Pyrolytic Organic-to-Inorganic Conversion of Precursors into AlN—A Review

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有機–無機変換プロセスによる AlN の作製（総説）

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Pyrolytic “organic-to-inorganic” conversion of precursors (preceramic materials) into aluminum nitride (AlN) has been investigated for the past few decades. AlN precursors can be classified based on their starting aluminum compounds (organoaluminum compounds, inorganic compounds containing aluminum, and metallic aluminum). The preparation of various AlN precursors and their conversion mechanisms during pyrolysis are reviewed.

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1. Introduction

PYROLYTIC organic-to-inorganic conversion of precursors (preceramic materials), which are typically organo-metallic and/or inorganic polymers possessing metal-nitrogen and/or metal-carbon backbones, is a novel route to obtaining non-oxide materials (Fig. 1).^{1)–5)} If precursors are liquid, fusible at relatively low temperatures or soluble in common organic solvents, this process can offer fabrication routes to ceramics and ceramic-based composites with desirable shapes, including coatings and fibers. Additional potential applications for this route include sintering aids and binders (Fig. 2).^{3)–5)} These applications are essentially unattainable by a conventional powder-processing route.⁴⁾ This route can also offer the preparation of ceramic materials possessing multiple metals (and semimetals), since precursors can exhibit atomic-scale homogeneity, leading to formation of highly homogeneous amorphous materials and ceramic composites

with better microstructures upon pyrolysis.

AlN^{6)–16)} has been considered as one of the attractive nitrogen ceramics with various properties, including high thermal conductivity, high electrical resistivity, low dielectric constant, high thermal and chemical stability and a low thermal expansion coefficient very close to that of silicon. In consideration of these intrinsic properties, AlN is expected to be a promising ceramic material for electronic and optoelectronic applications,^{7),17)–20)} such as heat sinks, hybrid substrates in integrated circuits, high power/frequency electronic devices and surface acoustic wave (SAW) devices. AlN powders have generally been prepared by carbothermal reduction of an alumina-carbon mixture,^{21)–25)} polymeric precursors containing an aluminum-oxygen network and a carbon source^{26),27)} and intercalation compounds^{28)–30)} under a nitrogen atmosphere, and by direct and floating nitridation.^{31)–33)} In addition, AlN films have been prepared by a chemical vapor deposition (CVD) process.^{34)–38)}

As a novel route to obtaining AlN, pyrolytic conversion of precursors has been investigated for past few decades. We review here the preparation of various AlN precursors based on the starting materials for aluminum source: from organo-aluminum compounds and inorganic compounds containing aluminum [such as AlH₃ (and its adduct), LiAlH₄, aluminum halides], and on their pyrolysis processes, as well as on

Fig. 1. Flow diagram for the preparation of ceramics via pyrolytic organic-to-inorganic conversion.

Fig. 2. Preparation of ceramic materials by precursor processing.

the pyrolytic conversion of precursors for other non-oxide ceramics and their composites. The preparation of AlN *via* an electrochemical technique using metallic aluminum is also described in this review.

2. Pyrolytic organic-to-inorganic conversion of precursors into non-oxide ceramics (and ceramic-based composites)

2.1 Design of precursors^{(1),(3),(5)}

Design of precursors is extremely important for obtaining useful precursors since successful applications of the pyrolytic organic-to-inorganic conversion process depend strongly on the properties and structure of precursors.

As mentioned above, to be useful, a precursor should usually be a liquid, or if a solid, it should be soluble in common organic solvents or fusible at relatively low temperatures in order to permit desired applications (such as fabrication of ceramics with desirable shapes). In addition, volatile products that evolve during pyrolysis should preferably be non-hazardous and nontoxic. A useful precursor should exhibit a high ceramic yield, moreover, leading to less shrinkage and a reduction in destructive effects caused by evolved gaseous species.

Many linear polymeric precursors, even when compounds with high molecular masses, exhibit negligible ceramic yields because of the generation and volatilization of low molecular mass compounds (e.g., cyclic species). Precursors exhibiting high ceramic yields should therefore possess cross-linked structures, but highly cross-linked structures generally exhibit very low solubility in common organic solvents.

In order to prepare a soluble precursor with a relatively high ceramic yield, two following strategies have been proposed. One is the introduction of bulky organic groups into a precursor, which can lead to formation of a soluble precursor, since the introduction of these groups can suppress the formation of a highly cross-linked structure. Materials obtained by pyrolysis of such precursors could contain undesirable carbon in the form of free carbon as well as carbides, however, which could lead to degradation of its potential, in particular, for the preparation of nitrides. Thus, the carbon content of soluble precursors (especially precursors for nitrides) should be as low as possible.

The other strategy is the use of oligomers,⁽³⁹⁾ or even monomers,⁽⁴⁰⁾ possessing reactive groups. Oligomers and monomers are generally soluble in common organic solvents, but they exhibit low ceramic yields because of their volatilization during pyrolysis. If cross-linking reactions occur before their volatilization, however, the ceramic yields can be increased. For the facile occurrence of cross-linking reactions, it is desirable for appropriate reactive (or potentially reactive) substituent groups (e.g., unsaturated organic groups or reactive bonds such as SiH, NH, BH and AlH) to be introduced into precursors. Thus, design of precursor is highly important for these strategies.

