction involving elimination of H_2 from Si-H and Si-Si bond formation was evidenced.

Further heating to 1000 °C resulted in the formation of a black solid which was poorly crystalline by XRD. Annealing at 1600 °C gave β-SiC as the only crystalline product. Efforts to obtain an accurate elemental analysis are still in progress. However, as is indicated by the comparison of the ^{13}C NMR spectra (Figure 3) and the TGAs in air (Figure 4) of the 1000 °C pyrolysis products obtained from the above polycarbosilane and the Union Carbide vinylic polysilane, the polycarbosilane-derived product appears to have much less free carbon. Moreover, as is suggested by the IR spectra in Figure 5 obtained for the 1000 °C powder before and after reaction with oxygen for an extended period at 1200 °C, the proportion of Si-O groups in the ceramic initially obtained from the pyrolysis must be very low indeed. The overall ceramic yield observed for this polycarbosilane was found to depend greatly on the heating rate used in the TGA experiment, as well as the degree of polymerization of the polymer. Char yields from 58 to 76 % were observed for the "high molecular weight" products at a heating rate of 10 °C/min. Holding at temperatures from ca. 80 to 200 °C to effect crosslinking resulted in improved char yields, with overall weight losses from initial polymer to SiC ceramic of less than 20%. This is close to the theoretical yield of 83%, assuming the polymer formula $[SiH_{1.85}Et_{0.15}CH_2]_n$ and "SiC" as the product.

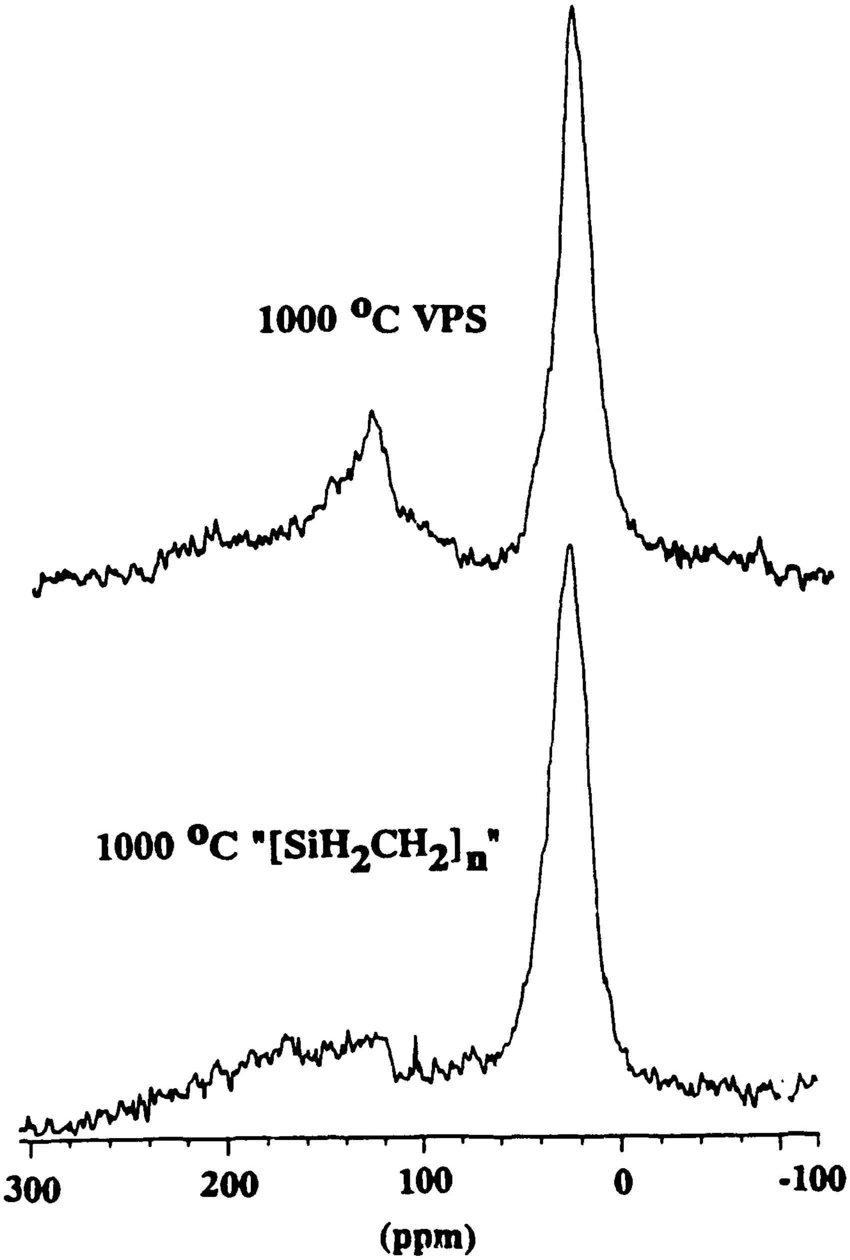

Figure 3. Solid state ^{13}C NMR spectra of ceramic products derived from VPS and "$[SiH_2CH_2]$"$_n$ at 1000°C in N_2.

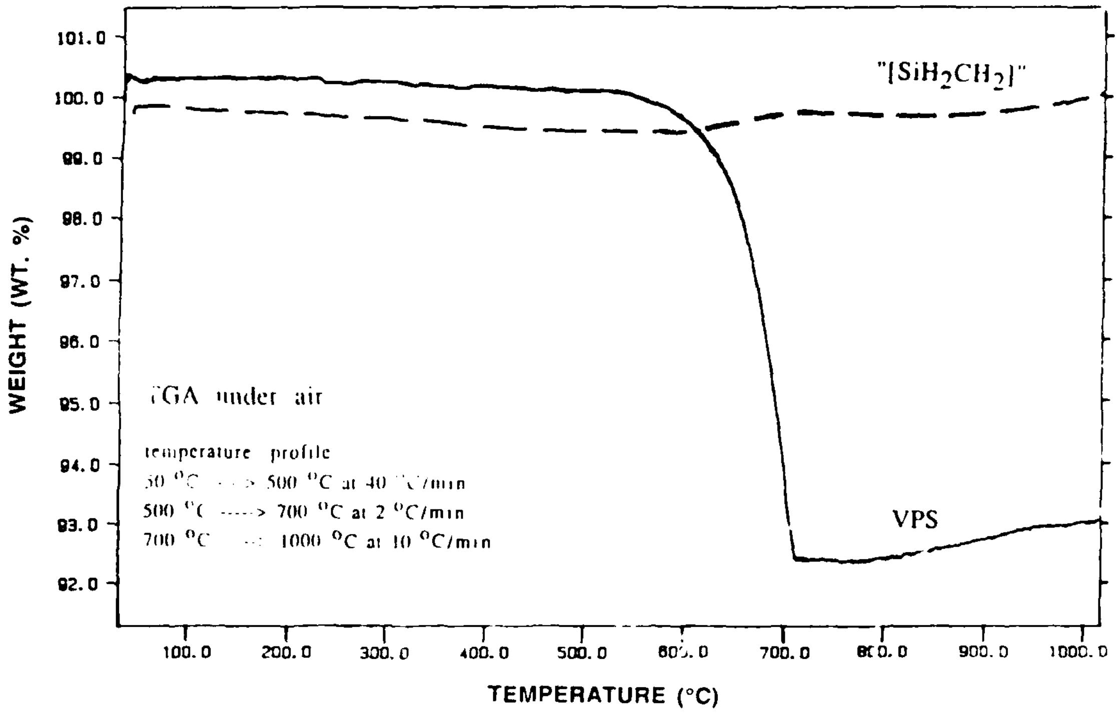

Figure 4. TGA (in air) of ceramic products derived from VPS and "[$SiH_2CH_2]_n$" at 1000°C in N_2.

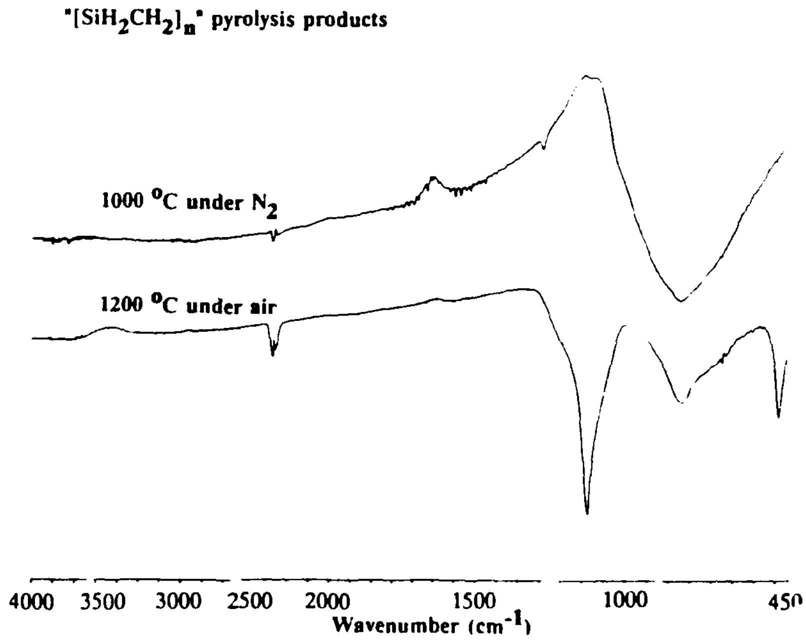

Figure 5. IR spectra of ceramic prepared from "[$SiH_2CH_2]_n$" at 1000°C before and after oxidation in air at 1200°C.

