

プレセラミック物質を用いた
窒化アルミニウム-窒化チタン固溶体の合成

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研究概要

セラミックス結晶の中には異なる元素を構造中に取り込むものがあり、このような化合物を固溶体と呼ぶ。均質な固溶体を粉末原料から合成するには、一般に高温でのプロセスを必要とする。一方、近年無機高分子（プレセラミック物質）を熱分解することによりセラミックスを合成する手法が確立されている。従ってこの手法を用いれば、出発物質であるプレセラミック物質の段階において分子レベルでの混合が可能となる。

本研究では低温で均質な窒化物セラミックス固溶体を得る手法を提案するため、耐磨耗性等の機械的特性及び耐酸化性に優れる(AI,Ti)Nセラミックスを取り上げ、2種の前駆体を均一に分散させる手法として、前駆体中にAl-N-Ti結合を持たせずに2種の前駆体をブレンドして前駆体を合成した。さらに、その熱分解過程を検討し、熱分解生成物のキャラクタリゼーションを行った。

1) 窒化チタン前駆体と窒化アルミニウム前駆体の可溶性を利用して、blend法により窒化チタン-窒化アルミニウムコンポジット(Ti-Al-N)前駆体を合成し、その前駆体の熱分解過程について検討した。TiN前駆体は $Ti(NMe_2)_4$ と $MeHNCH_2CH_2NHMe$ のアミン交換反応により合成したTi-N結合を有する可溶性オリゴマーであった。AlN前駆体は水素化リチウムアルミニウムとイソプロピルアミンとの反応により合成したAl-N結合を有する可溶性カゴ型化合物 $(HAlNPr^i)_m$ であった。Ti-Al-N前駆体中のTi:Al比が約1:2、2:1及び5:1になるようにTiN前駆体とAlN前駆体をベンゼンに溶解し、室温で攪拌後ベンゼンを除去するこ

とでTi-Al-N前駆体を得た。IR及び ^1H NMR分析により、Ti-Al-N前駆体にはTi-N-Al結合がほとんど存在していないと考えられた。Ti:Al=2:1の前駆体のTG曲線(He雰囲気)では前駆体成分の揮発を示唆するような急激な重量減少は観測されなかった。これはTi-Al-N前駆体が熱分解中に効率よく重合したためだと考えられた。また、前駆体の熱分解による重量減少が主に室温約500℃付近で起こり、約500℃~900℃温度範囲では僅か3%の重量減少しか観測されなかった。いずれのTi-Al-N前駆体でも $\text{NH}_3\text{-N}_2$ 雰囲気下で熱分解したところ、褐色固体が得られた。前駆体の収率は全て約30%で、理論収率と近い値が得られた。さらに、焼成物のTi:Al比もTi-Al-N前駆体のTi:Al比とほぼ一致していた。Ti:Al=5:1前駆体から得られた焼成物のXRDパターンでは岩塩型化合物の回折線のみが観測された。

Ti:Al=2:1前駆体を熱分解したところ、岩塩型化合物に加え2H-ウルツ鉱型AlNが結晶相として得られた。また、Ti:Al=1:2前駆体を熱分解したところ、2H-ウルツ鉱型AlNと岩塩型化合物からなるセラミックコンポジットが生成した。焼成物の格子定数及び組成分析から、これらの岩塩型化合物はTi(N,C,O)固溶体であると考えられ、格子定数から判断するとTi-Al-N系固溶体生成の可能性は低いものと考えられた。SEM観察により、いずれの焼成物も主に20-40nmの直径の粒子から構成されていることが分かった。

2) TiN前駆体単独の熱分解過程を検討するため、 $\text{Ti}(\text{NMe}_2)_4$ と各種ジアミン

($\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, $\text{Me}(\text{H})\text{NCH}_2\text{CH}_2\text{N}(\text{H})\text{Me}$, $\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NH}$)とのアミン交換反応

($\text{Ti}(\text{NMe}_2)_4$:ジアミン=2:1)によりTiN前駆体を合成した。 $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ と

$\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NH}$ から得られた前駆体は不溶性固体であり、非常に架橋した構造と推定された。一方、 $\text{Me}(\text{H})\text{NCH}_2\text{CH}_2\text{N}(\text{H})\text{Me}$ を用いた場合は、可溶性の油状生成物が得られた。油状生成物の ^{13}C NMRでは多数のシグナルが観測されたことから、 $\text{Me}(\text{H})\text{NCH}_2\text{CH}_2\text{N}(\text{H})\text{Me}$ を用いることによりある程度の構造制御に成功したものの、秩序を持った構造は得られなかったことがわかる。TGにより熱分解過程を検討したところ、前駆体の構造は大きく異なるものの、収率に非常に大きな差はなかった。また、3つの前駆体のTG曲線の形状は類似していた。従って、 $\text{Me}(\text{H})\text{NCH}_2\text{CH}_2\text{N}(\text{H})\text{Me}$ を用いた前駆体の熱分解初期段階において、重合反応が効率的に進行したものと推定された。

3) AlN前駆体の熱分解過程を検討するため、 $(\text{HAlNPr}^i)_m$ の熱分解過程を検討した。不活性雰囲気下での質量減少は240℃から始まり、320℃までは $(\text{HAlNPr}^i)_6$ の揮発を伴っていた。この温度領域で重合反応が進行しており、これはAl-N結合の切断とN上に生成する孤立電子対が他のケージを攻撃することによると考えられた。高温では飽和並びに不飽和炭化水素が生成しており、ラジカル反応が進行していたものと推定された。

研究発表

A) 本研究に関する論文

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B) 本研究に関連するもので、当該期間に発表した論文

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Pyrolytic Conversion of Precursors Prepared in $\text{Ti}(\text{NMe}_2)_4$ -Diamine Systems

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Precursors possessing Ti–N bonds were prepared by the reactions between $\text{Ti}(\text{NMe}_2)_4$ and each of three diamines $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, $\text{Me}(\text{H})\text{NCH}_2\text{CH}_2\text{N}(\text{H})\text{Me}$, $\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NH}$ ($\text{Ti}(\text{NMe}_2)_4$:diamine = 1:2), and were converted into ceramics by pyrolysis. The reactions with $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ and $\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NH}$ led to the formation of insoluble solids, whereas a soluble oil was obtained by the reaction with $\text{Me}(\text{H})\text{NCH}_2\text{CH}_2\text{N}(\text{H})\text{Me}$. The pyrolyses under argon gave carbon-rich $\text{Ti}(\text{N,C,O})$ phases, but those under NH_3 – N_2 resulted in the formation of $\text{Ti}(\text{N,C,O})$ phases with higher nitrogen contents. Despite the difference in precursor structures the pyrolysis behavior of three precursors under argon was rather similar, suggesting that the precursor obtained from $\text{Me}(\text{H})\text{NCH}_2\text{CH}_2\text{N}(\text{H})\text{Me}$ was effectively cross-linked during pyrolysis. © 1998 John Wiley & Sons, Ltd.

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INTRODUCTION

Titanium nitride (TiN) exhibits excellent properties, such as high hardness, high melting point, corrosion resistance and high electrical conductivity.¹ It has been used for various applications, including wear-resistant coatings and solar control

coatings for windows.^{2–4} Also, TiN has attracted increasing attention because of its use as diffusion barriers in integrated circuits.^{5,6} Traditional synthetic procedures for TiN are the nitridation of titanium metal and carbothermal reduction of TiO_2 under nitrogen, but recent studies on TiN synthesis have focused on chemical vapor deposition (CVD) processes for film preparation.¹ TiN films have been prepared mainly in TiCl_4 – NH_3 ⁷ and $\text{Ti}(\text{NR}_2)_4$ – NH_3 systems,^{8,9} and a variety of compounds possessing Ti–N bonds¹⁰ other than $\text{Ti}(\text{NR}_2)_4$ can also be used as precursors.

Another synthetic route to TiN is the pyrolysis of inorganic and organometallic compounds possessing Ti–N bonds. This chemical route is capable of TiN-film preparation, if precursors are soluble or spinnable.¹¹ Insoluble polymeric precursors were prepared by the ammonolysis of $\text{Ti}(\text{NMe}_2)_4$, and were converted into TiN powders via pyrolysis.^{12,13} Aminolysis of $\text{Ti}(\text{NMe}_2)_4$ led to the formation of soluble polymers which appeared to have ladder-like structures,^{14–16} and such precursors were converted into TiN powder and film via pyrolysis.^{15,16} TiN precursors were also prepared by the reactions between $\text{Ti}(\text{NMe}_2)_4$ and diamines $(\text{R}(\text{H})\text{NCH}_2\text{CH}_2\text{N}(\text{H})\text{R})$, $\text{R} = \text{H}, \text{Me}, \text{Et}$.¹⁶ If $\text{R} = \text{H}$, the product was an insoluble polymer, whereas the use of diamines with $\text{R} = \text{Me}$ and Et resulted in the formation of soluble precursors. TiN precursors can also be prepared electrochemically using titanium metal as a starting material.^{17,18}

This paper describes the preparation of TiN via reactions between $\text{Ti}(\text{NMe}_2)_4$ and three different kinds of diamines [$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, $\text{Me}(\text{H})\text{NCH}_2\text{CH}_2\text{N}(\text{H})\text{Me}$ and piperazine ($\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NH}$)]. Precursors were characterized spectroscopically, and were pyrolyzed under argon and NH_3 – N_2 atmospheres. Emphasis is placed upon the pyrolyzed products, which were characterized by compositional analysis and X-ray powder diffraction (XRD).

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EXPERIMENTAL

All the procedures were performed under a protective nitrogen atmosphere using a standard Schlenk technique or a globe box filled with nitrogen. Benzene and diamines (except piperazine) were freshly distilled using appropriate drying agents before use. Piperazine was dried under reduced pressure before use. Tetrakis(dimethylamino)titanium, $\text{Ti}(\text{NMe}_2)_4$, was used as received.

Precursors possessing Ti–N bonds were prepared on the basis of a previous report¹⁶ by the reactions of $\text{Ti}(\text{NMe}_2)_4$ with diamines (DAs) with $\text{Ti}(\text{NMe}_2)_4$:DA = 1:2. For ethylenediamine and its dimethyl derivative (*N,N'*-dimethylethylenediamine), an ideal reaction can be expressed by Eqn [1]:



where R = H or Me. About 4 g of liquid $\text{Ti}(\text{NMe}_2)_4$ was dissolved in 50 ml of benzene in a 200-ml three-necked flask. DA dissolved in 20 ml of benzene was dropped slowly into a $\text{Ti}(\text{NMe}_2)_4$ solution at room temperature with stirring. Then the resulting solution was gradually heated, and finally refluxed at 78 °C for 20 h.

When $\text{Ti}(\text{NMe}_2)_4$ was reacted with $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ and $\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NH}$, insoluble yellow precipitates were collected after the removal of the solvent and the volatile components under reduced pressure. By reaction between $\text{Ti}(\text{NMe}_2)_4$ and $\text{Me}(\text{H})\text{NCH}_2\text{CH}_2\text{N}(\text{H})\text{Me}$, however, a viscous black solution was obtained with the formation of a small amount of an insoluble precipitate, which was removed by filtration. The removal of the solvent gave a black oily product.

The precursors were characterized by IR spectroscopy (Perkin-Elmer FTIR-1640), and ^1H NMR (270 MHz, C_6D_6) spectroscopy was also applied for a soluble precursor. Thermogravimetric (TG) analyses of the precursors were carried out with a Shimadzu TGA-50 thermobalance at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under a helium flow.

The precursors were pyrolyzed in a tube furnace. About 0.5 g of precursor was placed in an Al_2O_3 boat, which was then introduced into an Al_2O_3 tube filled with argon or NH_3 . For pyrolysis under argon, the precursor was heated at 600, 1000, and 1500 °C for 2 h with a flow rate of 100 ml min^{-1} . For pyrolysis under NH_3 - N_2 , the precursor was first heated at 600 °C under NH_3 (30 mL min^{-1}), and cooled to room temperature. Then, the product

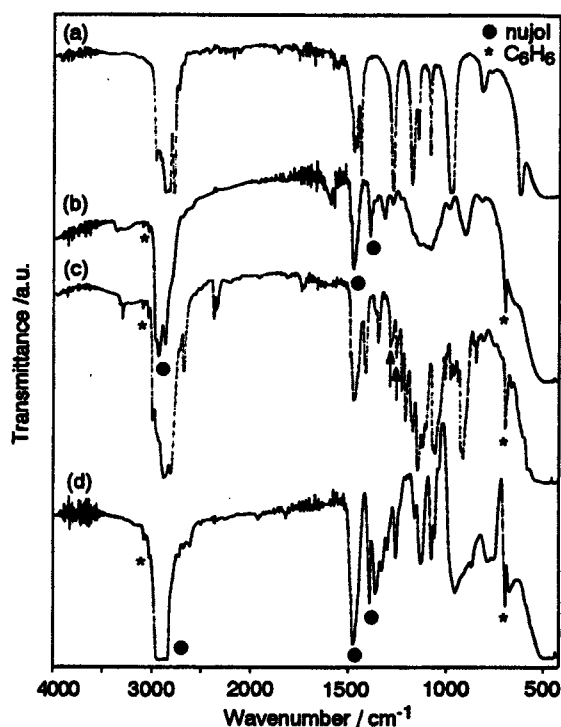


Figure 1 IR spectra of (a) $\text{Ti}(\text{NMe}_2)_4$, and of the reaction products of $\text{Ti}(\text{NMe}_2)_4$ with (b) $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (PreH), (c) $\text{Me}(\text{H})\text{NCH}_2\text{CH}_2\text{N}(\text{H})\text{Me}$ (PreMe) and (d) $\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NH}$ (PreP); the spectra (a) and (c) were obtained in the neat state, and the spectra (b) and (d) were obtained in Nujol.

pyrolyzed under NH_3 was heated again at 1350 °C for 8 h under N_2 (100 ml min^{-1}). The heating and cooling rate was $5\text{ }^\circ\text{C min}^{-1}$.