2.2 Precursors for non-oxide ceramics

The preparation of non-oxide ceramics (nitride and carbide) and their composites through pyrolysis of precursors was initially developed by Verbeeck, Winter, and Yajima and co-workers in 1970's.^{(41)–(45)} Yajima and co-workers prepared silicon carbide (SiC) by pyrolysis of poly(carbosilane) (PCS) obtained from poly(dimethylsilane), which was synthesized by alkali-metal-promoted dehalocoupling of chlorosilanes (Wurtz coupling).^{(43)–(48)} The conversion of poly(silane) (PS) into PCS, often called the Kumada rearrangement,^{(49)–(51)} occurs at $\sim 470^\circ\text{C}$ *via* a radical mechanism. Poly(carbosilane) with a 50–55% yield was obtained through this route. To

improve the synthesis (to increase the PCS yield and to lower the reaction temperature and time), PCS was prepared using Lewis acid catalysts (such as diphenylborosiloxane polymer).^{(52),(53)} The Yajima route has been employed for the commercial fabrication of such SiC fibers as “Nicalon (or Hi-Nicalon)” fiber (SiC_xO_y , Nippon Carbon Co., Ltd.)⁽⁵⁴⁾ and “Tyranol” fiber ($\text{SiTi}_x\text{C}_y\text{O}_z$, Ube Industries, Ltd.)⁽⁵⁵⁾

Numerous other PSs and PCSs have been widely prepared as SiC precursors *via* various synthetic methods.^{(56)–(59)} The preparation of PCSs was also advanced by ring-opening polymerization of various derivatives of 1,3-disilacyclobutane.^{(60)–(63)} Poly(silapropylene)s $[\text{Me}(\text{H})\text{SiCH}_2]_n$ (or poly[(methylchlorosilylene)methylene] $[\text{Me}(\text{Cl})\text{SiCH}_2]_n$) *via* H_2PtCl_6 -catalyzed ring-opening polymerization gave SiC with quite low ceramic yields due to their linear structures, and cross-linked polymers were consequently synthesized by further treatment.⁽⁶⁴⁾ PCSs were also prepared by Pt-catalyzed hydrosilylation of vinylchlorosilane $\text{SiH}(\text{CH}_2=\text{CH})\text{Cl}$.^{(65)–(67)} The increase in the introduction of vinyl groups led to high ceramic yields but gave rise to a higher carbon content in the resulting materials. Schilling et al.^{(68),(69)} revealed that SiC was obtained by pyrolysis of PCSs, which were synthesized *via* reactions of vinylmethylchlorosilane with other chlorosilane monomers (Me_3SiCl and/or Me_2SiCl_2).

Poly(dimethylsilane), described above, is a polymer that is insoluble and infusible, which is a large drawback as a precursor. West et al. prepared poly(silastylene)s possessing phenyl groups *via* sodium-promoted Wurtz coupling between PhMeSiCl_2 and Me_2SiCl_2 , leading to enhancement of their solubility in common organic solvents.^{(70)–(72)} Poly(methylsilane)s (PMS) prepared by dehalocoupling of dichloromethylsilane^{(68),(69),(73),(74)} exhibit quite low ceramic yields (15–20 mass%), and the resulting materials contained a 25 mass% excess of metallic silicon that crystallized at higher temperatures.⁽⁷³⁾ To achieve increases in ceramic yield and carbon content, modification of PMS *via* Pt-catalyzed hydrosilylation with organic or organosilicon compounds has been conducted.⁽⁷⁴⁾ Other approaches to increasing the ceramic yield of PMS have utilized various catalysts, such as transition metals^{(75),(76)} and boron compounds.^{(77)–(79)}

The preparation of silicon nitride (Si_3N_4) *via* pyrolytic conversion of poly(silazane)s, which typically possess an Si–N backbone, has been extensively investigated.^{(57),(80)} An oily poly(silazane) with the proposed formula of $[(\text{H}_2\text{SiNH})_{0.42}(\text{H}_2\text{Si}_{1.5}\text{N})_{0.58}]_n$ was prepared by ammonolysis of dichlorosilane (H_2SiCl_2) in polar solvents.^{(81),(82)} Pyrolysis of the oily polysilazane led to the formation of a brown solid, which contained $\alpha\text{-Si}_3\text{N}_4$, $\beta\text{-Si}_3\text{N}_4$ and a trace of metallic silicon. The cyclic silazane oligomers $(\text{R}^1\text{R}^2\text{SiNR}^3)_n$ (mainly $n=3\text{--}5$) were generally prepared *via* ammonolysis of organodichlorosilanes.^{(57),(80)} Since the average molecular masses of these compounds were low, they exhibited low ceramic yields.