Based on these observations it is clear that this polymer shows considerable promise for use as a SiC precursor. A variety of potential applications in the area of ceramic composites and nanostructures are currently under investigation. In addition, our efforts to fully characterize the pyrolysis process and the SiC product are continuing along with further work on the synthesis and structural modification of the polymer.

3. ACKNOWLEDGEMENT

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SILICON CARBIDE-ALUMINUM NITRIDE SOLID SOLUTIONS BY PYROLYSIS OF ORGANOMETALLICS

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ABSTRACT

SiC/AlN solid solutions and nanocomposites were prepared both by pyrolysis of single-component polymeric precursors derived from the reaction of cyclotrisilazanes with triethylaluminum and by copyrolysis of mixed organosilicon and organoaluminum precursors. The evolution of the final crystalline ceramic phases from the preceramic products of these pyrolyses was studied by XRD, TEM/EDS, and solid state ^{27}Al and ^{13}C magic angle spinning NMR spectroscopy, providing a detailed picture of the precursor-to-ceramic conversion process. The results of these studies are discussed in the context of the SiC/AlN phase diagram and the chemistry occuring during the conversion process.

INTRODUCTION

The SiC/AlN system has been the subject of much interest and investigation over at least the past 10 years [1-11]. This interest is due in part to the opportunity presented through solid solution formation to modify the properties of the component ceramic phases in particular ways; for example, the band gap, the thermal conductivity, thermal expansion, the hardness, the fracture toughness and the creep rate can be varied in a controlled manner [1-6]. But perhaps even more noteworthy is the prospect of effecting specific desired changes in the microstructure of the resultant ceramic product relative to that of the component ceramics. In particular, SiC occurs as various polytypes (3C, 2H, 4H, 6H, etc.) and undergoes phase transformations between these polytypes that can lead to exaggerated grain growth on temperature cycling. This is believed to be one of the reasons for the precipitous losses in strength that have been observed for polymer precursor-derived SiC fibers above 1400°C [8]. Unlike SiC, AlN has only one stable phase, which is isostructural and closely lattice matched to the wurtzite (hexagonal 2H) form of SiC. The addition of as little as 1-10 % AlN in hot-pressed SiC samples is reported to reduce grain size and improve microstructural uniformity [1-5]. Alloying AlN with SiC appears to stabilize the 2H structure which then resists structural transformation at high temperatures.

Ruh and Zangvil have published a tentative phase diagram for the SiC/AlN system that suggests the existence of a wurtzite-type 2H solid solution over a wide range of temperatures and compositions [7]. At temperatures above *ca.* 2100°C, a single 2H solid solution phase exists from about 23 % AlN to 100 % AlN. At temperatures less than *ca.* 1950°C and compositions from *ca.* 10 to 90 wt% AlN, 2H is the stable form; however, a miscibility gap exists, such that SiC- and AlN-rich 2H phases were observed.

The use of organometallic precursors to prepare SiC/AlN solid solutions has received relatively little attention. A patent has claimed the production of such solid solutions by pyrolysis of a mixture of a polycarbosilane and a poly(N-alkylaminoalane) under an inert atmosphere; however, a detailed characterization of the products of these reactions was not reported nor was the precursor-to-ceramic conversion process studied [9]. Paine and coworkers have evidenced, by X-ray powder diffraction and infrared spectroscopy, the formation of partially crystalline 2H SiC/AlN on pyrolysis of trimethylsilyl-substituted aluminum amide and imide in vacuo at 930°C [10].

The use of such organometallic precursor routes in the preparation and processing of these ceramic phases offers several potential advantages, including the prospect for: 1) improved control over composition, phase distribution and homogeneity; 2) lower processing temperatures; 3) finer-grained materials; and 4) the generation of useful final forms through solution or melt processing. In the particular case of SiC/AlN solid solutions, the high melting or infusible characteristics of these materials, along with the attendant low solid state diffusivities, render the production of the solid solution phases extremely difficult by the usual powder processing methods. Moreover, processing these solid solutions into continuous fiber, coatings, or ceramic matrices would clearly be problematic if not impossible.

In the context of our general interest in the design, synthesis and pyrolysis of organometallic precursors to specific phases and nanocrystalline composites in the Si-C-Al-O-N system, we have pursued the use of both single-component precursors and mixed organosilicon/ organoaluminum systems to prepare SiC/AlN solid solutions. Our initial work employing both a vinylic polysilane (VPS) and methylhydridopolycarbosilane (MPCS) as SiC sources, in copyrolysis with organoaluminum amides, yielded both 2H solid solutions and 3C-SiC/2H-AlN composites, depending on the AlN source employed [11].

We report here the results of both further copyrolysis experiments with diethylaluminum amide $[Et_2AlNH_2]_3$, employing a new polycarbosilane as the SiC source, and our pyrolysis studies of single-component precursors derived from the interaction of cyclotrisilazanes and triethylaluminum. Preliminary results from the latter study were recently reported at the 2nd International Ceramic Science and Technology Congress [12].

The SiC precursor source that was employed in the present studies was a new polycarbosilane of the approximate composition, $[SiH_{1.85}Et_{0.15}CH_2]_n$, prepared by Grignard coupling of chloromethyltrichlorosilane [13]. Our studies of this precursor indicate a near-quantitative conversion to apparently stoichiometric SiC on confined pyrolysis in N_2 to 1000°C [14]. It has a highly branched structure with $Si(C)H_3$, $Si(C)_2H_2$, $Si(C)_3H$, and $Si(C)_4$ microenvironments, and undergoes rapid crosslinking on heating to 150-250°C (or slowly at room temperature) to form a glassy, insoluble solid. It is unusual in that it gives SiC with little or no free carbon on pyrolysis; this precursor was used in the present study to provide better compositional control of the final solid solution product.

EXPERIMENTAL PROCEDURE

General

All precursor handling and preparation was done in a N_2-filled glovebox or with Schlenk techniques. The procedures used for precursor synthesis, handling, and characterization follow standard practice in organometallic chemistry [15] and have been described in detail in our earlier publications [11].

Transmission electron microscopy[$] samples of finely ground ceramic materials were prepared by dropping a suspension of the powder in hexane onto carbon-coated nylon grids and blotting away excess solvent. X-Ray diffraction measurements were made between $2\theta=10\text{-}80^{\circ}$[@]. TGA experiments were carried out in flowing, prepurified N_2 or NH_3 with a typical heating rate of $10^{\circ}C/min$[@@]. A special Lexan glove box was designed and built to house the TGA equipment so as to allow the handling of the air-sensitive precursors under an inert atmosphere. Annealing of 1000°C pyrolyzed ceramics was performed from 1600-1800°C in N_2 for 2h at the desired temperature in a two-chamber H_2-protected, molybdenum wound tube furnace.

Solid state ^{13}C and ^{27}Al NMR studies were performed at the Colorado State University Regional NMR Center. High-speed MAS NMR spectroscopy was carried out at 14.0 T on a Bruker AM-600 spectrometer using a high-speed MAS probe built in-house and tuned to 156.38 MHz [16-18]. Samples were spun in 4.5 mm O.D. cylindrical Vespel rotors at a speed of 12-14 kHz. Single pulse excitation using a 90 degree (2.3 μs) solids pulse was employed [19,20]. A 1.0s recycle delay was used in all cases. 1K data blocks (512-10,000 scans) were acquired using a 100 kHz spectral width and then zero filled to 4kB before Fourier Transformation using 50 Hz line broadening. ^{27}Al chemical shifts were referenced to aqueous 1M $Al(NO_3)_3$ (0.0 ppm). ^{13}C MAS NMR were acquired on a modified NT-100 spectrometer using cylindical Kel-F rotors [18] and an MAS probe built in-house and tuned to 25.27 MHz. Single pulse excitation using a 45 degree (2.5 μs) pulse was employed along with high power proton decoupling during data acquisition. 1kB data blocks (30,000-40,000 transients) were acquired using a 12 KHz spectral width and a 5.0s recycle delay. The resulting data were zero filled to 4kB and Fourier Transformed with 100 Hz line broadening. Carbon chemical shifts were referenced to liquid tetramethylsilane (TMS) whose chemical shift was taken to be 0.0 ppm.