The pyrolyzed residues were analyzed by XRD ($\text{CuK}\alpha$ Mac Science MXP³ diffractometer). The lattice parameters of the pyrolyzed residues were calculated by the non linear least-squares method. The amounts of nitrogen, oxygen and carbon in the pyrolyzed residues were measured with LECO TC-436 and CS-444LS instruments. The pyrolyzed residues were dissolved by treatment with aqua regia in a Teflon decomposition vessel at 130 °C for 24 h, and the amounts of titanium were determined by inductively coupled plasma emission spectroscopy (ICP; Nippon Jarrell Ash ICAP-575 II).

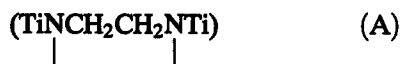
RESULTS AND DISCUSSION

The precursors prepared with $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ and piperazine [$\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NH}$] (hereafter PreH

and PreP, respectively) were obtained as insoluble solids, implying that they possess cross-linked structures. However, the average molecular weight should be much lower for the liquid precursor obtained from $\text{Ti}(\text{NMe}_2)_4$ and $\text{Me}(\text{H})\text{NCH}_2\text{CH}_2\text{N}(\text{H})\text{Me}$ (PreMe).

The IR spectra of the precursors, as well as that of $\text{Ti}(\text{NMe}_2)_4$, are shown in Fig. 1. After the reactions with each of the DAs, the $\nu(\text{Ti-N})$ band intensities¹⁹ of $\text{Ti}(\text{NMe}_2)_4$ (at 588 cm^{-1}) decrease dramatically, and new bands appear at $558\text{--}650\text{ cm}^{-1}$. Bradley and Gitlitz studied the IR spectra of $\text{Ti}(\text{NMe}_2)_{4-x}(\text{N}^n\text{Pr}_2)_x$, and reported that mixed species showed two $\nu(\text{Ti-N})$ bands near the position for Ti-NMe_2 and that for $\text{Ti-N}^n\text{Pr}_2$.¹⁹ Since only one $\nu(\text{Ti-N})$ band is observed for each of PreH and PreP, we assume that most of the NMe_2 groups are lost during the syntheses of PreH and PreP. This is further supported by the fact that the $\delta(\text{CH}_3)$ band¹⁹ of the NMe_2 groups ($\sim 1250\text{ cm}^{-1}$) is hardly detected in the IR spectra of these two precursors. In the IR spectrum of PreMe, a few bands assignable to $\nu(\text{Ti-N})$ are observed at 558 , 584 , and 650 cm^{-1} . In addition, bands attributable to the $\delta(\text{CH}_3)$ mode are observed at 1242 and 1274 cm^{-1} (as shown by arrows). Thus, PreMe appears to contain a small proportion of unreacted NMe_2 groups.

In the IR spectrum of PreH, weak bands due to $\nu(\text{N-H})$ and $\delta(\text{NH}_2)$ modes are observed. The number of H atoms attached to N (i.e. the number of NH) is twice the number of the NMe_2 groups in the $\text{Ti}(\text{NMe}_2)_4\text{-H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ system (in the other two systems, the number of NH is equal to that of the NMe_2 groups). Hence, the NH groups should be present even after the complete removal of the NMe_2 groups (which can be achieved with the equivalent number of NH groups; see Eqn [1] in the Experimental section). Based on the loss of most of the NMe_2 groups and the nominal $\text{NH}_2\text{:NMe}_2$ ratio (1:1), the presence of $\delta(\text{NH}_2)$ bands indicates that some nitrogen atoms should be present as imido bridges (Ti-N-Ti), which partly accounts for cross-linked structure formation. Imido-bridge structures have also been proposed for the precursors prepared between $\text{Ti}(\text{NR}_2)_4$ and primary amines, RNH_2 .¹⁴⁻¹⁷ It should also be expected that some of the $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ acts as a chelating agent¹⁶ and forms bidentate ligands bridging two titanium atoms (A).



The IR spectrum of PreP shows the absence of

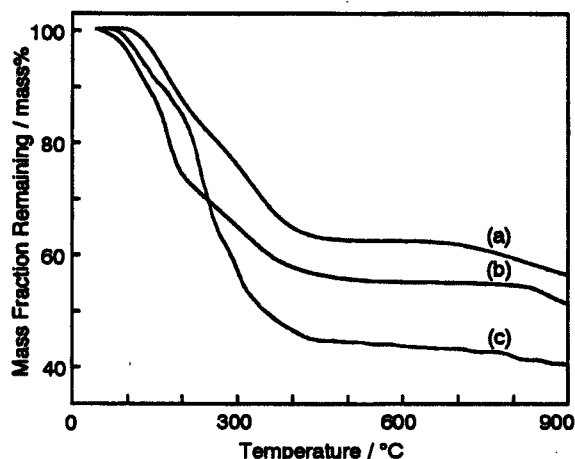


Figure 2 TG curves of the reaction products of $\text{Ti}(\text{NMe}_2)_4$ with (a) $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (PreH), (b) $\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NH}$ (PreP) and (c) $\text{Me}(\text{H})\text{NCH}_2\text{CH}_2\text{N}(\text{H})\text{Me}$ (PreMe) under He at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

NH groups, which is consistent with the loss of most of the NMe_2 groups. Since piperazine cannot act as a chelating reagent, piperazine should bridge two Ti atoms to form a cross-linked structure.

Oily PreMe is the only product that can be analyzed with $^1\text{H NMR}$. Many sharp signals were observed at 2–5 ppm (not shown), indicating the presence of various environments for the methyl groups. It should also be noted that no broad signals were observed, suggesting that the product is not highly polymeric. Seyferth and Mignani prepared TiN precursors in the same and very similar systems, and observed the formation of monomeric $[\text{Ti}(\text{RNCH}_2\text{CH}_2\text{NR})_2]$ with oligomers.¹⁶ Therefore we assume that PreMe consists of mixtures of monomeric and oligomeric species. The IR spectrum of PreMe shows the presence of a $\nu(\text{N-H})$ band at 3290 cm^{-1} , consistent with the presence of remaining NMe_2 groups.

The pyrolysis behavior of these three precursors was investigated by TG analyses (Fig. 2). All the precursors showed a two-step mass loss (room temperature to $\sim 500\text{ }^\circ\text{C}$ and $\sim 700\text{ }^\circ\text{C}$ upwards). The ceramic yield of PreMe is the lowest based on the TG results (40%, up to $900\text{ }^\circ\text{C}$), and the other two precursors show quite high ceramic yields of over 50% (the ceramic yield of PreH is higher than that of PreP).

When the precursors were pyrolyzed at $1500\text{ }^\circ\text{C}$ under argon, black residues were obtained. The ceramic yields of the precursors (Table 1) are between 20 and 30%, and these values are much

Table 1 Ceramic yields and characteristics of the pyrolyzed products for pyrolysis under Ar at 1500 °C for 2 h

	PreH	Precursor PreMe	PreP
Ceramic yield (mass%)	26	21	27
Loss of Ti (mass%)	33	44	31
Elemental analysis (mass%) ^a			
Ti	76.0 (1)	67.5 (1)	52.7 (1)
N	2.1 (0.09)	4.2 (0.21)	5.4 (0.35)
C	18.7 (0.98)	25.2 (1.49)	34.7 (2.63)
O	1.5 (0.06)	1.6 (0.07)	7.0 (0.40)
Total (mass%)	98.3	98.5	99.8
Lattice parameter (nm)	0.4321	0.4314	0.4285

^a Molar ratio in parentheses.

lower than the corresponding values obtained by TG analysis up to 900 °C. The ratios of Ti lost during pyrolysis are estimated from the amounts of Ti in the precursors and those in the 1500 °C pyrolysis residues (Table 1). PreMe shows the lowest ceramic yield and the highest Ti loss (consistent with TG results), but these values (yield and Ti loss) are not very different from those of the other precursors. Based on the difference in the precursor structures, PreMe, which appears to consist of monomeric and oligomeric species, is expected to show a much lower yield than those of the other cross-linked precursors. In addition, as shown in Fig. 2 the TG curve profile of PreMe is similar to those of the other two precursors, and no sharp mass loss (indicative of volatilization) is observed. Thus, we assume that the pyrolysis of PreMe leads to the formation of a cross-linked structure without considerable volatilization, and is finally converted into ceramic residue with a reasonable yield. Thus, PreMe is the most attractive precursor among the three examined because of its solubility.

The pyrolyses of the precursors under argon at 1500 °C resulted in the formation of well-crystallized single-phase rock-salt-type products. The XRD pattern of the product from PreH is shown in Figure 3 (c) and the lattice parameters of all the products are listed in Table 1. TiN is known to possess a rock-salt-type structure, and can form solid solutions with TiC and TiO.^{20–23} The observed lattice parameters are close to that of TiC (0.4327 nm)²⁰ rather than those of TiN (0.4240 nm)²⁰ and TiO (0.4178 nm).²⁴ The compositions of the products (Table 1) also reveal that the N:Ti ratios are very low [0.10:1 (PreH), 0.21:1 (PreMe) and 0.35:1 (PreP)], and considerable amounts of carbon are present. The presence of

carbon remaining in the residues obtained by pyrolysis under argon has also been reported previously.^{16,17}

It should be noted that the initial N:Ti ratios in the precursors should be 4:1 for PreMe and PreP [since the NMe₂ groups in Ti(NMe₂)₄ are replaced by the same number of -NMe (PreMe) or =N (PreP) groups, the N:Ti ratio should be maintained during the precursor synthesis] or equal to or above 2:1 for PreH [the N:Ti ratio ranges from 4:1 (the value for the 1:1 reaction) down to 2:1 (assuming that one NH₂ group reacts with two NMe₂ groups to form each imido bridge)]. Thus, it should be concluded that large amounts of nitrogen are lost during pyrolysis. In order to obtain further information, PreH was pyrolyzed at lower temperatures (600 and 1000 °C). After the pyrolysis at

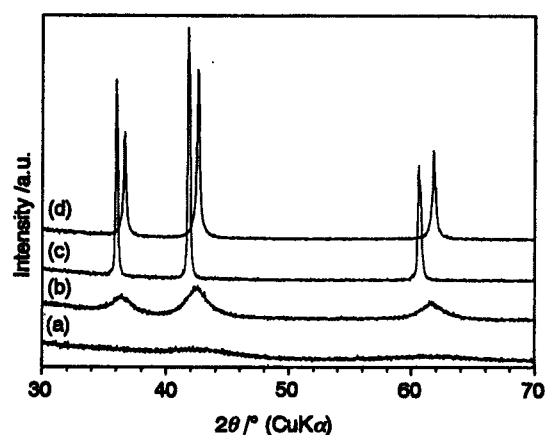


Figure 3 XRD patterns of the reaction product of Ti(NMe₂)₄ with H₂NCH₂CH₂NH₂ (PreH) pyrolyzed under argon at (a) 600 °C, (b) 1000 °C, (c) 1500 °C; and (d) pyrolyzed under NH₃-N₂ (for conditions see the Experimental section).

Table 2 Compositional characteristics of the reaction product of $\text{Ti}(\text{NMe}_2)_4$ with $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (PreH) pyrolyzed under argon

Pyrolysis temp.(°C)	Elemental analysis (mass%)				Total	Empirical formula
	Ti	N	C	O		
600	50.7	13.0	20.0	13.7	97.4	$\text{TiN}_{0.88}\text{C}_{1.58}\text{O}_{0.81}$
1000	51.4	8.5	20.9	9.9	90.7	$\text{TiN}_{0.57}\text{C}_{1.63}\text{O}_{0.58}$

Table 3 Ceramic yields and characteristics of the products of pyrolysis under $\text{NH}_3\text{-N}_2$ (at 600 °C for 2 h under NH_3 and subsequently at 1350 °C for 8 h under N_2)

	PreH	Precursor PreMe	PreP
Ceramic yield (mass%)	41	25	19
Loss of Ti (mass%)	1.0	27	34
Elemental analysis (mass%) ^a			
Ti	71.2 (1)	74.3 (1)	71.6 (1)
N	16.0 (0.77)	19.2 (0.89)	14.5 (0.69)
C	3.1 (0.17)	1.4 (0.08)	9.6 (0.54)
O	4.7 (0.20)	4.4 (0.18)	4.3 (0.18)
Total	95.0	99.3	100
Lattice parameter (nm)	0.4244	0.4243	0.4250

^a Molar ratio in parentheses.

600 °C, the product was amorphous, as shown by its XRD pattern [Fig. 3 curve (a)]. Since the N:Ti ratio is 0.88:1 (Table 2), a considerable amount of nitrogen was lost during the pyrolysis up to 600 °C. After the pyrolysis at 1000 °C, a poorly crystalline rock-salt-type phase was detected by XRD [Fig. 3 curve (b)]. A lower N:Ti ratio (0.57:1) indicated a further loss of nitrogen at 600–1000 °C (Table 2); this may be ascribed to the loss of nitrogen during the crystallization from an amorphous phase. The much lower N:Ti ratio for the 1500 °C pyrolysis product (0.10:1) shows that additional loss of nitrogen occurred at high temperature, consistent with the lower ceramic yield for the 1500 °C pyrolysis.

The pyrolyses under $\text{NH}_3\text{-N}_2$ resulted in the formation of light-brown solids. The XRD pattern of the pyrolyzed residue obtained from PreH is shown in Fig. 3 curve (d); all the pyrolyzed residues were single-phase $\text{Ti}(\text{N,C,O})$. All the lattice parameters of the products listed in Table 3 are close to that of TiN (0.4240 nm).²⁰ The yields range from 41% (PreH) to 19% (PreP), and are comparable with the reported value for the precursor prepared in the $\text{Ti}(\text{NMe}_2)_4\text{-Me}(\text{H})\text{NCH}_2\text{CH}_2\text{N}(\text{H})\text{Me}$ system in the same way.¹⁶ The compositional analysis reveals that N:Ti ratios range between 0.69:1 and 0.89:1 (Table 3). It is also revealed that the carbon contents are much smaller than those of the

corresponding products pyrolyzed under argon, consistently with the previous studies on TiN precursor pyrolysis.^{16,17} For the AlN precursor prepared in an $\text{AlR}_3\text{-H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ system, the amine-exchange reaction during pyrolysis under an NH_3 atmosphere was reported; NH_3 reacted with $\text{EtAlNCH}_2\text{CH}_2\text{NAlEt}$ to release $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$.²⁵ Thus, it appears that amine-exchange reactions also occur in the present systems, and the removal of DAs leads to the decrease in the carbon contents in the pyrolyzed products. The amount of Ti lost during the pyrolysis is very low for PreH (Table 3), which might be ascribed to the effective amine-exchange reaction and subsequent conversion into a highly cross-linked structure at lower temperature.