As poly(silazane)s with higher ceramic yields, methylhydridopolysilazanes were prepared *via* KH catalyzed dehydrocondensation of methylcyclasilazane $[\text{Me}(\text{H})\text{SiNH}]_n$.^{(82),(83)} The ceramic yields of these poly(silazane)s were relatively high (80–85 mass%) due to their cross-linked structures. The resulting material consisted of Si_3N_4 , SiC and a trace of free carbon. Blum et al. prepared cross-linked poly(silazane)s, moreover, *via* transition-metal-catalyzed dehydrocondensation.^{(84),(85)}

The thermal cross-linking reactions of various cyclic silazane oligomers $(\text{R}^1\text{R}^2\text{SiNR}^3)_n$ and the pyrolysis processes of the resultant cross-linked polymers have been investigated.^{(39),(85)–(88)} The ceramic yields and chemical compositions of

the resulting materials were heavily dependent on the organic substituents and the pyrolysis atmospheres. The oligomers possessing SiH and Si-CH=CH₂ or NH groups were easily converted into cross-linked structures at relatively low temperatures, leading to high-yield conversion into the resulting materials. The presence of the Si-CH₃ groups [not the Si-C_xH_{2x+1} groups ($x \geq 2$) or Si-phenyl groups] in the oligomers is favorable for the formation of Si-CH₂-Si intermediate links, which can lead to SiC formation in Si₃N₄ with further pyrolysis. Pyrolysis under an argon atmosphere gave ceramics with high yields and high carbon content, whereas pyrolysis under an NH₃ atmosphere resulted in the formation of pure Si₃N₄ due to nucleophilic and/or free-radical substitution by NH₃.

Isoda and co-workers prepared a novel soluble poly(silazane) (perhydropolysilazane) by ammonolysis of a dichlorosilane-pyridine complex.⁸⁹⁾ Continuous stoichiometric Si₃N₄ fiber was fabricated by the pyrolysis of perhydropolysilazane.⁹⁰⁾ This high-purity silicon nitride fiber possessed high strength, a modulus of elasticity, and thermal stability, which are properties suitable for reinforcing plastics, metals, glasses, and even ceramics.

As precursors for boron nitride (BN), Sneddon and co-workers prepared poly(borazylene) (B₃N₃H₄)_n obtained by dehydrocondensation of borazine (B₃N₃H₆) at moderate temperatures.^{91)–93)} Pyrolysis of poly(borazylene) at 1200°C led to the formation of white BN powders with high yields (>84 mass%). High-quality BN thin films on silicon were produced by spin-coating solutions of poly(borazylene).⁹⁴⁾ Since the cross-linking reactions occurred at low temperatures,⁹³⁾ however, it was difficult to adapt poly(borazylene) to applications requiring melt-processing. To overcome this drawback, new polymeric precursors to BN ceramics were prepared through reactions of poly(borazylene) with diethylamine (DEA), dipentylamine (DPA), and hexamethyldisilazane (HMD).^{95)–97)} The DPA–poly(borazylene) polymers led to the successful preparation of continuous polymer fibers (30–40 μm in diameter) with a melt-spun technique. Pyrolysis of the polymer fibers under ammonia gave high-quality BN ceramic fibers (30 μm in diameter).⁹⁵⁾

Paine and Narula prepared poly(borazinylamine) gels obtained by a reaction between hexamethyldisilazane and B-trichloroborazine.^{98),99)} Crystalline graphite-like BN (*h*-BN) was obtained by pyrolysis of poly(borazinylamine) gels at 1200°C. The formation of coatings and fibers was also achieved using these gels. Sneddon and co-workers investigated the preparation of B-vinylborazine *via* transition metal-catalyzed addition between borazine and acetylene and its polymerization (by thermal treatment^{100),101)} and free-radical initiation with AIBN¹⁰²⁾). Thermal polymerization of B-vinylborazine at 120°C led to the formation of an insoluble, rubbery polymer possessing a carbon-carbon backbone. A soluble polymer was moreover prepared by thermal polymerization of B-vinylborazine and borazine. In this case, borazine may play a role as a chain terminating reagent to cap the ends of the carbon-carbon backbone in the vinyl polymer. Pyrolysis of these polymers resulted in the formation of ceramic materials with B/N ratios of ~1.0.

2.3 Precursors for non-oxide ceramic-based composites

Ceramic-based composites have been recognized as attractive materials, since they provide a unique combination of characteristics and therefore offer tailoring and improvement of properties.¹⁰³⁾ Walker et al. first reported the preparation of non-oxide ceramic-based composites *via* pyrolytic organic-to-inorganic conversion.¹⁰⁴⁾ The preparation of precursors for

ceramic-based composites has since been extensively investigated, and the following three approaches have been proposed.¹⁰⁵⁾ In the first method, inorganic and/or organometallic precursors have been combined with reactive fillers such as pure, fine-grade metals and ceramics (as a second ceramic phase). This approach can provide improvement of their ceramic yields and suppress the evolution of gaseous species, with a resulting absence of change from the elemental compositions of the precursors to those of the resulting materials, while overcoming the intrinsic problem of shrinkage and porosity formation. In addition, when a metal powder is utilized and dispersed homogeneously, this second ceramic phase is also expected to be highly dispersed.