Precursors

Diethylaluminum amide, $[Et_2AlNH_2]_3$, was used as the precursor to AlN and prepared from the reaction of triethylaluminum with NH_3 as reported previously, except that dry hexane was used as the solvent [21]. The polycarbosilane, $[SiH_{1.85}Et_{0.15}CH_2]_n$ (HPCS), was obtained from the reaction of Cl_3SiCH_2Cl with Mg in diethylether [13]. The small amount of Et substitution arises from ether cleavage by the chlorosilane under extended reflux.

The single-component precursors to SiC/AlN were prepared under N_2 by direct reaction of either 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilazane (TMTVTS) or 1,1',3,3',5,5'-hexamethylcyclotrisilazane (HMTS) with triethylaluminum [12]. Reactions were performed using Si/Al molar ratios of 9, 3, and 1. Following the exothermic evolution of ethane, clear, water-like (Si/Al=9) or viscous (Si/Al=3,1) liquids were obtained. Heating these liquid products at 200-300°C produced viscous melts which solidified to yellowish glasses on cooling. Fibers could be drawn from these melts and converted to ceramic fibers by heating them rapidly to 1000-1400°C in N_2 or NH_3. In this manner, short lengths of a black ceramic fiber (10-100 μm in diameter) were obtained from hand-drawn precursor fiber heated in N_2.

Preparation of Precursor Mixtures

A homogeneous liquid containing a 2.1:1 molar (1:1 by weight) ratio of HPCS/$[Et_2AlNH_2]_3$ was prepared by thoroughly mixing the respective liquid precursors in a N_2-filled glove box. This mixture was proportioned for copyrolysis, hot-drop and TGA experiments.

Pyrolysis of Precursors

Copyrolysis of Mixture (Procedure A)

A *ca.* 10 g portion of the precursor mixture was transferred to a molybdenum boat and then loaded into a fused silica tube, equipped with roto-flow valves, in a glovebox. The fused silica tube was inserted into a programmable tube furnace and connected to gas inlet and outlet lines without exposure of the tube contents to the atmosphere. Initial pyrolysis was conducted in an NH_3 atmosphere, using a commercial purifier to remove residual O_2 and H_2O vapor from the anhydrous NH_3 source. The furnace temperature was increased, while flowing NH_3 through the furnace (0.2-0.4 scfh), from 25°C to 200°C in 1h, followed by a hold at 200°C for 4h, and then an increase to 300°C over 0.5h, with a hold at this temperature for another 4h. At this point the gas flow was switched from NH_3 to prepurified N_2 and the temperature was raised to 1000°C over 3.5h. After a 5h hold at 1000°C, the tube was furnace-cooled to room temperature and removed to the glove box for sample retrieval.

Hot Drop of Mixture (Procedure B)

A portion of the precursor mixture was transfered to a 5ml syringe fitted with a needle whose tip was covered with a small rubber septum. A fused silica reactor [11] was heated to 485°C in a sand bath with a constant stream of NH_3 (0.05 scfh) flowing through an inlet tube which extended to near the bottom of the reactor. The needle of the syringe was then pierced through a septum on the reaction vessel and the liquid mixture was "dropped" onto the heated bottom surface at a rate of 1 drop every 5-10s. White fumes were observed during the addition and the temperature of the reactor had increased to 510°C by the end of the addition. After complete addition of the mixture, the reaction vessel was flushed with N_2, cooled under N_2 flow, and transferred into the glovebox for sample collection. Subsequent heating to 1000°C was carried out in a molybdenum boat in the fused silica furnace tube as described in Procedure A after the switch from NH_3 to N_2 gas.

Pyrolysis of Single-Component Precursors (Procedure C)

Typically, 10-15 g portions of these precursors were loaded in the glovebox into the sealed furnace tube as described in Procedures A and B. The samples were directly pyrolyzed in flowing (0.05-0.1 scfh) N_2 by heating from 25°C to 1000°C in 10h, holding at 1000°C for an additional 10h, and cooling to ambient temperature. Samples were retrieved in the glovebox.

RESULTS

Copyrolysis of HPCS/Et_2AlNH_2 Precursor Mixture

TGA results for the mixture of the HPCS and $[Et_2AlNH_2]_3$ precursors (Figure 1) indicate a sizeable increase in char yield for the mixture as compared to those of the individual precursors alone. Essentially the same results were obtained by heating at a constant rate of 10^{o}C/min in N_2 or under conditions which simulated that of the bulk copyrolysis runs, *i.e.*, 5^{o}C/min to 200^{o}C under NH_3, hold for 2h at 200^{o}C, heating to 400^{o}C at 10^{o}C/min, then switching to N_2 for the final heating to 1000^{o}C. In either case, the overall weight loss to 1000^{o}C is only 6-10% more than that expected for a quantitative conversion of the mixture to SiC and AlN, whereas the individual precursors both gave char yields which were on the order of 27-30% under the same conditions (10^{o}C/min, under N_2) [22].

XRD data (Figure 2) for the 1000^{o}C samples obtained by either pyrolysis procedure A or B indicate little or no crystallinity, whereas after the 1600^{o}C anneal the crystallinity has obviously increased, although the crystallite sizes are apparently still quite small. By 1800^{o}C the 2H XRD pattern is clearly seen for all pyrolysis products.

TEM/EDS analyses performed on the ceramic powders derived from pyrolysis procedures A and B showed a significant difference in overall composition, despite the fact that these samples were derived from the same initial precursor mixture (Si/Al=2.1). Whereas the copyrolysis samples (procedure A) appeared to contain more Si than Al (Si/Al= *ca*. 3-10), the samples obtained from the hot drop appeared to be richer in Al (Si/Al= *ca*. 0.2-0.5). After the 1000^{o}C pyrolysis, both samples were largely amorphous;

after the 1600°C anneal, blocky crystallites of 10-50 nm were observed. Further annealing at 1800°C produced some slightly larger crystallites (50-500 nm), although most crystals were 20-50 nm in size; no grain sizes above 1μm were observed. As we observed previously for our precursor-derived SiC/AlN solid solution products [11], there appeared to be two distinct types of particles in these samples, an extremely fine-grained (<10 nm), material which was quite high in Al content and the larger blocky crystallites which were richer in Si than Al, but appeared to contain a significant proportion of both elements.

Single-component Precursor

The char yields for the single-component precursors, pyrolyzed in N_2 to 1000°C, ranged from 35-75%, increasing as the ratio of Si/Al decreased from 9 to 1, *i.e.*, as the amount of Al increased in the polymer [12], and also when the vinyl/methyl-substituted silazane, TMTVTS, was used instead of the methyl-substituted compound, HMTS (Figure 3). In all cases, the resulting ceramics were black glassy solids.

XRD indicated that all materials pyrolyzed to 1000°C were poorly crystalline. Heating to 1600-1800°C under N_2 induced crystallization, with the XRD patterns comparable to those obtained for the mixed-precursor ceramics and consistent with expectations for a 2H solid solution [12].

Solid state ^{27}Al and ^{13}C NMR results for the TMTVS-derived ceramic products are shown in Figures 4 and 5, respectively. The ^{27}Al spectra show a single, broad peak (with broad side bands) which sharpens somewhat and shifts to lower shielding as the temperature is increased from 1000°C to 1800°C. The peak at 113.2 ppm in the spectrum for the 1800°C sample is consistent with that observed at 114.3 ppm for the AlN derived from pyrolysis of the $[Et_2AlNH_2]_3$ precursor alone. The ^{13}C spectra have rather low signal-to-noise ratios; the presence of graphitic carbon from 180-100 ppm [23] is not seen in the 1600°C or 1800°C samples. Carbidic carbon (20 ppm) [23,24] is seen in both of these samples.

DISCUSSION

In our earlier studies of SiC/AlN solid solution formation by pyrolysis of mixed organometallic precursors, it was found that either 2H solid solutions or nanoscale composites of β-SiC and 2H AlN could be obtained, depending on the AlN precursor and the pyrolysis procedure employed. [11]. The use of $[i\text{-}Bu_2AlNH_2]_3$ as the AlN source led to a composite ceramic when a gradual copyrolysis was employed; on rapid heating (hot drop) or through the use of $[Et_2AlNH_2]_3$ as the AlN source, a 2H solid solution was obtained.

Two SiC sources were employed in our earlier work, a methylpolycarbosilane $[MeHSiCH_2]_n$ (MPCS) and a vinylic polysilane $[(vinyl)_xMe_yH_zSi]_n$ (VPS). Both polymers contain a considerable excess of carbon, relative to the unit Si/C ratio in SiC and. as was suggested by the elemental analyses, some of this excess carbon remains in the final ceramic products, presumably as free C.