CONCLUSIONS

Precursors possessing Ti–N bonds have been prepared from $\text{Ti}(\text{NMe}_2)_4\text{-DA}$ (diamine) systems using three different kinds of DAs [$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, $\text{Me}(\text{H})\text{NCH}_2\text{CH}_2\text{N}(\text{H})\text{Me}$, $\text{HN}(\text{CH}_2\text{CH}_2)_2\text{NH}$; $\text{Ti}(\text{NMe}_2)_4\text{:DA} = 1\text{:}2$], and their pyrolytic conversion processes and resultant ceramic residues were studied. The pyrolyses of these three precursors at 1500 °C under argon led to the

formation of carbon-rich products with ceramic yields of 20–30%. For all the precursors, the only crystalline phase was Ti(N,C,O), whose lattice parameters were close to that of TiC. Although the structure of the oily precursor using Me(H)NCH₂CH₂N(H)Me was very different from those of the other two cross-linked precursors, the pyrolysis results (TG curve, ceramic yield from 1500 °C pyrolysis and the amount of Ti lost during pyrolysis up to 1500 °C) were quite comparable with the corresponding values of the other two precursors; the precursor obtained from Me(H)NCH₂CH₂N(H)Me appeared to be converted into a cross-linked structure during pyrolysis. Pyrolysis under NH₃–N₂ effectively reduced carbon contents, and led to the formation of nitrogen-rich single-phase Ti(N,C,O).

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Pyrolytic Conversion of the Cage-Type Precursors into AlN

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Abstract

Aluminum nitride (AlN) was prepared via pyrolysis of cage-type poly(alkyliminoalane) [(HAlNR)_n] (R=Et, ⁱPr) under Ar or NH₃-N₂ atmospheres. Both (HAlNⁱPr)_n and (HAlNEt)_m were converted into ceramic residues with relatively high ceramic yields. The ceramic residues obtained via pyrolysis of the precursors under an Ar atmosphere contained considerable amounts of carbon, while most of carbon was removed during the pyrolysis under an NH₃-N₂ atmosphere. The only obtained crystalline phase was AlN, whose lattice parameters showed that isostructural Al₂OC was rarely dissolved in the lattices of the 2H wurtzite-type structures.

Introduction

Aluminum nitride (AlN) is one of the important nitride materials because of its high thermal conductivity [1]. AlN has been prepared mainly by the nitridation of Al metal and carbothermal reduction of alumina [2,3]. Chemical vapor deposition (CVD) processes have also been developed for AlN thin films [4].

Recently, the pyrolytic route to non-oxide ceramics attracts increasing attention, since this route can be used for various applications including fiber preparation and coating formation [5]. There have been various reports on the preparation of silicon carbide (SiC), silicon nitride (Si₃N₄), and boron nitride (BN) [5-8]. AlN can also be prepared by the pyrolytic route, and various systems have been reported [5,9,10]. A R₃Al-NH₃ system was studied extensively, and it was reported that the initially formed adduct R₃Al:NH₃ was converted into AlN via the formation of an intermediate (R₂AlNH₂)₃ [11-15]. A R₃Al-H₂NCH₂CH₂NH₂ (en) system was also examined with various R₃Al:en ratios, and the structures of the precursors and their pyrolytic conversion were investigated [15-18]. A AlH₃-NH₃ system is also capable for precursor synthesis, and different kinds of precursors were prepared by varying the AlH₃:NH₃ ratio [19-22]. AlN precursors can also be prepared electrochemically [20,23-27].

For AlN precursors, it is very difficult to prepare soluble polymers showing reasonable yields; thus most of AlN precursors were basically insoluble polymers, if they exhibit reasonable yields [20-22,26,27]. Some soluble oligomeric precursors can be converted into the precursors showing relatively high ceramic yields via their thermolysis at relatively low temperatures, but their solubility decreased simultaneously [16-18].

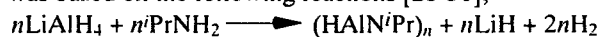
It is well-known that some compounds possessing Al-N bonds have cage-type structures. Such compounds are known as poly(alkyliminoalane) [(HAlNR)_n], and their preparation and structures have been well-established [28-32]. Cage-type compounds can be formed if R is bulky enough (such as ethyl (CH₃CH₂, Et) groups and isopropyl ((CH₃)₂CH, ⁱPr) groups), and the types of the cages depend on the bulkiness of the R groups [28-32]. On the contrary, if the bulkiness of R group is not sufficient (R=CH₃, Me), (HAlNMe)_n becomes a cross-linked polymer [33]. These compounds appear to be suitable for AlN precursors, and we have already reported preliminary pyrolysis results

of one of cage-type poly(alkyliminoalane), poly(isopropyliminoalane), under an Ar atmosphere [34].

This report describes the preparation of AlN from cage-type poly(alkyliminoalane), $(\text{HAlNR})_n$ ($R=\text{Et}, i\text{Pr}$). The precursors were converted into ceramic residues via pyrolysis under a reactive $\text{NH}_3\text{-N}_2$ atmosphere as well as an inert Ar atmosphere. Resultant ceramic residues were characterized by X-ray powder diffraction analysis (XRD) and elemental analysis. The morphology of the ceramic residues was studied by scanning electron microscopy (SEM).

Experimental

All the procedures for precursor synthesis and handling were performed under protective nitrogen atmosphere using the standard Schlenk technique [35] or a glove box filled with nitrogen. Preparation of the precursors was based on the following reactions [28-30];



The reaction between LiAlH_4 and $i\text{PrNH}_2$ at reflux gave a white solid after the removal of LiH and the solvent (heptane): $^1\text{H NMR}(\text{C}_6\text{D}_6)$ δ 1.40 (d, CH_3), 3.61 (sept, CH), 4.6 (br, AlH); $^{27}\text{Al NMR}$ δ 131 (HAlN_3); MS $m/e=495$ ($[\text{M}-15]^+$, 100 %); IR ($\nu_{(\text{Al-H})}$) 1854 cm^{-1} . The reaction between LiAlH_4 and $\text{EtNH}_2\text{-HCl}$ at reflux also gave a white solid after the removal of LiCl and the solvent (benzene): $^1\text{H NMR}(\text{C}_6\text{D}_6)$ δ 1.27 (tr, CH_3), 1.37 (tr, CH_3), 3.10 (q, CH_2), 3.22 (q, CH_2), 4.4 (br, AlH); $^{27}\text{Al NMR}$ δ 133 (HAlN_3); MS $m/e=568$ (M^+ , 28 %), 567 ($[\text{M}-1]^+$, 100 %), 566 ($[\text{M}-2]^+$, 78 %); IR ($\nu_{(\text{Al-H})}$) 1867 cm^{-1} , 1823 cm^{-1} . These results indicate that the main species were $(\text{HAlN}^i\text{Pr})_6$ and $(\text{HAlNEt})_8$ [28-31]. In $^1\text{H NMR}$ spectra of both $(\text{HAlN}^i\text{Pr})_n$ and $(\text{HAlNEt})_m$, additional weak peaks due to Et and $i\text{Pr}$ groups were observed, indicating the presence of other oligomeric species, though their amounts should be small. It should also be noted these two precursors were soluble in common organic solvents.

About 1 g of a precursor on a BN boat was placed in an Al_2O_3 tube and was pyrolyzed. $(\text{HAlN}^i\text{Pr})_n$ was converted via two-step pyrolysis under Ar; it was initially pyrolyzed at $1000\text{ }^\circ\text{C}$ for 2 h and subsequently heated at $1600\text{ }^\circ\text{C}$. For the pyrolysis of $(\text{HAlNEt})_m$ under Ar, the precursor was heated at $1600\text{ }^\circ\text{C}$ for 2 h. The Ar flow rate was 100 mL/min for these pyrolyses. For the pyrolysis under $\text{NH}_3\text{-N}_2$, the precursor was heated at $600\text{ }^\circ\text{C}$ for 2 h under an NH_3 flow (30 mL/min), and cooled to room temperature. Then the product pyrolyzed under NH_3 was heated again at $1350\text{ }^\circ\text{C}$ for 8 h under an N_2 flow (30 mL/min). The heating and cooling rate was $5\text{ }^\circ\text{C}/\text{min}$ in all the pyrolysis schedules.

The ceramic residues were characterized by XRD (Mac Science, MXP³) using monochromated $\text{CuK}\alpha$ radiation. The amount of aluminum was determined using inductively-coupled plasma emission spectroscopy (ICP; Nippon Jarrell Ash, ICAP-575 II). Typically, about 20 mg of a ceramic residue was dispersed in 30 ml of 12 mol/L HCl, and the mixture was heated at $120\text{ }^\circ\text{C}$ for 4 h using a teflon decomposition vessel [36]. The amounts of carbon, nitrogen and oxygen were determined by using Horiba EMIA-520SP and EMGA-2800 instruments. The morphology of the ceramic residues was studied using Hitachi S-2150 or JEOL JXA-8600 instruments.

Results and Discussion

When $(\text{HAlN}^i\text{Pr})_n$ was pyrolyzed under the Ar atmosphere, a black residue was obtained. (the ceramic yield; 32 %) On the contrary, its pyrolysis under the $\text{NH}_3\text{-N}_2$ atmosphere resulted in the formation of a white residue with a higher ceramic yield of 47 %. The pyrolysis of $(\text{HAlNEt})_m$ under the Ar atmosphere led to the formation of a black solid with a ceramic yield of 50 %. The pyrolysis under the $\text{NH}_3\text{-N}_2$ atmosphere led to the conversion into ceramic residue with a relatively high ceramic yield (57 %). For both the precursors, the ceramic yields for the pyrolysis under the Ar atmosphere are smaller than the corresponding yields for the pyrolysis under the $\text{NH}_3\text{-N}_2$ atmosphere. Table 1 lists the yields for all the pyrolysis.

The elemental analysis results of the ceramic residues are also summarized in Table 1. All the ceramic residues contained 20.8-23.5 % of nitrogen even after the pyrolysis under the Ar atmosphere,

Table 1. Ceramic yield, loss of aluminum, elemental analysis, lattice parameters for $(\text{HAlN}^i\text{Pr})_n$ and $(\text{HAlNEt})_m$ pyrolyzed under Ar and $\text{NH}_3\text{-N}_2$

	$(\text{HAlN}^i\text{Pr})_n$		$(\text{HAlNEt})_m$	
	Ar	$\text{NH}_3\text{-N}_2$	Ar	$\text{NH}_3\text{-N}_2$
ceramic yield /mass%	32	47	50	57
loss of aluminum /%	55	14	36	7
elemental analysis				
Al /mass% (molar ratio)	45.2 (1)	58.1 (1)	48.5 (1)	61.9 (1)
N /mass% (molar ratio)	20.8 (0.89)	28.9 (0.96)	23.5 (0.93)	28.7 (0.89)
O /mass% (molar ratio)	5.5 (0.20)	7.5 (0.22)	3.7 (0.13)	5.6 (0.15)
C /mass% (molar ratio)	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
lattice parameters/nm				
<i>a</i>	0.311(5)	0.310(9)	0.311(2)	0.311(0)
<i>c</i>	0.498(5)	0.497(6)	0.498(1)	0.497(7)

indicating that the nitrogen in the precursor was at least partly remained in the ceramic residues. On the contrary, the amount of carbon depends on the pyrolysis atmosphere; the pyrolysis under the Ar atmosphere led to the ceramic residues containing 17.1-20.6 % of carbon, while the carbon contents are less than 1 % for the ceramic residues pyrolyzed under the $\text{NH}_3\text{-N}_2$ atmosphere. In addition to nitrogen and carbon, some amounts of oxygen were detected for all the ceramic residues.

Based on the aluminum contents in the ceramic residues (Al_c), the theoretical aluminum contents in the precursors (Al_0), and ceramic yield (Y), the ratios of aluminum lost during the pyrolysis ($\Delta\text{Al}/\text{Al}_0$) can be calculated by the following equation and are listed in Table 1;

$$\Delta\text{Al}/\text{Al}_0 = [(\text{Al}_0 - Y \times \text{Al}_c) / \text{Al}_0] \times 100$$

During the pyrolysis of $(\text{HAlN}^i\text{Pr})_n$ under the Ar atmosphere, more than half of aluminum (55 %)

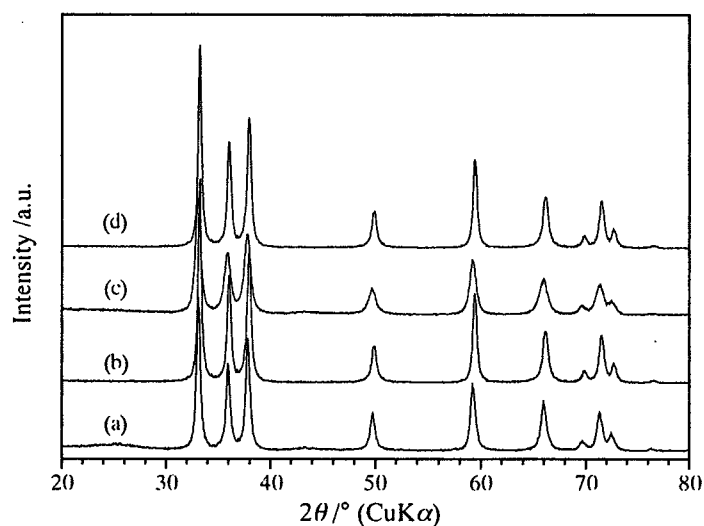


Fig. 1 XRD patterns of the ceramic residues: (a) $(\text{HAlN}^i\text{Pr})_n$ under Ar, (b) $(\text{HAlN}^i\text{Pr})_n$ under $\text{NH}_3\text{-N}_2$, (c) $(\text{HAlNEt})_m$ under Ar and (d) $(\text{HAlNEt})_m$ under $\text{NH}_3\text{-N}_2$.

was lost. The amount of aluminum lost during the pyrolysis was considerably reduced to 14 %, if the pyrolysis atmosphere was $\text{NH}_3\text{-N}_2$. Similarly, the amount of aluminum lost for the pyrolysis of $(\text{HAlNEt})_m$ (7 %) under the $\text{NH}_3\text{-N}_2$ atmosphere was much smaller than that for the pyrolysis under the Ar atmosphere (36 %). The lower Al loss for the pyrolysis under the $\text{NH}_3\text{-N}_2$ atmosphere should be ascribed to the formation of cross-linked structures via trans-amination reactions, which should lead to the release of amines (EtNH_2 and ${}^i\text{PrNH}_2$).