A second approach to the preparation of precursors for ceramic-based composites has employed the liquid-phase mixing of two (or more than two) single-component precursors. This approach makes it easy to achieve molecular-level homogeneity in the precursors.

A third approach is the preparation of single-source precursors. Single-source precursors typically possess heterogeneous M–N–M' and/or M–C–M' linkages, leading to atomic-level homogeneity of the elemental precursor compositions. Single-source precursors have also been prepared by tailoring single-component polymeric precursors with monomeric or oligomeric species.

As concerns the approach of blending of precursors with powder, the Si–M–C–N–O (M = Al, Ti, Cr, V, Zr, Nb, Mo, Ta, W, Si, B, CrSi₂, MoSi₂, etc.) composites were prepared from Si-based precursors such as poly(carbosilane)s, poly(silazane)s and poly(siloxane)s incorporating reactive filler particles.^{106),107)} Su et al. revealed that combining BN precursors with Ti powders led to the formation of TiB₂ and TiN by pyrolysis at 1450°C.¹⁰⁸⁾

As concerns the approach employing a blended precursor technique,¹⁰⁹⁾ Interrante et al. utilized combinations of an AlN precursor (Et₂AlNH₂)₃ with SiC precursors, vinylic poly(silane), methylhydridopolysilanes, or hydridopolysilane precursors and revealed that their pyrolysis led to the formation of nanocrystalline ceramic-based composites or solid solutions, such as SiC/AlN and Si₃N₄/AlN.^{110)–112)} A higher homogeneity could be achieved by rapid pyrolysis (the so-called “hot drop” approach) than by slow pyrolysis. Si₃N₄/BN composites were also prepared by pyrolysis of blended precursors obtained from vinylic poly(silane)s and poly(borazinylamine).^{112),113)} Moreas et al. prepared the blended precursors from allylhydridopolycarbosilane and poly(borazylene)s, leading to the formation of SiC/BN composites by pyrolysis.¹¹⁴⁾

Single-source precursors have mainly been prepared by ammonolysis or aminolysis of single-source monomeric species possessing heterogeneous linkages. Baldus et al. prepared highly cross-linked borosilicon imides by ammonolysis or aminolysis of Cl₃Si–NH–BCl₂ obtained from Cl₃Si–NH–Si(CH₃)₂ and BCl₃, leading to the formation of amorphous Si–B–N and Si–B–C–N materials by pyrolysis.¹¹⁵⁾ Janik et al. and Paciorek et al. prepared single-source precursors for Al–Si–N–C composites through reactions of (Me₃Si)₃Al·OEt₂ or [(SiMe₃)₂N]₃Al with ammonia in various molar ratios.^{116)–118)} As another approach to preparation of single-source precursors from monomeric species, Löffelholz et al. reported the preparation of precursors for Si–B–N and Si–Al–N composite by dehydrocondensation of two single-component monomers [Si(NHCH₃)₄ and Lewis-base adducts of alane or borane].¹¹⁹⁾ Single-source precursors have also been prepared by the modification of single-component polymeric precursors. Monomeric or oligomeric compounds were

bound to polymeric precursors as pendant side-chain groups *via* dehydrocondensation, deamination, dealkylation or dealcoholization. As a typical example, Hapke and Ziegler prepared Si-Ti-C-N composites by pyrolysis of poly(titanasilazane) obtained *via* deamination of poly(silazane) with $\text{Ti}(\text{NMe}_2)_4$.¹²⁰⁾ The chemical modification of Si-based polymers such as oligosilazanes, poly(silazane)s and poly(carbosilane)s has also been extensively investigated.^{110),121)–134)}

Among various ceramic composites, Si-B-C-N composites derived from polymeric precursors have lately drawn considerable attention because of their significant potentials (stemming from such characteristics as high thermal stability and oxidation resistance, high crystallization temperature and high ceramic yields). Sneddon and co-workers prepared Si-B-C-N precursors through reactions between boron compounds (borazine or the monofunctional boranes) and silazanes [tris(trimethylsilylamino)silane, 1,1,3,3,5,5-hexamethylcyclotrisilazane or poly(silazane)].^{97),135)–137)} Riedel *et al.* revealed that silicoboron carbonitride was obtained by pyrolysis of poly(borosilazane), which was prepared by ammonolysis of $\text{MeSi}(\text{Cl}_2)-\text{CH}_2\text{CH}_2-\text{BR}_2$.¹³⁸⁾ This composite was thermally stable up to 2000°C, suggesting that boron was effective in stabilizing the Si-C-N amorphous materials. Numerous studies on pyrolytic conversion of Si-B-C-N precursors have been summarized in recent reviews.^{80),97),139),140)}