In the present study, we have focused on the use of $[Et_2AlNH_2]_3$ as the AlN source for the mixed-precursor pyrolysis and, in order to avoid the introduction of excess carbon, we have employed a new precursor (HPCS) to SiC that has a near stoichiometric ratio of Si/C=1 [12]. HPCS is a highly branched polycarbosilane of the composition, $[SiH_{1.85}Et_{0.15}CH_2]_n$, that is known to undergo crosslinking by elimination of H_2 between SiH_n groups on heating between 100-300°C [14]. Thus, in our copyrolysis experiments, the temperature of the mixture of this precursor with $[Et_2AlNH_2]_3$ was held at 200°C for several hours to avoid the loss of volatile carbosilane oligomer fractions in HPCS. However, as is suggested by our TGA study of this mixture (Figure 1) even under the relatively rapid pyrolysis conditions (10 °C/min) employed in this TGA experiment, the overall char yield of the mixture is substantially enhanced relative to that of the individual precursors when studied under the same conditions alone. We conclude that a reaction between these two precursors occurs during the heating of the mixture between 200-500°C, which renders the precursors involatile and fixes the relative positions of Si and Al in the mixture during the subsequent pyrolysis. This would explain the observation that a 2H SiC/AlN solid solution is obtained as the eventual product of this pyrolysis.

The precise nature of the reaction between these two precursors is presently unknown; however, it is expected that Si-based radicals are formed by thermolysis of the Si-H bonds in the polycarbosilane near 200°C. These radicals can be trapped by the organoaluminum amide, which could lead to Si-N-Al linkages between these two precursors. Alternately, a reaction involving the relatively protonic (N)-H hydrogen atom of the organoaluminum amide and the relatively hydridic (Si)-H of the polycarbosilane could eliminate H_2 to form Al-N-Si bonds directly [25]. Efforts to test this hypothesis of Al-N-Si linkage formation in the heated polymer mixture are currently underway using solid state NMR spectroscopy. In any event, it is clear that the copyrolysis of this precursor mixture can be used to prepare an apparently homogeneous SiC/AlN solid solution in high yield.

Preliminary studies of this solid solution by using TEM/EDS and solid state ^{27}Al NMR spectroscopy suggest that, on annealing between 1600 and 1800°C, phase separation occurs to yield at least two distinct 2H solid solution phases. A similar situation was observed in our earlier studies [11] as well as in our investigation of the single-component precursors (see below). This is presumably a manifestation of the miscibility gap in the SiC/AlN phase diagram in the temperature regime where crystallization of the solid solution actually occurs [7].

The single-component precursors to SiC/AlN solid solutions are polyaluminosilazanes derived from the reaction of cyclotrisilazanes of the type $[RR'SiNH]_3$ (R = Me; R' = Me, vinyl) with Et_3Al. A reaction occurs at room temperature between these compounds, releasing ethane and presumably forming Si-N-Al bridges between at least partially intact silazane rings [20]. The substantial increase in viscosity that occurs on mixing the two liquid precursors, along with the eventual solidification on heating to form an insoluble glass, suggests a condensation polymerization process that eventually proceeds to form a three-dimensional network structure. In the case of the vinyl-substituted silazane, TMTVTS, IR spectra suggest that vinyl polymerization occurs along with Si-N-Al bond formation, contributing to the establishment of a network structure. It was found that, at an appropriate point in this thermally induced polymerization process, fibers could be hand drawn from the melt of the TMTVTS + Et_3Al polymer. These were successfully converted to amorphous ceramic fiber by heating rapidly in either N_2 or NH_3. In the latter case, a mixture of β-Si_3N_4 and AlN is the eventual crystalline product on thermally annealing at 1600°C, whereas under N_2 the only crystalline phase observed by XRD [12] is the 2H SiC/AlN solid solution. Based on the unusually high TGA yield observed for the

TMTVTS-derived polymer relative to the HMTS-derived polymer in particular (Figure 3), it is anticipated that the final ceramic product also contains a considerable amount of excess carbon.

The ^{27}Al and ^{13}C NMR data on the TMTVS-derived ceramic products (Figures 4 and 5) indicate that the final Al and C environments after crystallization at 1800^{o}C are similar to those in AlN and SiC, respectively; however, a closer examination of these spectra show a broadening that is not found in the pure phases, suggesting a distribution of environments. The substantial peak shifts that are observed in these spectra following the annealing of the 1000^{o}C sample at 1600^{o}C and finally 1800^{o}C, indicate further that a marked change in the local environment has occurred as this material crystallized. The initial ^{27}Al peak position observed for the amorphous 1000^{o}C product is consistent with an environment which contains both N and C. After heating to 1600^{o}C and then 1800^{o}C, the Al peak shifts to lower fields, approaching the 114.0 ppm position found for AlN. Similarly, the ^{13}C peak, which starts out with a value appropriate to graphitic carbon, shifts towards the position expected for C in SiC.

These observations are, in general, consistent with expectations based on the phase diagram for SiC/AlN which indicates a miscibility gap in this temperature regime, with AlN- and SiC-rich solid solution phases separating out on crystallization. Further NMR studies (including ^{29}Si NMR) of these solid solutions are planned, along with a full investigation of the homogeneous 2H solid solution phase which is anticipated on crystallization of the 1000^{o}C material above 2000^{o}C.

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[S] Philips CM12 coupled with Tracor Northern 5500 Analyzer
[@] Philips 1710W Automated Powder Diffractometer, equipped with a monochromater in the exit beam, CuKα radiation
[@@] Perkin Elmer Series 7 Thermal Analysis System

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Figure Captions

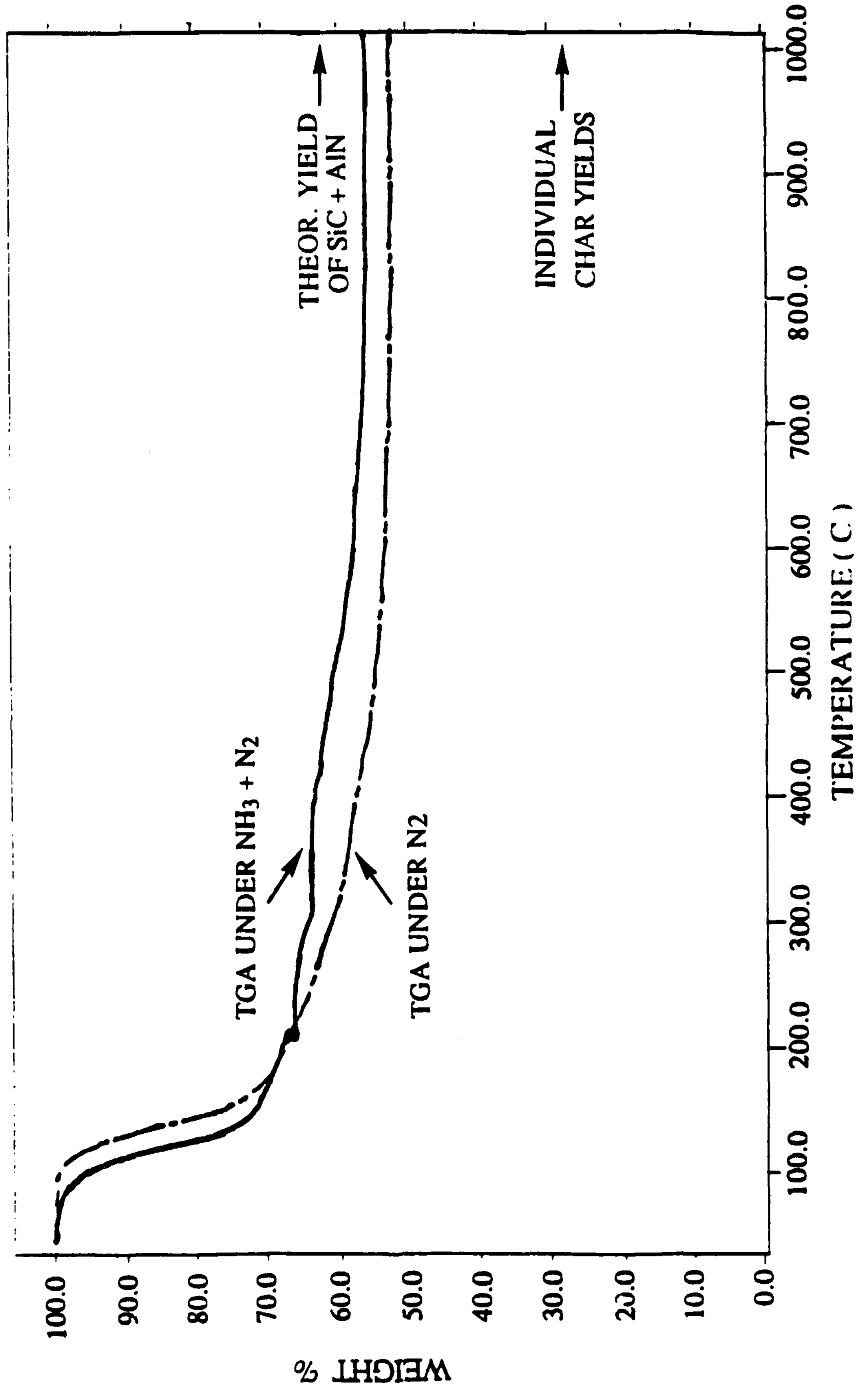
Figure 1. TGA curves for the pyrolysis of 2.1:1 molar (1:1 by weight) mixtures of HPCS/$[Et_2AlNH_2]_3$ in N_2 or N_2/NH_3. TGA under N_2 run at 10°C/min. For the N_2/NH_3 run, conditions simulating the copyrolysis were employed (see text). The sum of the char yields for the individual precursors are noted along with the theoretical yield of SiC + AlN.