Fig. 1 shows the XRD patterns of the ceramic residues. All the XRD patterns of the four ceramic residues are consistent with the formation of single-phase $2H$ wurtzite-type compounds. Isostructural Al_2OC , whose lattice parameters ($a=0.319$ nm, $c=0.509$ nm) are slightly larger than those of AlN , is known to form solid-solutions with AlN [37,38]. Since the ceramic residues contained aluminum, nitrogen, oxygen, and carbon, the possibility of the formation of $\text{AlN-Al}_2\text{OC}$ solid solutions should be considered. Hence, the lattice parameters of the $2H$ wurtzite-type compounds were precisely determined. All the values listed in Table 1 are consistent with the previously-reported values for AlN ($a=0.310\text{-}0.3114$ nm, $c=0.496\text{-}0.4986$ nm) [37,39]; the $2H$ wurtzite-type compounds in the ceramic residues should be essentially pure AlN , and oxygen and carbon are hardly present in the $2H$ wurtzite-type structures. Thus, carbon in the ceramic residues pyrolyzed under Ar is probably present as amorphous free carbon. Oxygen, which should not be present in the precursors ideally, may be introduced via the oxidation during handling and pyrolyzing of the precursors and/or the hydrolysis of the ceramic residues after exposure to air; the presence of oxygen is probably ascribed to the formation of hydroxide, oxide and/or oxynitride of aluminum. This is consistent with the N/Al ratios below unity for all the ceramic residues (Table 1).

Fig. 2 shows scanning electron micrographs of the ceramic residues obtained by the pyrolyses of $(\text{HAlN}{}^i\text{Pr})_n$ and $(\text{HAlNEt})_m$ under the Ar atmosphere. Both the ceramic residues show very smooth surface. These two ceramic residues actually consist of small particles.

Conclusions

We have demonstrated that the cage-type compounds of poly(alkyliminoalane) [$(\text{HAlNR})_n$ ($\text{R}=\text{Et}$, ${}^i\text{Pr}$)] are excellent AlN precursors because of their relatively high ceramic yields and their high solubility in common organic solvents. The pyrolysis under the Ar atmosphere led to AlN

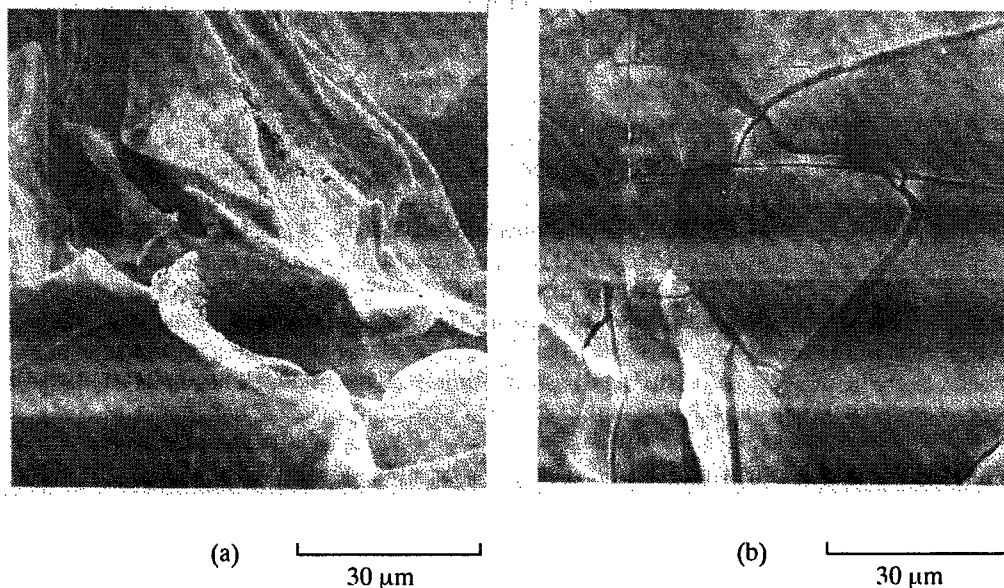


Fig. 2 Scanning electron micrographs of the ceramic residues; (a) $(\text{HAlN}{}^i\text{Pr})_n$ under Ar and (b) $(\text{HAlNEt})_m$ under Ar.

crystallization with the formation of considerable amounts of amorphous free carbon, while essentially carbon-free AlN was obtained via pyrolysis under the NH₃-N₂ atmosphere. These results revealed that the cage-type compounds (HAINR)_n (R=Et, ^tPr) are promising AlN precursors, though they do not possess polymeric structures.

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Pyrolytic Conversion of Blended Precursors into Ti-Al-N Ceramic Composites

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Pyrolytic preparations of Ti-Al-N ceramics from three blended precursors were investigated. The precursors were prepared by stirring $(\text{HA1N}^{\text{tPr}})_m$ and an aminolysis product of $\text{Ti}(\text{NMe}_2)_4$ with $\text{MeHNCH}_2\text{CH}_2\text{NHMe}$ in C_6H_6 . IR and ^1H NMR analyses suggested that essentially no Ti-N-Al bonds were present in the precursors. Pyrolysis of the precursors under $\text{NH}_3\text{-N}_2$ led to the formation of brown solids with ceramic yields of about 30%, and the Ti-Al ratios in the pyrolyzed products were close to those of the precursors. XRD analysis of the pyrolyzed product from the precursor with Ti:Al=5:1 indicated the formation of a NaCl-type compound as the only crystalline phase. Pyrolysis of the precursor with Ti:Al=2:1 led to the formation of AlN besides the major NaCl-type compound. A ceramic composite containing AlN and the NaCl-type compound was formed by pyrolysis of the precursor with Ti:Al=1:2.

Key Words : Ceramic composite, Aluminum Nitride, Titanium Nitride, Precursor, Pyrolysis

I. Introduction

In recent years, considerable attention has been given to ceramic composites because of their superior properties compared to single-component ceramics.^{1,2} Ceramic composites consisting of two or more binary nitrides often exhibit improved properties.^{3,4} TiN-AlN ceramic composites are expected to be useful for antifriction materials and heating materials because of their high thermal conductivity, high hardness, excellent wear resistance and excellent oxidation resistance.⁵⁻⁷ Powder techniques are the traditional synthetic procedures for TiN-AlN ceramic composites. However, chemical vapor deposition (CVD) processes have been applied to study the preparation of TiN-AlN composite films recently.⁸

Pyrolytic conversion of precursors has been widely applied for the preparations of the simple carbides and nitrides of various main group elements and transition metals,^{3,9,10} and is currently being investigated as an alternative route for the preparations of non-oxide ceramic composites.⁴ The use of such a preceramic route in preparation and processing ceramic composites offers several potential advantages, including improved control over composition, grain size, homogeneity, and lower processing temperatures.^{4,11} In addition, the route provides a method for the formation of shapes, such as fibers and coatings, if the preceramic materials are soluble or fusible.⁹ Syntheses of non-oxide ceramic composites using precursors have been mainly reported for systems such as Si-C-

N, Si-B-C-N, and Si-Al-N.^{4,11,12} Although considerable researches on precursors for TiN, TiC and AlN have been reported,^{3,9,10} there is only one report on the preparation and pyrolysis of a precursor for a ceramic composite in a Ti-Al-N system as far as we know.¹³

Most of preceramic approaches that have been explored for composite preparation are the syntheses of single-source molecular precursors that contain heterogeneous linkages such as M-N-M', because a molecular level homogeneity of the components in the initial precursor system can be obtained through these approaches.^{4,12,14,15} However, if the single-component precursors are miscible liquids or solids soluble in organic solvents, the homogeneity can also be achieved by blending two precursors with the desired composition at a molecular level.¹² The blended precursors are usually soluble in organic solvents since no reactions between the two single-component precursors are expected. Syntheses of ceramic composites using blended precursors have been reported for systems such as boron containing $\text{Si}_3\text{N}_4/\text{BN}$ and $\text{Si}_3\text{N}_4/\text{AlN}$ composites.^{4,12}

This paper describes the preparations of Ti-Al-N ceramics by the pyrolysis of the precursors essentially without Ti-N-Al bonds. We have previously reported the preparations of AlN and TiN by the pyrolysis of a cage-type compound $(\text{HA1N}^{\text{tPr}})_m$ and an aminolysis product of $\text{Ti}(\text{NMe}_2)_4$ with $\text{MeHNCH}_2\text{CH}_2\text{NHMe}$, respectively.^{16,17} Herein, they were employed as sources to AlN and TiN respectively. Pyrolytic conversion of the blended precursors was investigated by compositional analysis, X-ray powder diffrac-

tion (XRD) and scanning electron microscopy (SEM).

II. Experimental

All the procedures were performed under a protective nitrogen atmosphere using a standard Schlenk technique or a glove box filled with nitrogen. All the organic solvents and amines were freshly distilled by using appropriate drying agents before use.

The AlN precursor $(\text{HAlN}^i\text{Pr})_m$ was prepared based on a previous report.¹⁹ Examinations of this $(\text{HAlN}^i\text{Pr})_m$ by ^1H , ^{13}C , and ^{27}Al NMR revealed that it was present mainly as a cage-type hexamer. In addition, signals due to tetramer were also observed in ^1H and ^{13}C NMR. The IR spectrum showed the presence of a (Al-H) stretching band at 1860 cm^{-1} .¹⁹ The bands at 1165 , 1139 , 834 cm^{-1} and the bands at 1379 , 1365 cm^{-1} were assigned to $-\text{CH}(\text{CH}_3)_2$ skeletal bands and bending bands respectively.¹⁹

The TiN precursor possessing Ti-N bonds was prepared based on a previous report by the reaction of $\text{Ti}(\text{NMe}_2)_4$ with $\text{N,N}'$ -dimethylethylenediamine with $\text{Ti}(\text{NMe}_2)_4$:diamine=1:2.²⁰ Examinations of the black oily product by ^1H , ^{13}C NMR suggested that it was a mixture of monomeric and oligomeric species with various environments of the methyl groups. The IR spectrum showed the presence of a few bands assignable to Ti-N stretching bands at 556 , 590 , 650 cm^{-1} . In addition, the presence of C-H bending bands at 1242 , 1274 cm^{-1} and a N-H stretching band at 3290 cm^{-1} suggested that the product contained a small amount of unreacted-N(H)Me groups.^{17,19}

The blended precursors were prepared as follows. After the TiN precursor was dissolved in 30 ml of benzene in a 100 ml three-neck flask, the AlN precursor was added with approximate molar ratios of Ti:Al=5:1, 2:1 or 1:2. The mixed solution was stirred for 1 h to ensure homogeneity. Removal of benzene gave the blended precursors.

The precursors were pyrolyzed in a tube furnace. About 0.5 g of each precursor was placed in a BN boat, which was then introduced into an Al_2O_3 tube filled with NH_3 . The precursor was first heated at 600°C for 3 h under NH_3 (30 mL/min), then cooled to room temperature. The product pyrolyzed under NH_3 was heated again at 1350°C for 8 h under N_2 (100 mL/min). The heating and cooling rates were $5^\circ\text{C}/\text{min}$.

The precursors were characterized by using IR (Perkin-Elmer FTIR-1640), ^1H and ^{13}C NMR (JEOL JNM-270X, 270.16 MHz) spectroscopy. Thermogravimetric (TG) analysis of the precursors was carried out by using a Shimadzu TGA-50 thermobalance at the heating rate of $10^\circ\text{C}/\text{min}$ under a He flow. The pyrolyzed products were analyzed by using XRD (Cu K α ; Mac Science MXP³ diffractometer). The lattice parameters of the pyrolyzed products were calculated by the non-linear least-squares method. The amounts of nitrogen, oxygen and carbon in the pyrolyzed products were measured by using LECO TC-436 and CS-444LS instruments. After the pyrolyzed products

were dissolved with aqua regia in a teflon decomposition vessel at 130°C for 24 h, the amounts of titanium and aluminum were determined by inductively coupled plasma emission spectroscopy (ICP, Nippon Jarrell Ash ICAP-575 II). The morphology of the pyrolyzed products was investigated using SEM (Hitachi S4500-S).

III. Results and Discussion

The blended precursors were dark brown waxy liquid (Ti:Al=5:1) or orange brown highly waxy liquid (Ti:Al=2:1, 1:2). The Ti-Al molar ratios of the precursors determined by ICP analysis were 4.8:1, 2.3:1, 1:1.8 for precursors with Ti:Al=5:1, 2:1, 1:2, respectively.

Examination of the blended precursors by IR and ^1H NMR spectroscopies showed that some reactions occurred during blending the $(\text{HAlN}^i\text{Pr})_m$ and the aminolysis product of $\text{Ti}(\text{NMe}_2)_4$ with $\text{MeHNCH}_2\text{CH}_2\text{NHMe}$. The ^1H NMR signals at 1.21 ppm due to the $-\text{CH}_3$ of the $(\text{HAlN}^i\text{Pr})_m$ disappeared and a broad peak appeared at 1.15-1.55 ppm in the spectra of the blended precursors. The IR spectra of the blended precursors showed that the bands at 1005 cm^{-1} and 1285 cm^{-1} assignable to the $(\text{HAlN}^i\text{Pr})_m$ also disappeared. Contrary to these spectroscopic changes for AlN precursors, the ^1H NMR spectra of the blended precursors showed that the profiles of the signals of the methyl groups of $\text{Ti}(\text{NMe}_2)_4$ with $\text{MeHNCH}_2\text{CH}_2\text{NHMe}$ were essentially unchanged, indicating that the reactions between the $(\text{HAlN}^i\text{Pr})_m$ and the aminolysis product of $\text{Ti}(\text{NMe}_2)_4$ with $\text{MeHNCH}_2\text{CH}_2\text{NHMe}$ were very limited. These results suggest that essentially no Ti-N-Al bonds are formed during blending the $(\text{HAlN}^i\text{Pr})_m$ and the aminolysis product of $\text{Ti}(\text{NMe}_2)_4$ with $\text{MeHNCH}_2\text{CH}_2\text{NHMe}$.