2.4 Investigation of pyrolytic organic-to-inorganic conversion process

Investigation of the pyrolytic process, as well as characterization of the precursors and the resulting materials, is highly important for designing precursors with high ceramic yields and controlling the chemical compositions of the resulting materials. Information concerning pyrolytic behavior can be obtained by using thermogravimetry (TG), especially thermogravimetry associated with continuous mass spectrometry (TG-MS).⁸⁷⁾ The gaseous species evolved during pyrolysis can be analyzed using gas chromatograph-mass spectrometry (GC-MS) and gas chromatograph-infrared (GC-IR) spectroscopy.¹⁴¹⁾ GC-MS can provide direct identification of the evolved gaseous species. The functional groups of the evolved gaseous species can be determined by means of GC-IR. In addition, investigation of the pyrolytic process can be conducted using IR and solid-state magnetic nuclear resonance (NMR) spectroscopy,¹³⁶⁾ which can determine the surrounding environments of elements as well as the functional groups presented in intermediate solids during pyrolysis. The pyrolytic organic-to-inorganic conversion processes, which possibly include the dissociation (bond scission) reactions and cross-linking reactions (e.g., addition reaction, condensation reaction, etc.), can therefore be clarified by the combination of these analyses.

3. AlN precursors

Practical investigations of pyrolytic organic-to-inorganic conversion into AlN were first reported in 1986.^{16),142)} Since then, the preparation of AlN from organometallic/inorganic precursors has been extensively investigated. Main interest was initially focused on the fabrication of AlN (powder, film and fiber). The mechanism of conversion into AlN during pyrolysis and the preparation of precursors for AlN-based composites have recently been pursued. Besides development of AlN precursors, precursors for AlN-based composites have been prepared through the use of oligomeric AlN precursors as building blocks as well as of single-source precursors, as shown by the following typical examples. Interrante *et al.* prepared a viscous Al-B-N precursor from $(\text{EtNH})_3\text{B}$ and

$(\text{Et}_2\text{AlNH}_2)_3$, leading to the formation of homogeneously dispersed AlN particles in a *t*-BN matrix.¹⁴³⁾ They also prepared SiC/AlN, $\text{Si}_3\text{N}_4/\text{AlN}$ composites using $(\text{Et}_2\text{AlNH}_2)_3$.^{109)–111)} Al-Si-N-C^{144),145)} and Ti-Al-N¹⁴⁶⁾ composites were obtained by pyrolysis of precursors prepared by the combination of $(\text{HAl}^i\text{Pr})_n$ with $[\text{Me}(\text{H})\text{SiNH}]_m$ or an aminolysis product of $\text{Ti}(\text{NMe}_2)_4$, respectively.

This section describes the preparation of AlN precursors and their pyrolytic organic-to-inorganic conversion. Here we classify AlN precursors into the following three categories based on the starting compounds:

- 1) AlN precursors from organoaluminum compounds
- 2) AlN precursors from inorganic compounds containing aluminum [such as AlH_3 (and its adduct), LiAlH_4 and aluminum halides]
- 3) Electrochemical preparation of AlN (starting from metallic aluminum)

The CVD process related to organometallic compounds possessing an Al-N backbone is described as well.

3.1 AlN precursors from organoaluminum compounds

Wiberg suggested that products prepared by reactions between Me_3Al and ammonia were converted into AlN upon pyrolysis in 1948.¹⁴⁷⁾ Further development of this trialkylaluminum chemistry was advanced by Interrante and co-workers.^{16),148)–151)} The adducts $\text{R}_3\text{Al}\cdot\text{NH}_3$ from R_3Al and ammonia were thermally converted into R_2AlNH_2 with a loss of alkane (RH).

The thermal decomposition mechanism of the adduct $\text{Me}_3\text{Al}\cdot\text{NH}_3$ in solution are shown in Fig. 3.^{148),149)} The structure of the dialkylaluminum amide R_2AlNH_2 was typically cyclic trimer $(\text{R}_2\text{AlNH}_2)_3$ with a six-membered $(\text{AlN})_3$ ring in a crystalline state, but equilibrium between the trimer and dimer was present in solutions. The trimer/dimer ratio decreased with increase in the sizes of the organic substituents on aluminum, and NH_3 strongly catalyzed this trimer-dimer conversion. (Fig. 4)^{148),150)} Pyrolytic conversion into the alkylaluminum imide polymer $(\text{RAINH})_n$ from $(\text{R}_2\text{AlNH}_2)_3$ was proposed as shown in Fig. 5.¹⁵¹⁾ The heterolytic cleavage of an Al-N bond in an $(\text{AlN})_3$ ring and the subsequent attack of a nitrogen terminal ($=\text{N}:$), which was generated by this

Fig. 3. Proposed mechanism for the thermal decomposition of $\text{Me}_3\text{Al}\cdot\text{NH}_3$.¹⁴⁸⁾

$[(\text{HNCH}_2\text{CH}_2\text{NH})\text{AlR}_2]_2$. Further heat treatment of $\text{RAl}[(\text{HNCH}_2\text{CH}_2\text{NH})\text{AlR}_2]$ gave insoluble solids, which ex-

hibited relatively higher ceramic yields (59–85 mass% under an N₂ atmosphere) than those of untreated products RAl[(HNCH₂CH₂NH)AlR₂]₂ [27–41 mass% under an N₂ atmosphere (1000°C)].