Figure 2. XRD powder patterns for ceramics obtained by a) Copyrolysis/Procedure A, and b) Hot Drop/Procedure B for HPCS/$[Et_2AlNH_2]_3$.

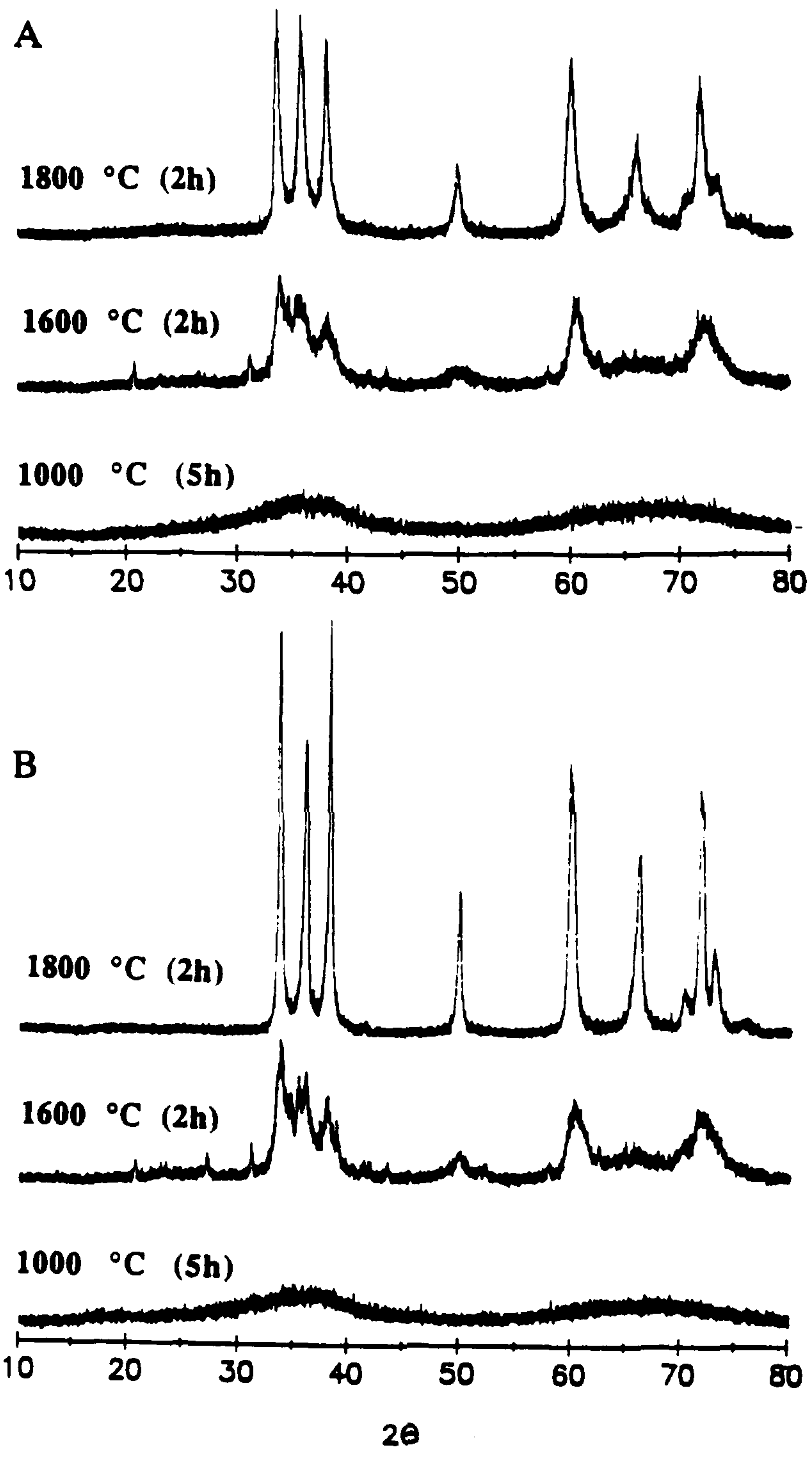
Figure 3. TGA curves for the N_2 pyrolysis of a) TMTVS and b) HMTS single-component precursors. Heating rate was 10°C/min.

Figure 4. Solid state ^{27}Al MAS NMR spectra for TMTVS (Si/Al=3) samples pyrolyzed to 1000°C and annealed at 1600°C and 1800°C in N_2. Peak positions are noted. Spectra of $[Et_2AlNH_2]_3$ samples that were heated to 1000°C and 1600°C are shown for comparison. Spinning side bands (*) are seen as small, broad bands on each side of the main peak.

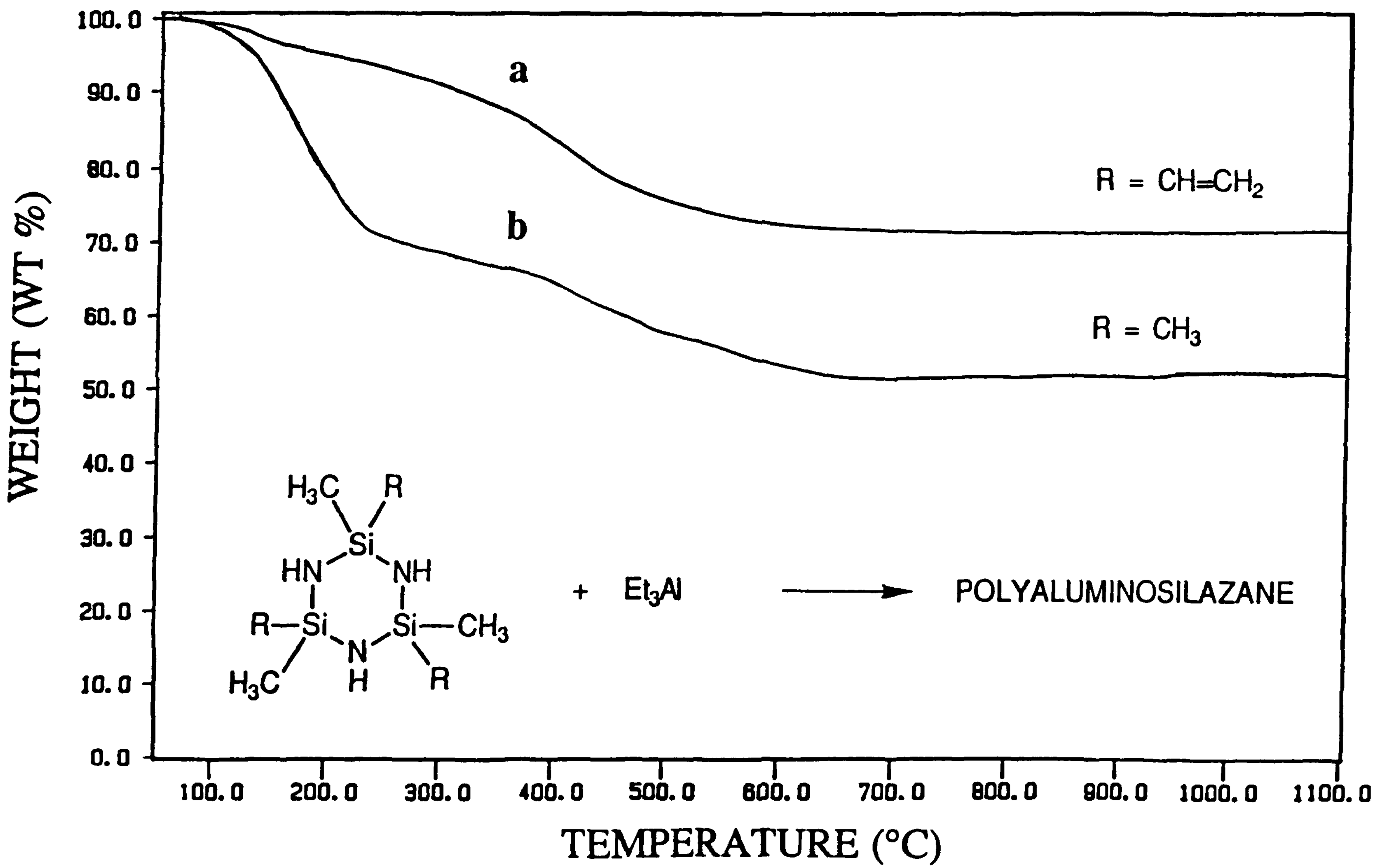
Figure 5. Solid state ^{13}C MAS NMR spectra for TMTVS (Si/Al=3) samples pyrolyzed to 1000°C and annealed at 1600°C and 1800°C in N_2.