Table 1. Ceramic Yields and some Characteristics of the Pyrolyzed products

Precursor/Ti:Al	5:1	2:1	1:2
Ceramic yield/mass %	30.6	29.6	30.9
Loss of Ti/mass%*	4.1	4.3	8.0
Loss of Al/mass%*	7.9	10.2	12.3
Element analysis			
Ti/mass% (molar ratio)	59.82(1)	56.40(1)	34.11(1)
Al/mass%(molar ratio)	6.77(0.20)	13.41(0.42)	33.36(1.74)
N/mass%(molar ratio)	18.11(1.03)	17.46(1.06)	21.20(2.13)
C/mass%(molar ratio)	4.38(0.29)	5.19(0.37)	3.45(0.40)
O/mas%(molar ratio)	5.18(0.25)	5.63(0.30)	5.77(0.51)
Total/mass%	94.26	98.69	97.89
lattice paramete/nm			
NaCl-type compound	0.4243	0.4245	0.4246
2H-wurtzite compound			a=0.3111 c=0.4976

*The loss $[E_{L(M)}]$ of metal (M=Ti or Al) during the pyrolysis was calculated from the amounts of the metal in the precursor $[W_{P(M)}]$ and in the pyrolyzed residue $[W_{R(M)}]$.
 $E_{L(M)} = [W_{P(M)} - W_{R(M)}] / W_{P(M)} \times 100$ Y: ceramics yield

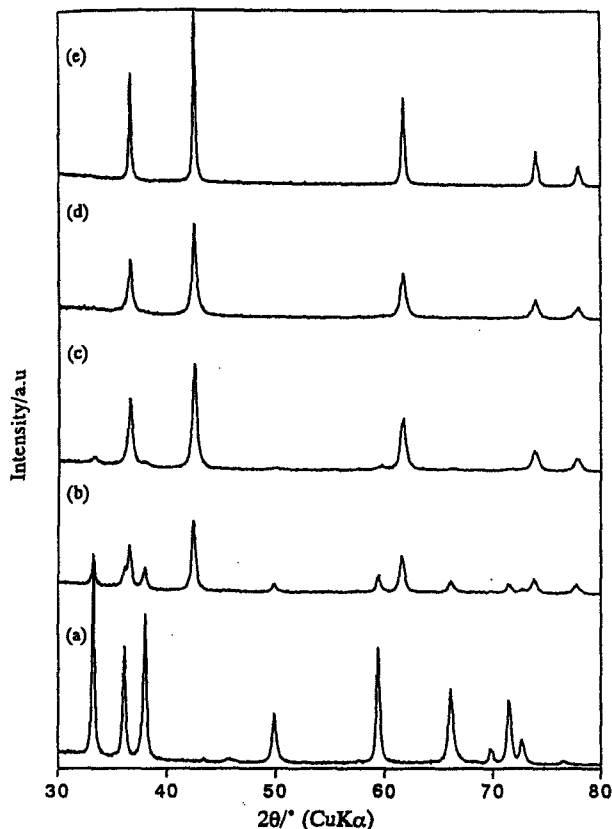


Fig. 1. XRD patterns of the products pyrolyzed from (a) precursor AlN, (b) precursor Ti:Al=1:2, (c) precursor Ti:Al=2:1, (d) precursor Ti:Al=5:1 and (e) precursor TiN.

Thermogravimetric analysis of the precursor with Ti:Al=2:1 indicated that no sharp mass loss occurred. Fifty seven of mass loss occurred at the temperature below $\sim 500^\circ\text{C}$, and only 3% of mass loss was observed at the temperature range of $\sim 500^\circ\text{C}$ - 900°C . This suggested that the decomposition of the organic groups should occur mainly at the temperature below $\sim 500^\circ\text{C}$. The ceramics yield at 900°C was up to 40%, which is higher than the theoretical one (about 29% for conversion of all the titanium and aluminum in the precursors into TiN and AlN). The excessive mass compared to the theoretical yield is probably due to the fact that carbon has been retained either as free carbon or as a mixture of free carbon and carbide. The presence of carbon remaining in the residue obtained by the pyrolysis of the AlN precursor or the TiN precursor under Ar has also been reported previously.^{16,17}

Pyrolysis of the blended precursors under NH_3 flow at 600°C for 3 h and subsequently under N_2 at 1350°C for 8 h gave brown solids in all cases. All the precursors have ceramic yields of about 30% that are close to the theoretical ones (Table 1). The amounts of titanium and aluminum lost during the pyrolysis are very small. These results are probably due to the effective amine-exchange reactions between the precursor and NH_3 , and subsequent conversion into highly cross-linked structures at

lower pyrolysis temperature.^{17,21} It is probable that the formation of the highly cross-linked structures partially suppressed the loss of Al- and Ti-containing species, which led to the conversion with a reasonable ceramic yields.

It should also be noted that the Ti-Al molar ratios of the pyrolyzed products showed in Table 1 are very close to those of the blended precursors (4.8:1, 2.3:1 and 1:1.8 for precursors with Ti:Al=5:1, Ti:Al=2:1 and Ti:Al=1:2 respectively). About 5% of carbon is present in the products (Table 1), even though the amine-exchange reactions during the pyrolysis under NH_3 atmosphere could reduce a carbon content in a pyrolyzed product.²¹ Furthermore, considerable amounts of oxygen, which was probably introduced during the pyrolysis, are present in the products (Table 1). The presence of carbon and oxygen in the TiN/AlN residues obtained by the pyrolysis of a titanium aluminum polyimide under NH_3 has also been reported previously.¹³

The XRD pattern of the pyrolyzed product from precursor with Ti:Al=5:1 indicates the formation of a NaCl-type compound as an only crystalline phase (Fig. 1d). As the Al content in the blended precursor increases, weak 2H-wurtzite type compound peaks appear in the XRD pattern of the pyrolyzed product from precursor with Ti:Al=2:1 (Fig. 1c). Pyrolysis of the precursor with Ti:Al=1:2 leads to the formation of a ceramic composite containing a 2H-wurtzite type compound and an NaCl-type compound in the pyrolyzed product (Fig. 1b).

The lattice parameters of the NaCl-type compounds in the products are slightly larger than that of TiN (0.4242 nm^{22}), and unnegligible amounts of carbon and oxygen are present in the products (Table 1). TiN possesses a NaCl-type structure and can form solid solutions with TiC that also possesses a NaCl-type structure with a larger lattice parameter (0.4327 nm^{22}); the formation of a TiN-TiC solid solution will give a larger lattice parameter as compared to that of TiN.²³ TiO (0.4178 nm^{23}) is also soluble in TiN, and has a little effect on the lattice parameter of TiN when the content of TiO is below 40% (molar percentage).²³ Thus, the observed lattice parameters of the NaCl-type compounds can be reasonably explained by assuming that the NaCl-type compounds are Ti(N, C, O) phases.

A (Ti, Al)N solid solution is also known as a metastable phase with an NaCl-type lattice.²⁴ The absence of the peaks attributable to any Al-containing phase (including the 2H-wurtzite type compound) in the XRD pattern of the pyrolyzed product from the precursor with Ti:Al=5:1 implies the possibility of the formation of a (Ti, Al)N solid solution, besides the possibility that the crystallization of the 2H-wurtzite type compound has been retarded. If the (Ti, Al)N solid solution formed, the lattice parameter of the (Ti, Al)N solid solution should be smaller than that of TiN.²⁵ Thus, the observed lattice parameters which are slightly larger than TiN are not consistent with the formation of (Ti, Al)N solid solution. Since Jaschek and Rüssel reported that the (Ti, Al)N solid solution was obtained

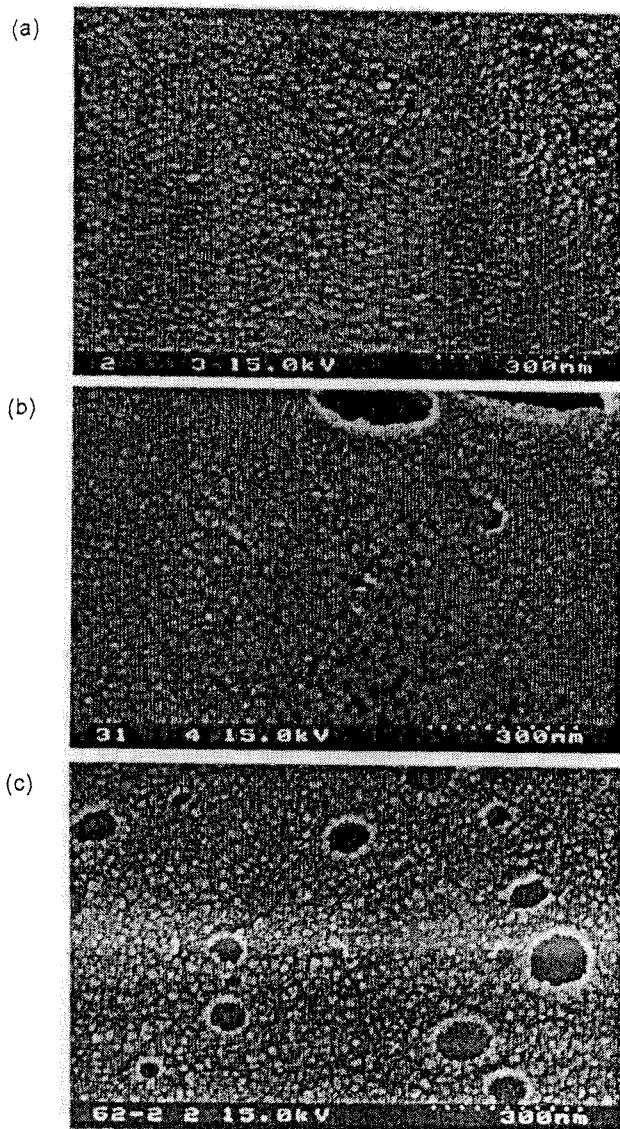


Fig. 2. SEM of the products pyrolyzed from (a) precursor with Ti:Al=1:2, (b) precursor with Ti:Al=2:1 and (c) precursor with Ti:Al=5:1.

by pyrolysis of a titanium aluminum polyimide under NH_3 below 1200°C ,¹³⁾ we can not exclude the possibility of the formation of (Ti, Al)N solid solutions from our precursors at lower temperatures. By pyrolyzing the precursor with Ti:Al=1:2 at 1000°C , only the NaCl-type compound formed, but the XRD peaks are too broad for closer inspection. The formation of a Ti-containing solid solution would be possible by assuming a (Ti, Al)(N, C, O) solid solution, but, as far as we know, there is no study which reports the presence of a (Ti, Al)(N, C, O) solid solution.

The lattice parameters of the 2H-wurtzite type compound in the pyrolyzed product from precursor with Ti:Al=1:2 are $a=0.311(1)$ nm and $c=0.497(6)$ nm, very similar to the reported values of AlN ($a=0.310\text{--}0.3114$ nm, $c=0.496\text{--}0.4986$ nm^{26,27)}, indicating that the 2H-wurtzite type com-

pound should be an AlN phase. Thus, as shown in the XRD pattern, a ceramic composite consisting of a hexagonal AlN and a NaCl-type compound has formed when the precursor with Ti:Al=1:2 was pyrolyzed at $1,350^\circ\text{C}$, consistent with the previous report.¹³⁾ The XRD peaks of the 2H-wurtzite type compound for the product with Ti:Al=2:1 were too broad for lattice parameter determination, but we assume that the 2H-wurtzite type compound was also AlN with this ratio.

The mean crystallite sizes calculated from XRD patterns using the Scherrer equation were about 20 nm for the NaCl-type compounds in all the three products, and about 30 nm for AlN in the product from precursor with Ti:Al=1:2. These XRD results are well consistent with the following SEM results. SEM examination of the pyrolyzed product from the precursor with Ti:Al=1:2 showed that the product mainly consists of very fine particles with diameters of 20-40 nm (Fig. 2a). In addition, some aggregated particles (consisting of smaller particles of 30-100 nm) were also observed (not shown). The products from the precursor with Ti:Al=2:1 and 5:1 show morphology similar to the aforementioned one, and particles with diameters of 20-40 nm are mainly observed by SEM (Fig. 2b and 2c). Besides the major small particles, larger spherical particles with diameters of 30-100 nm (Ti:Al=2:1) or aggregated particles (diameter: 30-200 nm) consisting of smaller particles (<30 nm) (Ti:Al=5:1) were observed (not shown). It should also be worth noting that the surfaces of the products from precursor with Ti:Al=5:1 and Ti:Al=2:1 are porous.

IV. Conclusions

Three blended precursors essentially without Ti-N-Al bonds have been prepared by mixing the $(\text{HAlN}^i\text{Pr})_m$ and an aminolysis product of $\text{Ti}(\text{NMe}_2)_4$ with $\text{MeHNCH}_2\text{CH}_2\text{-NHMe}$ homogeneously, and their pyrolytic conversion behavior was investigated. Pyrolysis of the precursors under $\text{NH}_3\text{-N}_2$ at 1350°C led to the formation of brown solids with ceramic yields close to the theoretical ones. The Ti:Al ratios in the pyrolyzed products were consistent with those of the precursors. Only NaCl-type compound formed when was pyrolyzed the precursor with Ti:Al=5:1. On the other hand, pyrolysis of the precursor with Ti:Al=2:1 led to the formation of AlN besides the major NaCl-type compound. A ceramic composite consisting of AlN and the NaCl-type compound has formed when the precursor with Ti:Al=1:2 was pyrolyzed.