Jensen reported the preparation of AlN precursors *via* thermal polymerization of aluminum imine complexes [RCH=NAl(^{*i*}Bu)₂]₂.^{159,160} These precursors were thermoplastic and soluble in aprotic solvents, and exhibited low oxygen and moisture sensitivity. Pure AlN was obtained by pyrolysis of [CH₃CH=NAl(^{*i*}Bu)₂]₂ with a relatively high ceramic yield. (65 mass%: pyrolyzed at 1000°C under an N₂ atmosphere)

3.2 AlN precursors from inorganic compounds containing aluminum, such as AlH₃ (and its adduct), LiAlH₄ and aluminum halides

An aluminum imido polymer (HAlNH)_n containing no carbon, has been actively pursued because the presence of carbon in precursors for nitrides can lead to the formation of undesirable carbon. Wiberg and May first reported the reaction mechanism between AlH₃ and ammonia with two different Al : N ratios (Al : N = 1 : 1, 1 : 3) in 1955.¹⁶¹ This approach was reinvestigated by Maya (Al : N = 1 :

3)¹⁴² and Ochi et al. (Al : N = 1 : 1, 1 : 3),¹⁶² as shown in **Scheme 2**. Maya prepared an insoluble polymeric precursor [Al(NH₂)_{0.864}(NH)_{1.069}]_n through a reaction between AlH₃·Et₂O and ammonia with the 1 : 3 reaction (Scheme 2A). AlN was obtained by pyrolysis of [Al(NH₂)_{0.864}(NH)_{1.069}]_n at 600°C. A similar result was reported by Ochi et al. By using the reaction system with an Al : N = 1 : 1 ratio, Ochi et al. also prepared a product, which was soluble in THF. (Scheme 2B)¹⁶² This soluble product was slowly polymerized to form a gel (HAlNH)_n. The residue of the gel (HAlNH)_n pyrolyzed at 1100°C in a vacuum contaminated the residual carbon from THF solvent.

Rokensub and Roesky prepared an insoluble amide-imide polymer [Al(NH₂)NH]_n from AlH₃(NMe₂)₂ and ammonia.¹⁶³ Crystalline AlN without impurities (in particular a very low carbon content, lower than 0.3%), was obtained by pyrolysis of this insoluble polymer under an NH₃ atmosphere. The authors suggested that the reason for the absence of impurities is that two alkylamino groups stabilized the aluminum hydride, protecting it against coordination of oxygen-containing impurities such as ether.

AlN precursors were synthesized, furthermore, by employing lithium aluminum hydride (LiAlH₄). Janik et al. investigated the reactions of LiAlH₄ with NH₄X (X = Cl, Br), N₂H₄ and N₂H₄·HCl, leading to the formation of an insoluble polymer:¹⁶⁴

The insoluble polymer obtained from LiAlH₄ and NH₄Br contained 5–10 mass% of diethyl ether solvent. The ceramic yield of this polymer was 85–87 mass% up to 1000°C. Pyrolysis in a vacuum or under an N₂ atmosphere gave a black powder containing crystalline AlN, suggesting the presence of residual carbon originated from diethyl ether.

Coffman et al. obtained a cyclic trimer (H₂AlNMe₂)₃ from LiAlH₄ and dimethylamine hydrochloride (Me₂NH·HCl).¹⁶⁵ The cyclic trimer (H₂AlNMe₂)₃ was pyrolyzed under a nitrogen atmosphere to yield metallic aluminum, whereas its polymerized product was converted into AlN and Al–O–N

Comparison of the 2:1 and 1:1 R₃Al:en Systems

Fig. 6. Suggested pathway for the thermal decomposition of the R₃Al-en adducts.¹⁴⁸

Scheme 2. Reaction schemes for AlH₃–NH₃ systems with (A) AlH₃ : NH₃ = 1 : 3 and (B) AlH₃ : NH₃ = 1 : 1 ratios.¹⁶²

Table 1. Ceramic Yields of Insoluble AlN Precursors from the R₃Al-en Adducts¹⁴⁸

R ₃ Al : en		2 : 1		1 : 1		3 : 2	
		R=Me	R=Et	R=Me	R=Et	R=Me	R=Et
Ceramic yields / mass%	N ₂	70	64	37	45	85	59
	NH ₃	56	55	53	49	75	31

ceramics. (75.5 mass%; pyrolyzed at 1200°C under an N₂ atmosphere)

AlN precursors were also prepared from aluminum halide as an aluminum source. The aluminum amino-imino polymer [Al(NH₂)NH]_n was prepared from AlBr₃ and KNH₂.¹⁴²⁾ AlN was obtained by pyrolysis of [Al(NH₂)NH]_n at 800°C in a vacuum.