WEIGHT %
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
TEMPERATURE (C)
100.0
200.0
300.0
400.0
500.0
600.0
700.0
800.0
900.0
1000.0
TGA UNDER NH$_3$ + N$_2$
TGA UNDER N2
THEOR. YIELD OF SiC + AlN
INDIVIDUAL CHAR YIELDS

[illegible]

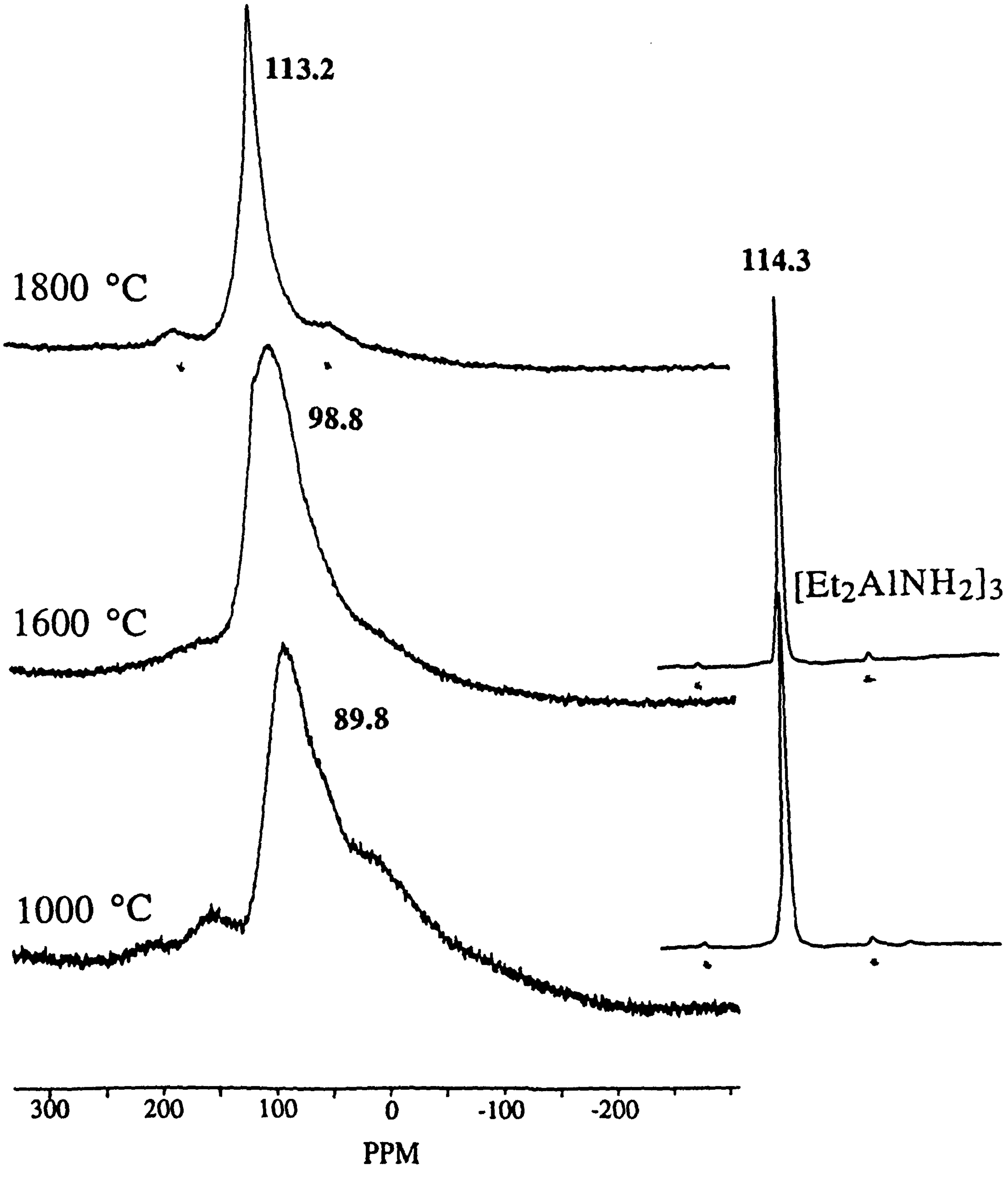


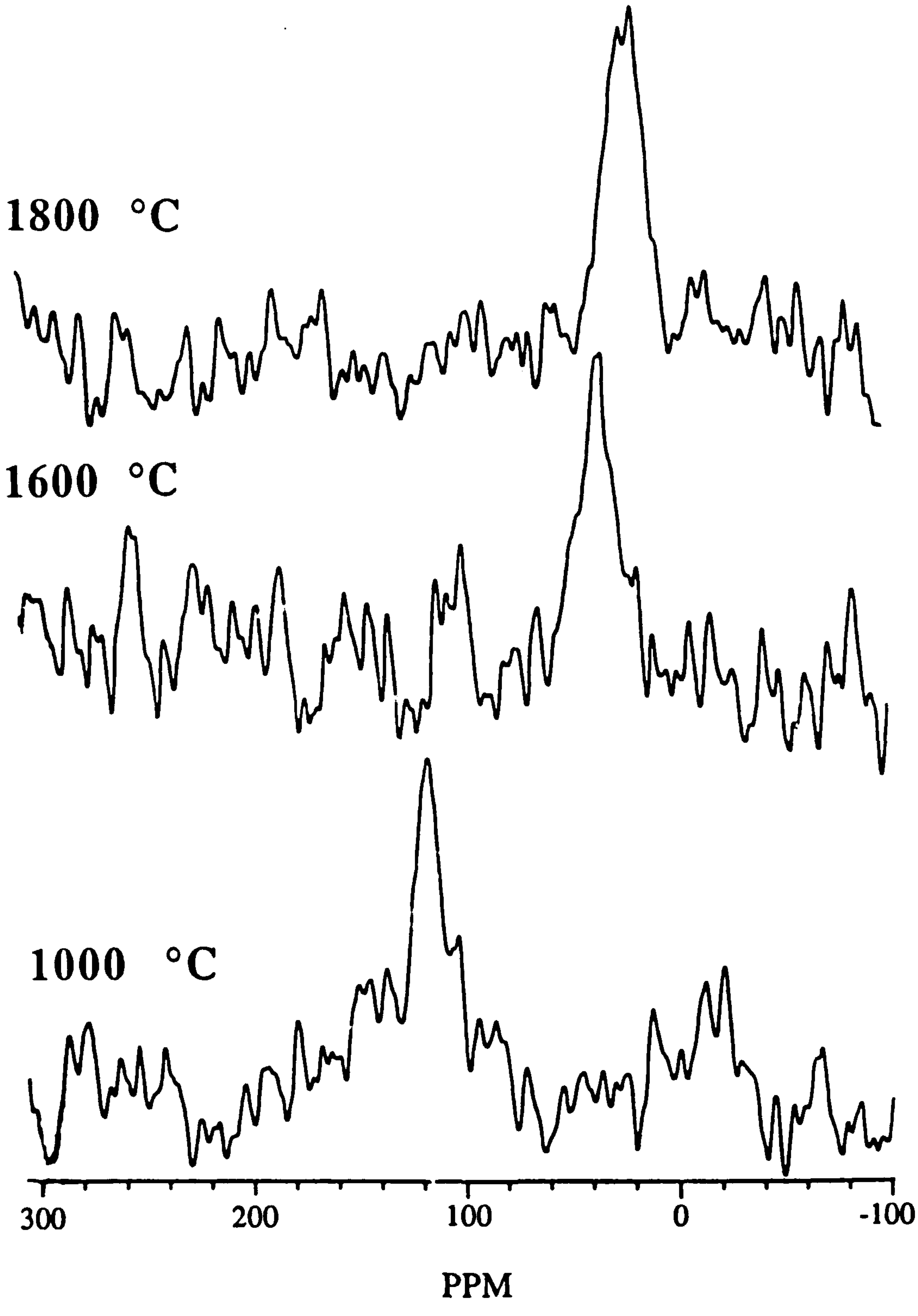
A
1800 °C (2h)
1600 °C (2h)
1000 °C (5h)
10
20
30
40
50
60
70
80
B
1800 °C (2h)
1600 °C (2h)
1000 °C (5h)
10
20
30
40
50
60
70
80
2θ