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Pyrolysis of poly(Isopropyliminoalane) to Aluminum Nitride

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Abstract:

The pyrolysis processes of poly(isopropyliminoalane) were investigated by analyzing evolved gases mass-spectrometrically and residual solids spectroscopically. The major mass loss (between 240 and 540 °C) consisted of two different pyrolysis stages. At the first stage (240-320 °C), (HAIN¹Pr)₆ was continuously detected as a gas, and the precursor was converted into a cross-linked structure. A polymerization mechanism without releasing organic compounds is proposed, and the formation of (HAIN¹Pr)₆ during polymerization besides its evaporation is suggested. The second stage (320-560 °C) involved the formation of various organic compounds, and radical processes are proposed for their formation.

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I. Introduction

Pyrolytic conversion of preceramic materials, typically organometallic and inorganic polymers possessing metal-nitrogen and/or metal-carbon bonds, provides novel routes to non-oxide ceramics.¹⁻³ If preceramic materials are soluble in organic solvents or fusible at relatively low temperature, one can obtain ceramic materials with desirable shapes, for example, fibers and films. The preceramic materials can also be used potentially for sintering aids and binders.³

Aluminum nitride (AlN) is one of important nitride ceramics because of its high thermal conductivity.⁴ In addition, AlN films are currently attracting increasing attention because of their possible use for electronic and optoelectronic applications.^{5, 6} Preparation of AlN via pyrolytic processes has also been extensively investigated, and many systems have been reported for the synthesis of AlN precursors so far.^{3, 7-9}

Generally, precursors are polymeric to avoid the loss of the precursors by volatilization,¹ but oligomers¹⁰ and even small molecules¹¹ can also be converted into ceramics via polymerization during their pyrolysis. Cyclic oligomers are possible candidates as preceramic materials, if their volatilization is sufficiently suppressed and effective polymerization occurs during pyrolysis. For the use of very volatile compounds, such as borazine (HBNH)₃, pressure pyrolysis technique was applied,¹² but some cyclic species have been converted into non-oxide ceramics via usual pyrolysis. As a borazine-derivative, (CH₃NH)₃B₃N₃H₃ was converted into BN by the pyrolysis under NH₃.¹³ Also, cyclic poly(silazane), (MeSiHNNH)_n, was applied to Si₃N₄/SiC synthesis; (MeSiHNNH)_n showed low ceramic yield (20%), so that it was polymerized using KH before pyrolysis to improve its ceramic yield.¹⁴ Among AlN precursors, cyclic (R₂AlNH₂)₃ was isolated as an intermediate during the conversion of R₃Al:NH₃ into AlN.⁹ The pyrolysis of (Et₂AlNH₂)₃ gave a ceramic residue with a ceramic yield of 28 % (under N₂ up to 1000 °C,

theoretical yield: 40.5%), and the pyrolysis mechanism of $(R_2AlNH_2)_3$ was proposed to be initiated by ring-opening.¹⁵ The cluster compounds containing five- and four-membered rings were also pyrolyzed to form AlN, but higher ceramic yields were achieved by polymerizing the cluster compounds thermally before pyrolysis.¹⁶

It has been known for years that some compounds possessing Al-N bonds exhibit cage-type structures.¹⁷ Cage-type compounds, as well as cyclic compounds, can be used as preceramic materials, and we have reported the successful pyrolytic conversion of these cage-type compounds, poly(alkyliminoalanes) $[(HAINR)_n]$ ($R=Et, iPr$), into crystalline AlN.¹⁸⁻²¹ In spite of their relatively low molecular mass, they gave ceramic residues with moderate ceramic yields (for $R=iPr$, 32 % (Ar) and 47 % (NH_3-N_2); for $R=Et$, 50 % (Ar) and 57 % (NH_3-N_2)) without polymerization before pyrolysis.²¹ In terms of the pyrolysis of poly(isopropyliminoalane) $[(HAINiPr)_n]$ whose major component is a cage-type hexamer (Figure 1),²² it was shown that mineralization was essentially completed by the pyrolysis at 1000 °C under Ar to form an amorphous solid containing AlN₄ environment.¹⁸ To clarify the conversion mechanism, the mineralization step of this precursor should be further investigated.

This paper describes the detailed investigation on the pyrolysis of poly(isopropyliminoalane) at lower temperatures. The analyses of evolved gases and spectroscopic characterization of pyrolyzed residues were conducted to clarify the pyrolysis processes. In particular, we focus on the polymerization reactions during the pyrolysis, which should play an important role for the conversion of oligomeric $(HAINiPr)_n$ into AlN.

Figure 1

II. Experimental Procedure

(1) Preparation and Characterization of $(HAINiPr)_n$

All the procedures were performed under a protective nitrogen atmosphere using standard Schlenk technique.²³ Poly(isopropyliminoalane) was prepared according to the previous report;²⁴



Typically, LiAlH₄ (4.3 g, 1.1x10⁻¹ mol) was dispersed in 120 ml of dry *n*-heptane, and ^{*i*}PrNH₂ (6.0 g, 1.0x10⁻¹ mol) in dry *n*-heptane (30 ml) was slowly added to the suspension. The mixed suspension was stirred at 0 °C for 1 h, and further stirred at reflux for 20 h. After filtration for the removal of LiH, *n*-heptane was distilled off to yield a white solid.

The product was characterized by nuclear magnetic resonance spectroscopy (NMR) using a JEOL NM-GSX-400 spectrometer. ¹H NMR (400 MHz, C₆D₆) showed the presence of a doublet (CH₃) at 1.4 ppm and a septet (CH) at 3.6 ppm, both consistent with hexamer [(HAlN^{*i*}Pr)₆] formation.^{24, 25} Weak signals due to other oligomers (mainly tetramer) were also present.^{24, 26} A very broad signal due to AlH groups was also observed at ~ 4.6 ppm. ¹³C NMR (135 MHz, C₆D₆) results were also consistent with the reported value for the hexamer (28.0 ppm (CH₃), 49.7 ppm (CH)).²⁵ In an ²⁷Al NMR spectrum (104 MHz, C₆D₆), a broad signal was observed at 132 ppm. This was slightly different from the reported value (123 ppm)²⁵ probably due to the difference in the magnetic fields. Infra-red spectroscopy (IR; Perkin Elmer IR-1640) revealed the presence of a broad ν_(Al-H) band centered at 1855 cm⁻¹ (see Figure 4 a).²⁷ A mass spectrum of the product (JEOL, SX-102A) was also consistent with the hexamer formation;²⁷ *m/e* (EI, 70 eV), 496 ([M-14]⁺, 20), 495 ([M-15]⁺, 100). Relative intensities of other fragments were less than 10.

(2) Thermogravimetry-Mass Spectrometry (TG-MS) analysis.

A TG curve was recorded on a Shimadzu TGA-50 thermobalance. About 10 mg of the precursor was heated up to 900 °C at a rate of 10 °C/min

under a He flow (30 mL/min). The thermobalance was coupled with a Shimadzu GCMS-QP1100EX quadrupole mass spectrometer via stainless steel capillary, which was heated in accordance with the heating schedule of the thermobalance up to 250 °C. Mass spectra were obtained with an ionization energy of 70 eV in the range from 10 to 1000 amu, and were recorded at 9.9 second intervals. The temperature of the ion source was 250 °C.

When various gaseous compounds formed simultaneously, evolved gases were analyzed by gas chromatography (GC) for separating gases before mass spectrometric analysis (TG-GCMS). The gases were trapped during the TG measurement in the temperature range corresponding to the gas evolution, and the trapped gases were analyzed by GC-MS using the same instrument (Shimadzu GCMS-QP1100EX). The columns were packed with silica gel or 2,6-diphenyl-*p*-phenylene oxide. The trap, which was cooled by dry ice, was also packed with the materials used for the GC-columns.

(3) Tube Furnace Pyrolysis.

The precursor was pyrolyzed using a tube furnace under a He flow (100 mL/min) in order to obtain residual solids without exposure to air and to collect gases evolved during pyrolysis. The precursor was placed on a BN boat, and introduced into a quartz tube filled with He. Then it was heated at a rate of 5 °C/min up to 300, 400, and 500 °C, and subsequently cooled without holding time at the highest temperatures. The pyrolyzed products were analyzed by IR using nujol (300 °C-pyrolyzed product) and KBr disk (400 °C- and 500 °C-pyrolyzed products) techniques. IR samples were prepared in a glove bag filled with nitrogen. The evolved gases were trapped using liquid nitrogen and analyzed by GC-MS using the aforementioned instrument.

III. Results

Figure 2 shows a typical TG curve of the precursor. The ceramic yield is typically 39 % up to 900 °C. Up to 240 °C, a small mass loss (~7 %) is observed, and a further larger mass loss is observed from 240 °C to 560 °C. The mass spectra collected during the TG analysis were classified into only three groups; 1) those collected from room temperature to ~240 °C, 2) those collected from ~240 °C to ~320 °C, and 3) those collected from ~320 °C to ~560 °C. Thus, we describe the pyrolysis process in the following three sections.

Figure 2

(1) From room temperature to ~240 °C.

All the mass spectra at this temperature range corresponded to $^i\text{PrNH}_2$ (not shown). When the precursor was pyrolyzed in the tube furnace at 300 °C, however, $^i\text{PrNH}_2$ was not trapped. Thus, $^i\text{PrNH}_2$ should form *via* the hydrolysis of the precursor by a trace of water in the TG-MS equipment.

When the precursor was pyrolyzed at 160 °C in a three-neck flask under a nitrogen atmosphere, the precursor melted partially and volatilization of gaseous species was observed. The $^1\text{H-NMR}$ analysis of the remaining product mainly showed the signals due to $(\text{HAIN}^i\text{Pr})_6$; most of the oligomers except $(\text{HAIN}^i\text{Pr})_6$ disappeared. Thus, the oligomers except $(\text{HAIN}^i\text{Pr})_6$ (for example, tetramer) would be converted into $(\text{HAIN}^i\text{Pr})_6$ or other polymeric structures.

(2) From ~240 to ~320 °C.

Above 240 °C, the intensity of the total ion chromatogram (TIC) became very intense, consistent with the large mass loss in the TG curve. In this temperature range, all the mass spectra were similar. Figure 3 illustrates a mass spectrum collected at 300 °C, where the total amount of evolved gases

was maximum. The base peak is the fragment at m/e 495, which is also the base peak of $(\text{HAIN}^i\text{Pr})_6$ (its relative molecular mass is 510; the fragment at m/e 495 corresponds to a $[\text{M}-15]^+$ ion (see experimental section)).²⁷ In addition, during the tube furnace pyrolysis, a white powder was condensed at the cold downstream part of the reaction tube before the trap, and ^1H NMR analysis of the condensed product indicated that the main species in the condensed powder was $(\text{HAIN}^i\text{Pr})_6$. Since the molecular mass of $(\text{HAIN}^i\text{Pr})_6$ is relatively small, it is likely that $(\text{HAIN}^i\text{Pr})_6$ volatilized in this temperature range. The mass spectrum (Figure 3) also contains small fragments that cannot be assigned to $(\text{HAIN}^i\text{Pr})_6$, which appears to be consistent with the presence of weak unassignable signals in the ^1H NMR spectrum of the condensed powder.

————— **Figure 3** —————

The pyrolysis in the tube furnace at 300 °C resulted in the formation of an yellow powder which is insoluble in benzene, indicating that the precursor was converted into a polymeric cross-linked structure in this temperature range. The IR spectrum of the residue pyrolyzed at 300 °C (Figure 4 b) shows the presence of a strong $\nu_{(\text{Al-H})}$ band at $\sim 1850 \text{ cm}^{-1}$.²⁷ Thus, at least a large portion of Al-H bonds survives after the pyrolysis at 300 °C.

————— **Figure 4** —————

(3) From ~ 320 to ~ 560 °C.

All the mass spectra collected by the TG-MS analysis in this temperature range were similar. Since these spectra can not be interpreted easily, the gases evolved in this temperature range in the thermobalance were collected and analyzed using GC-MS (TG-GCMS). GC-MS analysis for the gases evolved by the tube furnace pyrolysis in the same temperature range was also conducted. Unsaturated hydrocarbons (C_2H_4 , C_3H_6 , C_4H_8 ,

C₅H₁₀, C₆H₁₀, C₉H₁₂), saturated hydrocarbons (CH₄, C₂H₆, C₃H₈), and CH₃CN were identified by both the techniques.

Since the base peak at m/e 41 corresponds to intense fragments of most of the species evolved (except CH₄, C₂H₄, C₂H₆), the temperature profile of this fragment should reflect the gas evolution behavior (Figure 2 c). The intensity of this fragment increases rapidly at ~ 320 °C, where the detected amount of (HAINⁱPr)₆ was drastically decreased (indicated by the behavior of the fragment at m/e 495; see Figure 2 b). Above 340 °C, the intensity of the fragment at m/e 41 decreases gradually, and the fragment is hardly detected above 560 °C, where the TG curve almost levels off.

IR analysis provides further information on the residual solids (Figure 4). After the treatment up to 400 °C, $\nu_{(Al-H)}$ bands are absent, but the $\nu_{(C-H)}$ bands are still observed at around 2900 cm⁻¹ (Figure 4 c). Upon heating up to 500 °C, neither $\nu_{(C-H)}$ nor $\nu_{(Al-H)}$ bands are detected (Figure 4 d).