A reaction between AlCl₃ and hexamethyldisilazane [(Me₃Si)₂NH] occurred at 60–100°C to form the compounds (Cl₂AlNHSiMe₃)₂ with the simultaneous loss of one mol of Me₃SiCl.^{166),167)} Thermolysis of (Cl₂AlNHSiMe₃)₂ at 170–200°C led to the formation of a polymer (ClAlNH)_n and further pyrolysis of (ClAlNH)_n in a vacuum or under an NH₃ atmosphere gave crystalline AlN.¹⁶⁸⁾ Riedel et al. revealed that the residue pyrolyzed above 1000°C contained a small amount of silicon and carbon and suggested that all the carbon atoms seemed to be bonded to silicon as SiC.¹⁶⁹⁾ Hyodo et al. prepared an AlN precursor through a reaction between AlCl₃ and ethylenediamine. Pyrolysis at 1200°C for 5 h led to formation of crystalline AlN.¹⁷⁰⁾

Poly(alkyliminoalane)s are well-known cage-type compounds possessing an Al–N backbone and have usually been prepared via the following three reaction:¹⁷¹⁾

Table 2 summarizes the aggregation degree of poly(alkyliminoalane)s, and their structures are demonstrated in **Fig. 7**.^{172),173)} A novel cage-type compound, H₆Al₆(NⁱPr)₄[NSi(NMe₂)₃]₂, has recently been prepared by a reaction of H₂NSi(NMe₂)₃ with (HAINⁱPr)₆.¹⁷⁴⁾

Pyrolytic organic-to-inorganic conversions of (HAINⁱPr)_n^{175)–178)} (*n* is mainly 6) and (HAINet)_n^{177),179),180)} (*n* is mainly 8) to AlN have been investigated. **Table 3** summarizes the ceramic yields and chemical compositions of the pyrolyzed residue. The residues pyrolyzed under an Ar atmosphere consisted of crystalline AlN and amorphous carbon. The residues pyrolyzed under an NH₃/N₂ atmosphere, on the contrary, were white solids possessing an extremely small amount of carbon (0.1–0.5 mass%). A possible reaction during pyrolysis under an NH₃/N₂ atmosphere was an amine-exchange reaction as follows:

The loss of aluminum in the pyrolysis of these oligomers under an NH₃/N₂ atmosphere was suppressed, as compared with that under an Ar atmosphere. The lower loss could be ascribed to a cross-linking reaction involving the NH bonds formed by the amine-exchange reaction.

The pyrolytic conversion of these oligomers can be divided into two stages.^{178),180)} In the first stage, the heterolytic cleavage of Al–N bonds led to formation of nitrogen terminals (=N:), which attacked aluminum atoms in another cage (with further attacks following), resulting in cage-opening polymerization. (**Fig. 8**) In the second stage, the alkenes were generated via two possible mechanisms: (A) homolytic cleavage of C–N bonds and subsequent β-elimination of hydrogen radicals; and (B) concerted β-elimination. (**Scheme 3**) The alkanes were also generated by hydrogen abstraction of radicals (as shown in Scheme 4C).

The poly(alkyliminoalane) structures can be modified by using two different kinds of amines. To achieve further increases in ceramic yields, AlN precursors possessing C=C bonds were prepared from LiAlH₄, allylamine hydrochloride (allylNH₂·HCl) and EtNH₂·HCl.¹⁸¹⁾ The ceramic yields of

Table 2. Aggregation Degree of (HAINR)_n and their Structures^{171)–173)}

R	aggregation degree ^a	structure ^b
Me	—	highly cross-linked
Et	8	cage-type
ⁿ Pr	6, 7, 8	cage-type
ⁱ Pr	4, 6	cage-type
ⁿ Bu	6, 7, 8	cage-type
ⁱ Bu	6	cage-type
^s Bu	6	cage-type
^t Bu	4	cage-type
C ₈ H ₁₁	4, 6	cage-type

^a main components. ^b see Fig. 7

Fig. 7. Structure of poly(alkyliminoalane) [(HAINR)_n, *n* = 4, 6, 7, 8].¹⁷²⁾

Table 3. Ceramic Yields, Loss of Aluminum and Chemical Compositions of the Residues Pyrolyzed of (HAINⁱPr)_n and (HAINet)_n^{175)–177),179)}

	(HAIN ⁱ Pr) _n		(HAINet) _n	
	Ar	NH ₃ -N ₂	Ar	NH ₃ -N ₂
ceramic yield / mass%	32	47	50	57
loss of aluminium / mass% ^a	55	14	36	7
elemental analysis				
Al / mass%	45.2 (1)	58.1 (1)	48.5 (1)	61.9 (1)
N / mass%	20.8 (0.89)	28.9 (0.96)	23.5 (0.93)	28.7 (0.89)
O / mass%	5.5 (0.20)	7.5 (0.22)	3.7 (0.13)	5.6 (0.15)
C / mass%	20.6 (1.03)	0.5 (0.02)	17.1 (0.79)	0.1 (0.004)
total / mass%	92.1	95.0	92.8	96.3

^a The loss of aluminum [Loss (Al)] during pyrolysis can be calculated by the following equation, based on the aluminum in the ceramic residue (C_{Al}), the aluminum in precursors (P_{Al}) and the ceramic yield (Y). Loss (Al) [%] = [(P_{Al}Y × C_{Al}) / P_{Al}] × 100