100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
WEIGHT (WT %)
100.0
200.0
300.0
400.0
500.0
600.0
700.0
800.0
900.0
1000.0
1100.0
TEMPERATURE (°C)
a
b
R = CH=CH2
R = CH3
H3C
R
Si
HN
NH
R
Si
N
H
Si
CH3
H3C
R
+ Et3Al
POLYALUMINOSILAZANE

Figure 1


113.2
1800 °C
114.3
98.8
[Et$_2$AlNH$_2$]$_3$
1600 °C
89.8
1000 °C
300
200
100
0
-100
-200
PPM


1800 °C
1600 °C
1000 °C
300
200
100
0
-100
PPM

Publication No. 11

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NOVEL POLYMERIC PRECURSORS TO Si-C-Al-O-N CERAMIC COMPOSITES

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ABSTRACT

Si_3N_4/AlN, SiC/AlN, and mixed Si-C-Al-O-N and Si-Al-O-N ceramic composite powders were prepared by the controlled pyrolysis of one-component polymeric precursors to 1000 °C in either N_2 or NH_3, followed by annealing to 1600-1800 °C in N_2. The polymers were prepared by the reaction of 1,3,5-trimethyl, 1,3,5-trivinyl-cyclotrisilazane with either triethylaluminum or diethylaluminum ethoxide.

INTRODUCTION

Ceramics in the Si-C-Al-O-N system consist of mixtures of Si- and Al-containing carbide, nitride, oxide, oxycarbide, and oxynitride compounds with uni- or multi-dimensional networks of (Si, Al)(C, O, $N)_{4-6}$ units. Si-C-Al-O-N ceramics are attractive candidates for high-temperature structural applications with thermal and mechanical properties comparable to SiC and Si_3N_4. The oxygen-containing ceramics provide improved oxidation resistance and are generally easier to process than the carbides or nitrides alone[1-3].

Conventional processing of Si-C-Al-O-N composite powders often involves intimate mixing of combinations of the component ceramic powders, followed by shaping and densification at elevated pressures and temperatures[4-9].

Organometallic precursors to ceramics are currently of interest because they offer potential advantages, over traditional powder methods, such as 1) processing at lower temperatures, 2) control of the stoichiometry and microstructure in the resulting ceramic and 3) the ability to form coatings and fibers due to solubility and tailorable rheology of the precursors.

Several researchers produced polymer-derived ceramics by pyrolyzing either two or more "molecularly mixed" organometallic precursors to the various phases in the composite[10-14] or single component polymers which contained all elements of the desired ceramic composition[15-18]. Yu and Mah[10] prepared oxynitride and Si-Al-O-N ceramics fron a mixture of precursors to SiO_2N_2 and Al_2O_3. Interrante and co-workers[11-13] prepared ceramic composites and solid solutions containing Si, Al, and C or N from mixtures of alkylaluminum amide precursors to AlN and polysilane or polycarbosilane precursors to SiC/Si_3N_4. Recently, single component polymeric precursors to SiC/SiO_2[15], SiC/Al_2O_3[15], SiC/AlN[16], as well as $Si_3N_4/SiC/C$[17] and Si-C-B-N[18] ceramic composites were reported.

This study describes the preparation of single component polymeric precursors from the reaction between a vinyl-, methyl-substituted cyclic trisilazane and alkylaluminum or alkylaluminum alkoxide compounds. Controlled pyrolysis of these precursors in N_2 or NH_3 produces mixed phase ceramic nanocomposites containing Si, Al, N, C, and/or O.

EXPERIMENTAL PROCEDURE

All chemicals were handled in either a N_2-filled glovebox or with Schlenk techniques, respecting the pyrophoric nature of alkylaluminum compounds and the moisture sensitivity of high surface area ceramic powders. N_2 and anhydrous NH_3 were purified in-line prior to use to remove traces of moisture and O_2: N_2 - over activated copper catalyst and 3Å molecular sieves; NH_3 - over a mixture of flaked KOH and molecular sieves, and then a commercial purifier[19a].

Thermogravimetric analyses[19b] of all polymers were performed in flowing (0.05-0.1 SCFH) N_2 or NH_3, typically at heating rates of 5-10 °C/min. Bulk pyrolysis experiments to 1000 °C were performed using an elastomer-sealed fused silica tube with inlet and outlet valves, which allowed the passage of flowing (0.2-0.4 SCFH) gas. Samples were heated in molybdenum foil boats at 2-5 °C/min and held at the desired temperature for 6-10 hours. Portions of samples heated to 1000 °C were further heated in flowing N_2 in a gastight alumina tube at temperatures up to 1800 °C at heating rates of 6-10 °C/min. Samples were annealed for 2-4 hours and cooled overnight in the sealed furnace.

XRD[19c] and TEM/SAD[19d] were used to investigate the crystallinity of the resulting ceramics. Solid state ^{29}Si, ^{13}C and ^{27}Al MAS NMR[19e] and FT-IR[19f] provided information regarding the chemical reactions between the starting materials and local bonding environments in the products.

The source of Si was 1,3,5-trimethyl, 1,3,5-trivinylcyclotrisilazane $[(CH_2{=}CH)(CH_3)SiNH]_3$. The source of Al was either triethylaluminum,

$(CH_3CH_2)_3Al$, or, to prepare Al- and O-containing ceramics, diethylaluminum ethoxide $[(CH_3CH_2)_2AlOCH_2CH_3]_2$, which was prepared as previously described[20] and purified by vacuum distillation at 65-70 °C at 1 mm Hg.

Two series of precursor polymers were prepared. Polyaluminosilazanes (PAS) were obtained by reacting the silazane with triethylaluminum without solvent at 25 °C in Si/Al ratios of 9, 3, and 1. Reaction occurred immediately as evidenced by the exothermic reaction and evolution of gas bubbles. Polymers ranged in viscosity from runny liquids (Si/Al=9) to taffy-like fluids (Si/Al=3 and 1). Some polymers continued to increase in viscosity over several months (Si/Al=3 and 1), producing a clear glass in one case (Si/Al=3). Polyoxyaluminosilazanes (POAS) were prepared by reacting the silazane directly with diethylaluminum ethoxide to give Si/Al ratios of 3, 1.5, 1, 0.67, and 0.33. These mixtures were refluxed at 110 °C for 2 hours and further refluxed at 250 °C for an additional 6 hours. Upon cooling, colorless viscous liquids (Si/Al=0.33) to slightly yellow solids (Si/Al=3) were obtained.

Polymeric fibers were hand-drawn from the melt of several precursor compositions after the polymers had been heated between 200-300 °C in N_2. These fibers were subsequently heated in N_2 or NH_3 to 1000-1400 °C to yield black or white ceramic fibers (10-100 μm in diameter), respectively.

RESULTS

The char yields for PAS polymers pyrolyzed in N_2 ranged from 35-75%, increasing as the ratio of Si/Al decreased from 9 to 1, *i.e.* as the amount of Al increased in the polymer. In all cases, the resulting ceramics were black glassy solids. Char yields for PAS pyrolyzed in NH_3 varied from 15-48%, with solids ranging in color from dark grey to white. POAS polymers gave char yields of 35-60% in N_2 (black solids) and 30-50% in NH_3 (white solids).

XRD indicated that all materials pyrolyzed to 1000 °C were poorly crystalline, regardless of atmosphere. Heating PAS-derived composites to 1600-1800 °C produced α-SiC/AlN following pyrolysis in N_2 (Figure 1a) or α-, β-Si_3N_4/AlN if pyrolysis was done in NH_3 (Figure 1b). Heating POAS-derived ceramics to 1600 °C produced SiC, AlN, and mixed Al-O-N phases after pyrolysis in N_2, or β-Si_3N_4, AlN, Al_2O_3 and mixed Al-O-N phases in NH_3. The local bonding environment of Al was investigated with solid state ^{27}Al MAS NMR, which showed phase separation of AlN_4 tetrahedra, AlO_6 octahedra, and mixed $Al(O,N)_{4-6}$ species[21] in the POAS-derived composites (Figure 2). TEM analysis of POAS-derived composites showed several crystal morphologies which depended on the Si/Al ratio in the starting polymer. Blocky crystals were observed in the composite with Si/Al=3 (Figure 3a), while both needle-like and blocky crystals were observed in the pyrolysis product of Si/Al=0.67 (Figure 3b).

Nanocrystallites (5-500 nm) were typically observed in samples that were poorly crystalline by XRD powder patterns.