IV. Discussion

The polymerization reactions during pyrolysis at the first pyrolysis stage (240-320 °C) to form a cross-linking structure is the key issue for (HAINⁱPr)₆ with relatively low molecular mass. In the temperature range of 240-320 °C, (HAINⁱPr)₆ polymerizes probably with its simultaneous volatilization. Differential thermal analysis (DTA) results of (HAINⁱPr)₆ revealed that (HAINⁱPr)₆ decomposed above 245 °C,²⁸ which is well consistent with the onset temperature of the large mass loss observed in the present TG results. The exothermic peak starting at 245 °C was observed in the DTA curve,²⁸ indicating that polymerization was detected by DTA (note that volatilization (such as boiling and sublimation) should give endothermic peaks in DTA curves).²⁹

Sauls *et al.*¹⁵ reported that heterolytic cleavage of the Al-N bonds in [(R₂AlNH₂)₃ (R=Me, Et) occurred even below ~150 °C. Thus, we also

consider the heterolytic cleavage of the Al-N bonds for the initiation of the pyrolysis of $(\text{HAlN}^i\text{Pr})_6$ at the first stage (240-320 °C). An $\text{R}_3\text{Al}:\text{NH}_3$ adduct thermally underwent polymerization by losing alkane (RH) to give $(\text{RAINH})_n$ via the formation of an intermediate $(\text{R}_2\text{AlNH}_2)_3$.^{9, 15} On the contrary, no organic compounds were observed during the pyrolysis of the precursor at the first stage. Thus, we consider the following reaction mechanism without the formation of organic compounds for the polymerization at this stage. The heterolytic Al-N bond cleavage in $(\text{HAlN}^i\text{Pr})_6$ results in the formation of nitrogen terminals $(=\text{PrN}:)$ (as shown in Figure 5), which were considered to attack aluminum atoms.^{15, 30} An attack of a nitrogen terminal to aluminum atom in another cage could lead to the opening of two cages that are linked by a newly-formed Al-N bond (Figure 5). This ring-opening reaction also results in the formation of a new nitrogen terminal that can further attack another aluminum atom. Repeated cleavage of the Al-N bonds in many cages and subsequent attacks to other cages should result in the formation of a polymeric structure. This polymerization mechanism involving no AlH groups is consistent with the IR results which revealed that a large portion of the AlH groups remained after the pyrolysis at 300 °C (Figure 4 b).

Figure 5

The formation of small fragments is also possible by the combination of multiple attacks of nitrogen terminals and Al-N bond cleavage localized at the same cage (or in a small area for polymerized parts). It is likely that such small species tend to aggregate,³¹ and the most probable species formed via aggregation is $(\text{HAlN}^i\text{Pr})_6$, that was continuously detected by TG-MS over 80 °C. When the precursor was converted into ceramic residue via two-step pyrolysis (1000 °C for 2 h and 1600 °C for 2 h) under Ar, 55 % of aluminum in the precursor was lost.¹⁹ Thus, the loss of $(\text{HAlN}^i\text{Pr})_6$ at this stage possibly via polymerization and volatilization appears to account for the loss of aluminum mainly.

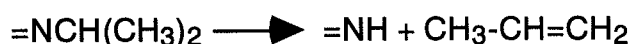
Formation of various hydrocarbons at the second stage (above 320 °C) indicates that the cleavage of the C-C and C-N bonds occurs. (HAIN/Pr)₆ is hardly detected at this stage (Figure 2 b), suggesting that the pyrolysis mechanism is completely changed at 320 °C.

The C₃H₆ formation should involve the C-N bond cleavage, and two possible mechanisms can be proposed based on the previous reports;

1) the homolytic C-N bond cleavage and the subsequent β elimination of a hydrogen radical:³²

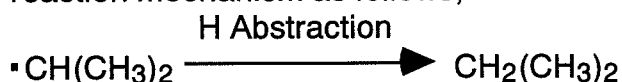


2) the concerted β elimination:³³



Generally, radicals play an important role for the thermal degradation of organic polymers above 300-400 °C.³⁴ In addition, the reactions of poly(carbosilanes)³⁵ and poly(silazanes)³⁶ at higher temperature ranges were reported to be radical processes. Furthermore, Distler *et al.*³⁷ observed radical formation during the pyrolysis of Al(NHⁿPr)₃. Thus, we assume that the radical processes were dominant in this temperature range, and the C₃H₆ formation was ascribed to the reaction path involving the homolytic C-N bond cleavage (reaction mechanism 1).

During the pyrolysis of poly(silazanes), radicals (R[•], H[•]) formed during pyrolysis were considered to abstract hydrogen atoms from SiH, NH, and CH groups.³⁶ Therefore, the formation of C₃H₈ can be interpreted based on the above reaction mechanism as follows;



The formation of hydrocarbons other than C₃H₆ and C₃H₈ should involve the homolytic C-C bond cleavage, and radical reactions (combination, β elimination, and hydrogen abstraction) are also considered to be involved.

The loss of the AlH groups up to 400 °C (Figure 4 c) and that of the CH groups up to 500 °C (Figure 4 d), therefore, could be attributed to hydrogen abstraction reactions involving radicals.

Finally we point out three characteristics of cage-type (HAINⁱPr)₆ as a preceramic material;

(1) Its oligomeric structure. Though its molecular mass (510) appears to be insufficient to suppress the volatilization completely, a part of (HAINⁱPr)₆ was involved in the polymerization at ≥ 240 °C.

(2) The cleavage of the Al-N bonds at low temperature to form a polymeric structure without deposition of aluminum metal. Although AlN formation via polymerization was also reported for cyclic (R₂AlNH₂)₃,¹⁵ simple pyrolysis of another ring-type compound (H₂AlNMe₂)₃ resulted in the formation of aluminum metals.^{38, 39} Thus, it is essential that the cleavage of Al-N bonds leads to the polymerization reaction, not to the Al metal deposition.

(3) The presence of three Al-N bonds per one aluminum or nitrogen atom. It is known that linear polymers normally show very low ceramic yields.¹ On the contrary, polymers containing rings or cages exhibit relatively high ceramic yields, because multiple bond cleavage is required for liberation of volatile molecules.¹ Similarly, the advantage of this cage-type compound is the presence of three Al-N bonds per one atom, which can suppress the liberation of volatile molecules to a certain extent.

V. Conclusions

We have demonstrated that poly(isopropyliminoalane) was converted into a ceramic residue via two pyrolysis stages, which were characterized by different gas evolution behavior. (HAINⁱPr)₆ was the main evolved gas at the first pyrolysis stage (240-320 °C), where the precursor was converted into the cross-linked structure. The proposed pyrolysis mechanism of the precursor at this stage involves the heterolytic Al-N bond cleavage and subsequent attack

of the nitrogen terminal formed to aluminum atoms in other cages. Besides evaporation, the formation of $(\text{HAlN}^i\text{Pr})_6$ during the polymerization is suggested. Various organic compounds formed at the second stage (320-560 °C), and the formation mechanisms of typical gases (C_3H_6 and C_3H_8) are proposed based on radical processes with homolytic C-N bond cleavage. These results suggest that the cage-type compounds can be effective preceramic materials, if their pyrolysis mechanisms involve polymerization for the conversion of the cross-linked structure at relatively low temperature.

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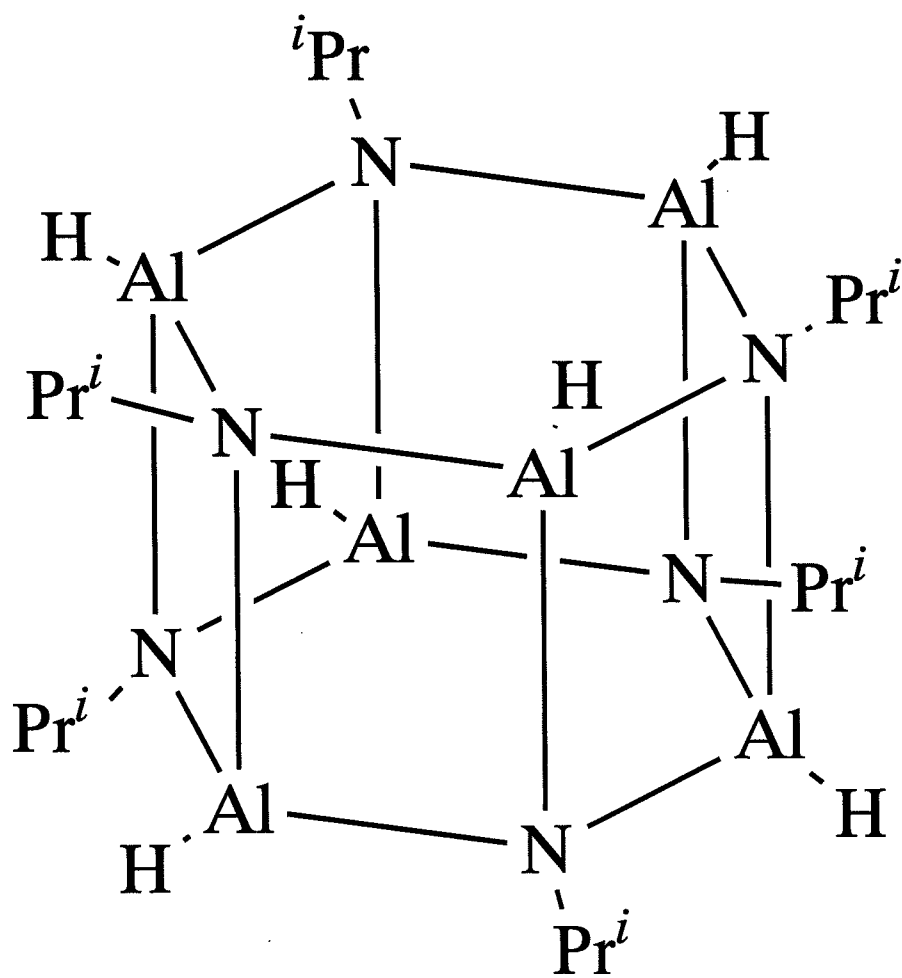


Figure 1. Idealized structure of $(\text{HAlN}^i\text{Pr})_6$.

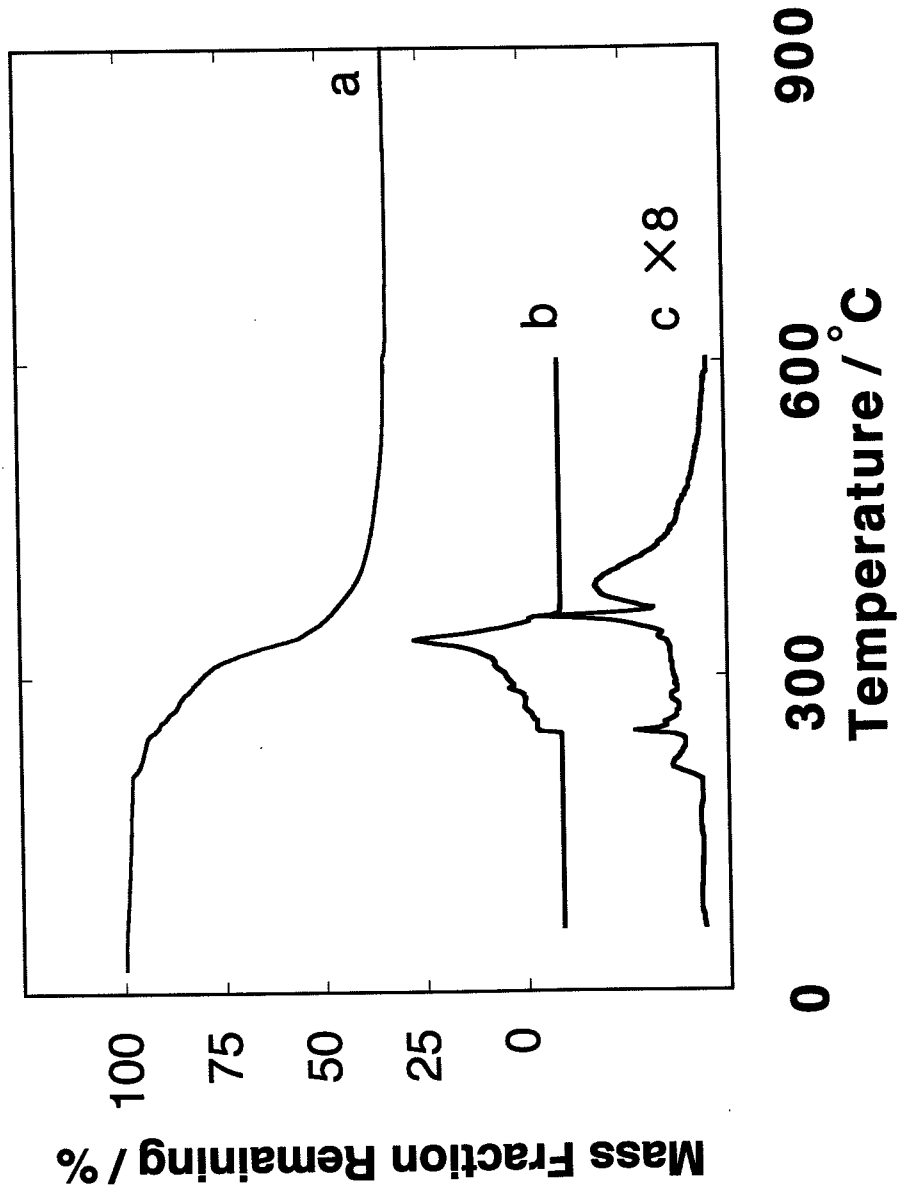


Figure 2. Typical TG curve of poly(isopropyliminoalane) under a He flow (a) with the variation in the intensity of fragments during simultaneous TG-MS analysis ((b) fragment at m/e 495; (c) fragment at m/e 41).