Fig. 8. Proposed mechanism for the thermal polymerization of $[HAINCH(R)CH_3]_n$. ($R = H, CH_3$)¹⁷⁸

(A)

(B)

(C)

Scheme 3. Proposed mechanism for the formation of alkanes and alkenes during pyrolysis of $[HAINCH(R)CH_3]_n$. ($R = H, CH_3$)¹⁷⁸

these precursors were higher than those of $(HAINet)_n$ and $(HAIN^iPr)_n$, a result which could be ascribed to cross-linking involving a hydroalumination reaction and possibly polymerization of allyl groups during pyrolysis. To improve the solubility of insoluble poly(methyliminoalane) $(HAINMe)_n$, poly(methyl iminoalane-co-dimethyl aminoalane)s were prepared.¹⁸² The partial substitution of dimethylamino groups for methylimino groups in $(HAINMe)_n$ resulted in the formation of a soluble polymeric/oligometric precursor. The ceramic yields of these precursors were close to those of $(HAINet)_n$ and $(HAIN^iPr)_n$, and these precursors had possible advantages for achieving desirable rheological properties because of their polymeric structures.

3.3 AlN films and imido compounds possessing an Al-N backbone prepared via the CVD process

For the preparation of AlN films via the CVD process using AlN precursors, Interrante et al. prepared smooth, transparent AlN films, which were deposited on silicon and silica substrates at 400–800°C in a low temperature chemical vapor deposition system using a cyclic trimer $(Me_2AlNH_2)_3$.¹⁸³ They also investigated the reaction mechanism during the CVD process and the influence of temperature on the trimer-dimer equilibrium by identification of the gas-phase product using a molecular beam-mass spectrometer.^{184,185} Timoshkin et al. revealed that the formation of imide compounds (clusters) during the CVD processes was feasible both thermodynamically and kinetically.¹⁷² The authors suggested that the CVD processes are capable of offering a route to the fabrication of nanoparticles with the desired stoichiometries using these

Fig. 9. Proposed in-cell chemistry leading to formation of an AlN precursor.¹⁹²

clusters as single-source precursors.

3.4 Electrochemical preparation of AlN

AlN precursors also have been prepared by electrolysis of metallic aluminum in solutions, which consist of an alkylamine, a solvent and a supporting electrolyte or liquid ammonia. The electrochemical preparation of AlN was first reported by Maya in 1986.¹⁴² An aminoalane $Al(NH_2)_3$ was prepared by anodic oxidation of metallic aluminum in liquid ammonia containing KNH_2 and NH_4Br . Rüssel et al.^{186–190} reported that anodic oxidation in an electrolyte consisting of a primary amine, acetonitrile and tetrabutylammonium bromide gave an intermediate compound $[Al(NHR)_3]$. Further heating of $Al(NHR)_3$ in a vacuum at 150°C led to the formation of a polymeric gel. A crystalline AlN powder was obtained by pyrolysis of this polymeric gel at 1200°C (42 mass%). AlN coatings¹⁸⁸ and oxynitride glass¹⁹⁰ were also prepared from the polymeric gel. Crooks et al., on the other hand, prepared a insoluble polymer $[Al(NH_2)(NH)]_n$ and a by-product $[Al(NH_3)_6Br_3]$ in an electrolyte consisting of ammonium bromide and ammonia (Fig. 9).^{191–193} During pyrolysis of this mixture in NH_3 up to 600°C, NH_3 condensation of the polymer occurred, followed by elimination of NH_3 from both the polymer and $Al(NH_3)_6Br_3$ and/or sublimation of $Al(NH_3)_6Br_3$. After pyrolysis at 1100°C in NH_3 , only an AlN powder was obtained. In addition to the preparation of the AlN powder, this polymer was used for AlN coating onto an Si substrate by an electrophoresis technique. Shimada et al. prepared AlN powders and films by the combined method of electrolysis of metallic Al in isopropylamine and further pyrolysis.¹⁹⁴

4. Conclusions

This review presents an overview of the preparation of precursors possessing an Al-N backbone and their conversion into AlN. Since Al-N bonds are easily formed via a Lewis acid-base reaction, most polymeric compounds possessing the Al-N backbone have highly cross-linked structures and are thus basically insoluble in common organic solvents. Formation of such cross-linked structures can be suppressed by using a primary amine with a bulky substituent, but AlN precursors possessing bulky substituents can lead to high carbon content in resulting materials, which is a large drawback in the preparation of nitrides due to the resulting degradation of their potential. Cyclic and cage-type AlN precursors are usually soluble, on the other hand, but exhibit low ceramic yields. The ceramic yields of these soluble precursors are expected to increase with post-treatment, which can give rise to degradation of their solubility. In order to capitalize on the advantages of the pyrolytic organic-to-inorganic conversion process, the

development of AlN precursors with high solubility, high ceramic yields and low carbon content will be consequently required.

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