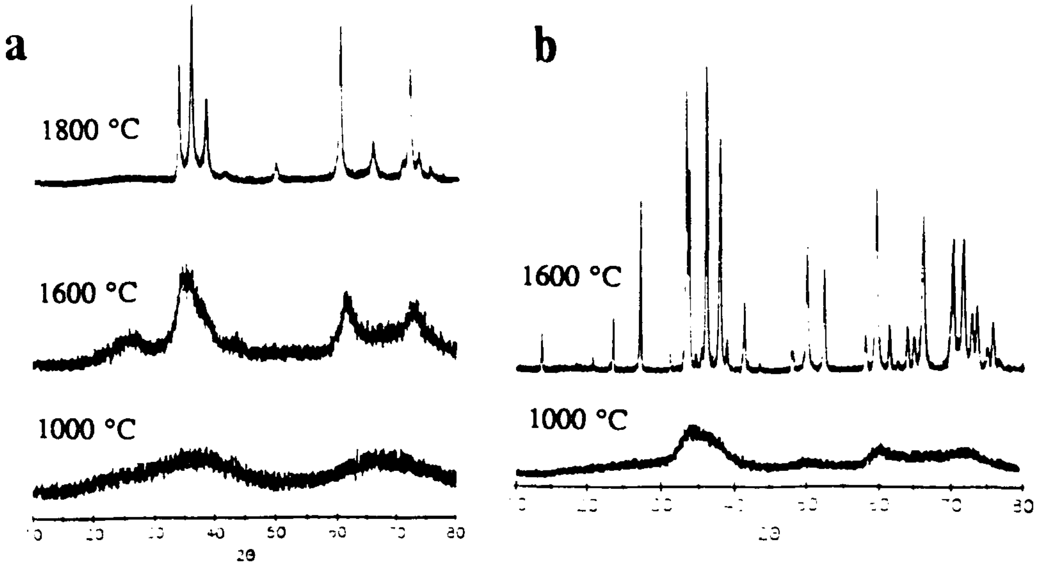


Figure 1. XRD Patterns for PAS-derived composites a) Si/Al=9, N_2 pyrolysis, N_2 anneal (α-SiC/AlN product), b) Si/Al=3, NH_3 pyrolysis, N_2 anneal (α-, β-Si_3N_4/AlN product).

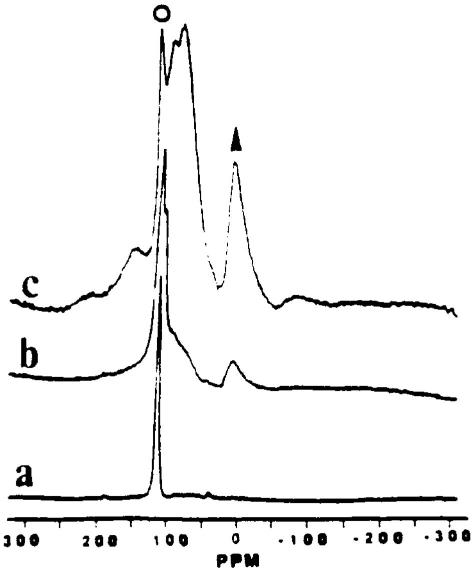
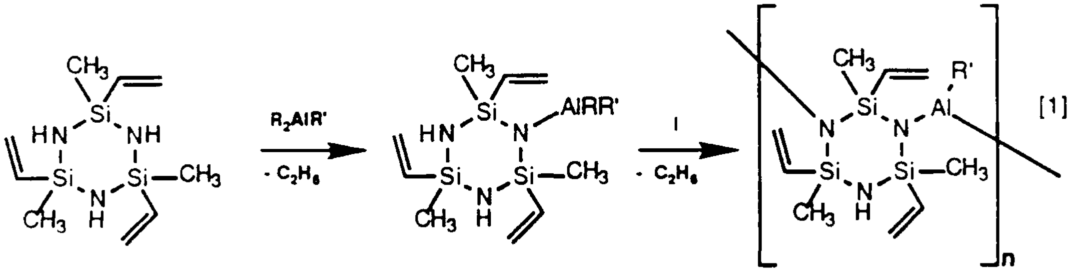


Figure 2. ^{27}Al solid state MAS NMR spectra of POAS-derived composites (NH_3 pyrolysis, 1600 °C N_2 anneal) showing formation of AlN_4 (o), AlO_6 (▲), and mixed $Al(O,N)_{4-6}$ phases. a) Si/Al=3, b) Si/Al=1.5, c) Si/Al=1.

DISCUSSION

PAS and POAS polymers are formed by a known condensation reaction which occurs between the N-H groups of the silazane and the organoaluminum compound to form a new Al-N bond and evolve ethane[22] (Reaction 1). Further Al-N bonding by Lewis acid-base interaction involving the trigonal Al and N atoms in this structure is likely, leading to further polymerization and potential cross-linking. This mechanism is supported by the immediate exothermic evolution of gas, identified as ethane by GC, that occurred during the preparation of the polymers (POAS polymers required slight warming, suggesting a slower reaction rate) and FT-IR spectra which showed a decrease in the concentration of N-H functionality upon reaction. Heating the polymers causes further extension of the Al-N network with loss of more ethane along with coupling of the vinyl groups, ultimately leading to a highly cross-linked product. Solid state ^{13}C MAS NMR showed that the vinyl groups reacted completely between 200-300 °C.



[1]

1

$R = C_2H_5$, $R' = C_2H_5$ or OC_2H_5

We have found that single component polymeric precursors can provide homogeneous sources of mixed phase ceramic composite powders. These precursors can also be pulled into polymeric fibers, which can then be pyrolyzed to produce ceramic fibers. The phase distribution and crystallite size can be controlled by proper choice of pyrolysis atmosphere, heating rate, annealing temperature and time, and the Si/Al ratio in the starting polymer.

NH_3 provides a source of N and aids in the removal of C-containing species[12,23], thereby providing a convenient route to prepare nitride ceramics. AlN and Al_2O_3 are known to influence the relative distribution of α- and β- Si_3N_4[24], and we observe that the presence of Al-O-N species in the POAS-derived composites causes the preferential formation of β-Si_3N_4 over α-Si_3N_4 at 1600 °C.

We are employing polymeric precursors to make ceramic nanocomposites which are expected to exhibit novel and potentially useful mechanical properties such as high toughness[25] and even ductility[25,26].

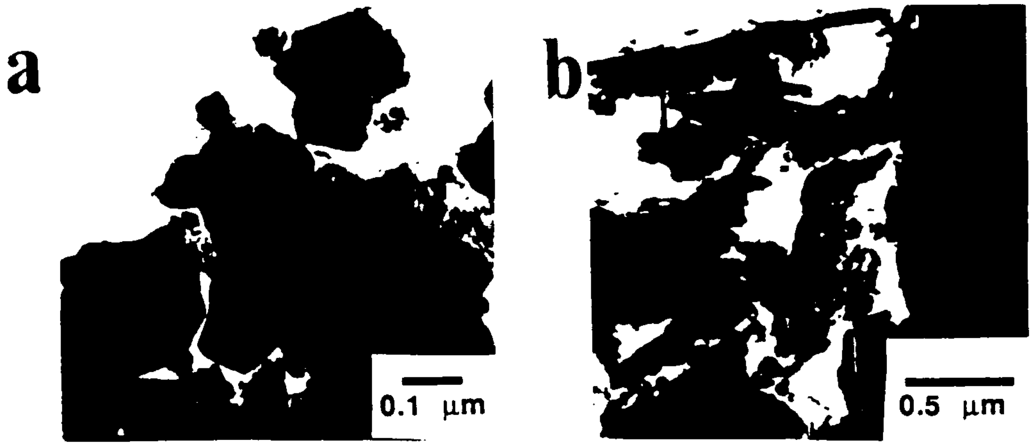


Figure 3. Transmission electron micrographs of POAS-derived ceramic composites (NH_3 pyrolysis, 1600 °C N_2 anneal). a) Si/Al=3, b) Si/Al=0.67.

ACKNOWLEDGEMENTS

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COMPLETED PROJECT SUMMARY

1. TITLE: ORGANOMETALLIC PRECURSOR ROUTES TO Si-C-Al-O-N CERAMICS

2. PRINCIPAL INVESTIGATOR: L.V. INTERRANTE

3. INCLUSIVE DATES: 1 July 1989 - 31 March 1991

4. CONTRACT/GRANT NUMBER: AFOSR-89-0439

5. TOTAL COST: $140,000

6. SENIOR RESEARCH PERSONNEL: Dr. T. Trout
   Dr. W. Schmidt
   Dr. F. Sauls

7. JUNIOR RESEARCH PERSONNEL: Mr. C. Whitmarsh
   Mr. Z. Jiang
   Mr. H-J. Wu

8. PUBLICATIONS

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