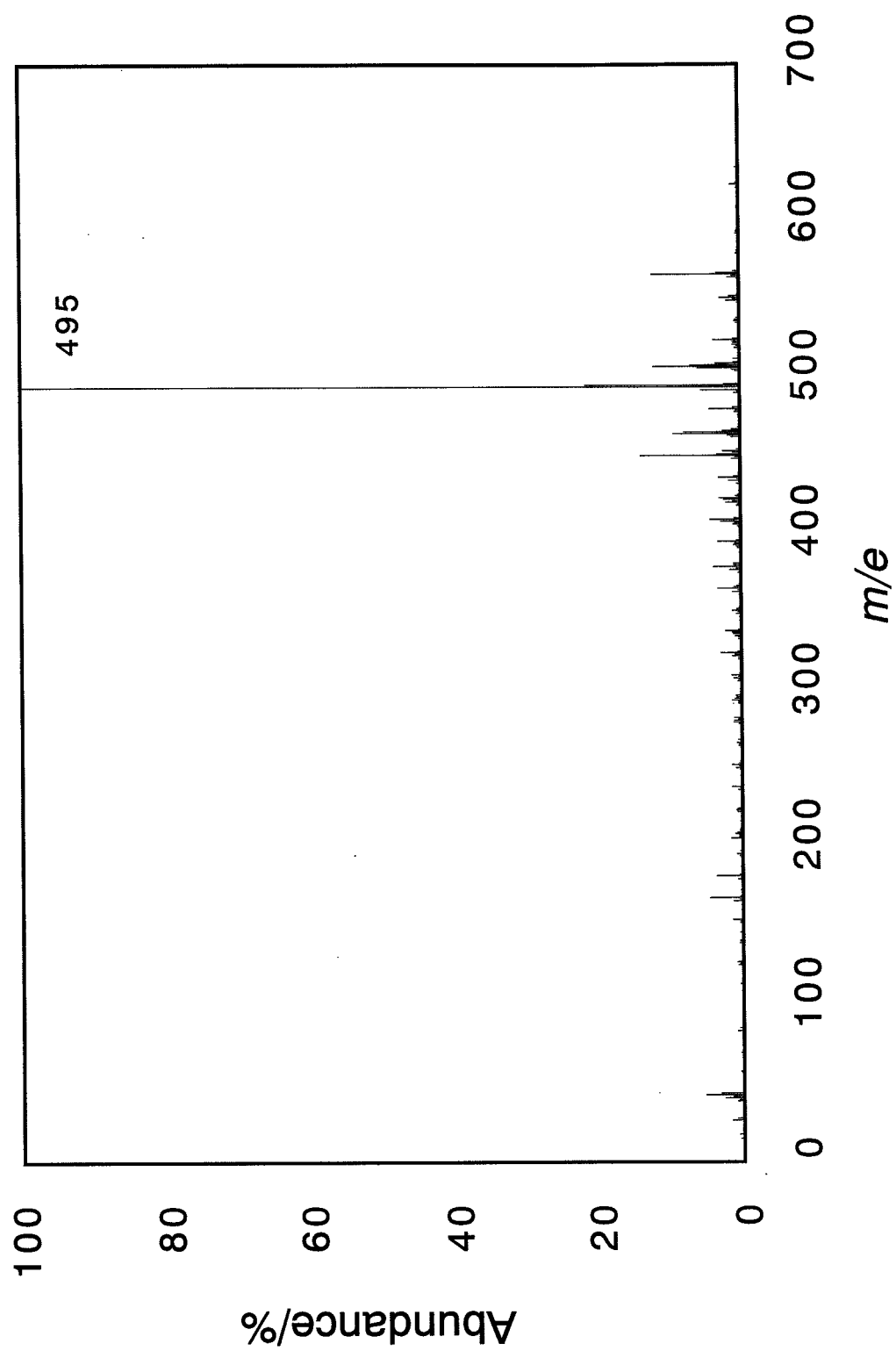


Figure 3. Mass spectrum collected during the pyrolysis of poly(isopropyliminoalane) at 300 °C.

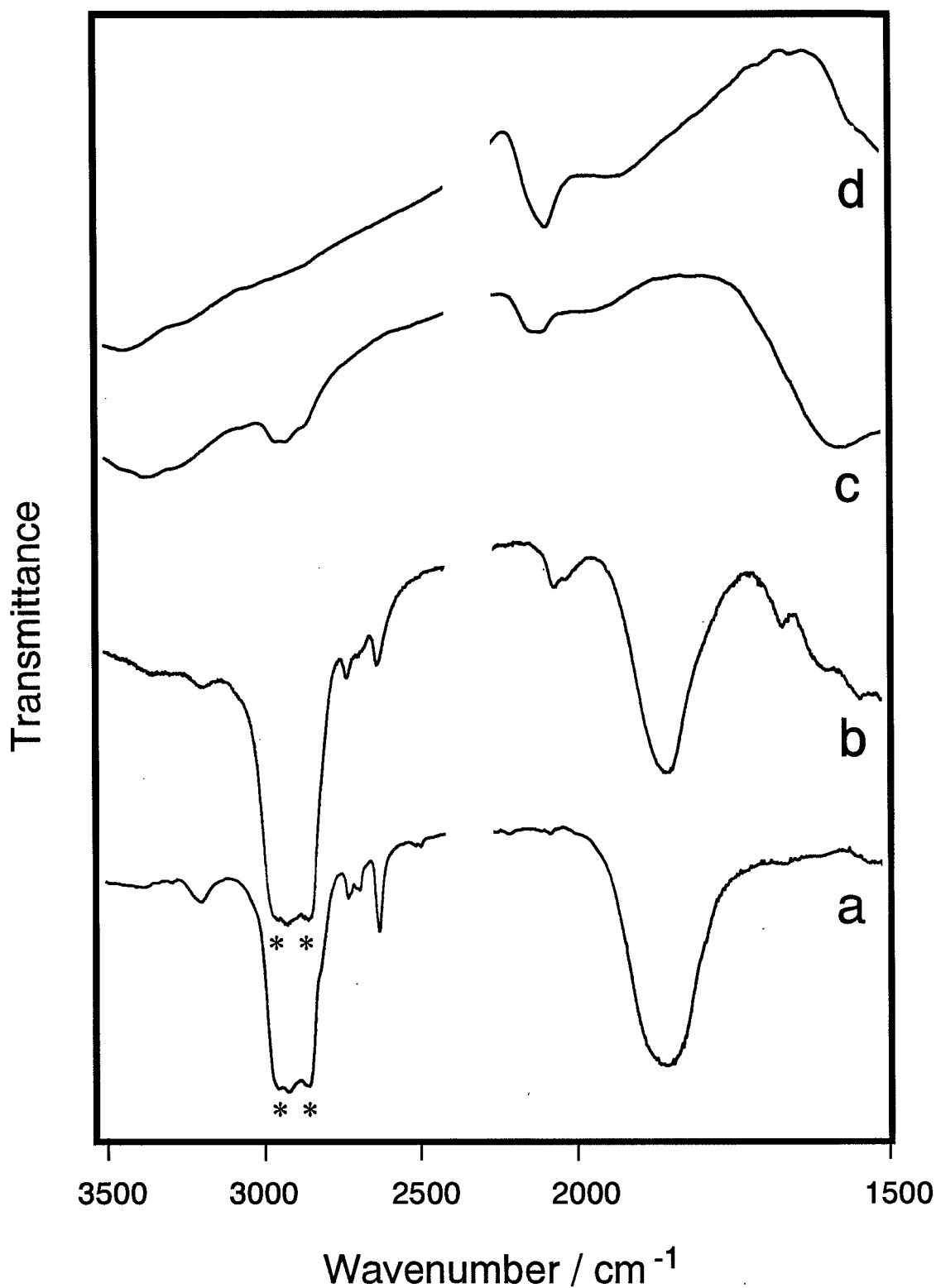


Figure 4. IR spectra of (a) poly(isopropyliminoalane) and (b)-(d) pyrolyzed poly(isopropyliminoalane) under a He flow (at (b) 300 °C, (c) 400 °C, and (d) 500 °C). (a) and (b) are collected using nujol technique (bands due to nujol are marked by asterisks), and (c) and (d) are collected using KBr-disk technique.

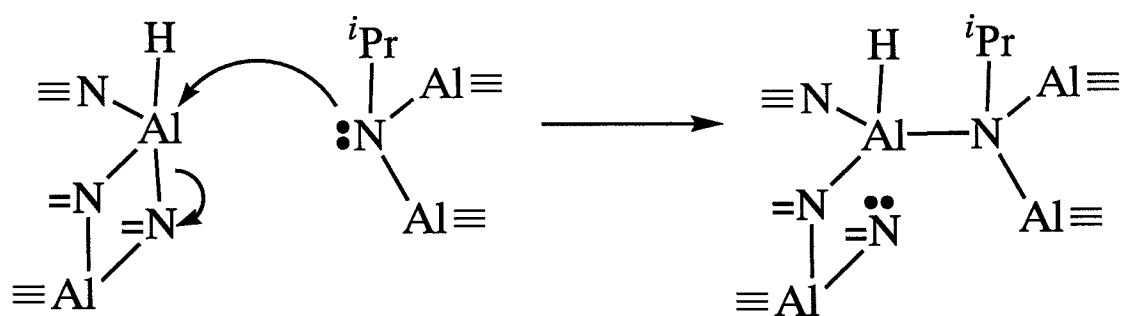
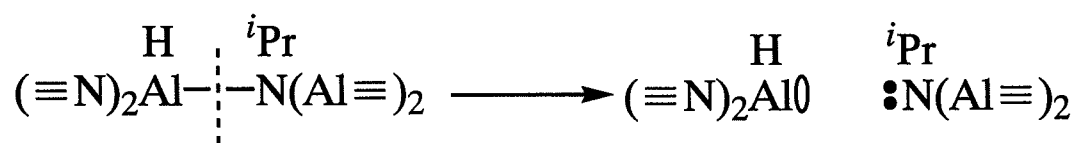


Figure 5. Schematic representation of the thermal polymerization mechanism of $(\text{HAIN}^i\text{Pr})_6$.

Preparation of a Soluble Precursor by an Aminolysis Reaction of $Zr(NEt_2)_4$ and Its Pyrolytic Conversion into ZrN

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A novel soluble precursor with a Zr-N-Zr backbone structure was prepared by an aminolysis reaction of $Zr(NEt_2)_4$ with Pr^iNH_2 . Pyrolysis of the precursor under NH_3-N_2 atmospheres led to the formation of ZrN as a main crystalline phase with a ceramic yield of 45.2%. Aggregated particles consisting of very minute particles with diameters of 50-300 nm were obtained.

Zirconium nitride (ZrN) exhibits beneficial properties, such as high melting point, hardness, excellent chemical durability and interesting optical properties.¹ Thin films of ZrN have been used for various applications, including wear-resistant coatings, diffusion barriers in integrated circuits and coating for solar control windows.²⁻⁴ ZrN powders have been prepared commercially by direct nitridation of metallic zirconium and carbothermal reduction of ZrO_2 under nitrogen.¹ Chemical vapor deposition (CVD) process has been investigated for the preparation of ZrN films.⁵

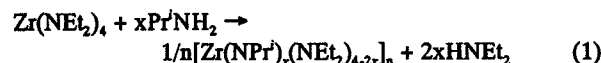
Pyrolytic conversion of inorganic and organometallic compounds into non-oxide ceramics provides an alternative route for the preparation of films and fibers via liquid phase, but it is required that the precursors are soluble or fusible for such applications.^{2,6} Extensive work has been reported on the preparation of carbides and nitrides of various main group elements, such as SiC, Si_3N_4 , BN, and AlN by this chemical route.^{2,6,7} This chemical route has also been developed for the preparation of transition metal nitrides.² Insoluble polymeric precursors with highly cross-linked structures were prepared by the ammonolysis of transition metal dialkylamides⁸ or *via* an electrochemical route,⁹ and were converted into transition metal nitrides *via* pyrolysis. Soluble precursors which were converted into TiN or Ti(N,C) powders, fibers and films *via* pyrolysis were prepared by the aminolysis of $Ti(NMe_2)_4$, since the formation of highly cross-linked structures was suppressed by the introduction of bulky organic groups into the precursors.¹⁰⁻¹² A soluble precursor which was converted into δ -NbN *via* pyrolysis was also prepared by an aminolysis reaction of $Nb(NEt_2)_4$.¹³ Bartlett investigated the aminolysis reactions of $Zr(NEt_2)_4$ with excess primary alkylamines ($Zr(NEt_2)_4:RNH_2=1:15$, R=Bu, Pr, Et),¹⁴ but the resultant polymeric products (proposed formula: $[Zr(NR)(NHR)_2]_n$) were insoluble in organic solvents. Only one soluble ZrN precursor $[(CH_3)_3Si]_2NH \cdot ZrCl_4$ was reported, but a corrosive HCl by-product evolved during the pyrolysis.¹⁵

Here we report the preparation of a precursor possessing a Zr-N-Zr backbone structure by an aminolysis reaction of tetrakis(diethylamino)zirconium ($Zr(NEt_2)_4$) with isopropylamine (Pr^iNH_2). Since isopropyl groups are branched, it is expected that the aminolysis reaction will lead to the formation

of a soluble product. The precursor was pyrolyzed under NH_3-N_2 atmospheres, and the pyrolyzed product was characterized by compositional analysis, X-ray powder diffraction analysis (XRD), and scanning electron microscopy (SEM).

All the procedures were performed under a protective nitrogen atmosphere using the standard Schlenk technique¹⁶ or a glove box filled with nitrogen. $Zr(NEt_2)_4$ was prepared and distilled (b.p. 120 °C at 0.1 mmHg) based on a previous report.¹⁷ The IR and ¹H NMR data were consistent with previous reports for $Zr(NEt_2)_4$.¹⁸ ¹H NMR (ppm): 1.11 (triplet, $-CH_2CH_3$), 3.34 (quadruplet, $-CH_2CH_3$); IR (cm^{-1}): 1000, 1152 ($\nu(NC_2)$), 550-578 ($\nu(Zr-N)$). Elemental analysis exhibited an empirical formula of $ZrN_{4.3}C_{15.6}H_{40.2}$, which approximately corresponds to $Zr(NEt_2)_4$.

The precursor was prepared by the reaction of $Zr(NEt_2)_4$ with Pr^iNH_2 (Zr : Pr^iNH_2 = 1:5) according to an ideal reaction expressed by Eq. (1).



$Zr(NEt_2)_4$ was dissolved in toluene in a three-neck flask, and Pr^iNH_2 in toluene was slowly dropped into the $Zr(NEt_2)_4$ solution at about 5 °C with stirring. The mixed solution was stirred for 2 h at about 5 °C. Then the resultant solution was gradually heated, and finally refluxed for 16 h. An orange solid, which was soluble in benzene and toluene, was obtained after the separation of a small amount of insoluble yellow solid by filtration and removal of toluene under a reduced pressure.

The ¹H NMR spectra of the precursor, $Zr(NEt_2)_4$, and Pr^iNH_2 are shown in Figure 1. In the ¹H NMR spectrum of the precursor, a quadruplet at 3.34 ppm due to the $-CH_2CH_3$ of $Zr(NEt_2)_4$ is hardly detected, and many weak signals appear at 3.00-4.80 ppm. In the region for a triplet at 1.11 ppm (for $Zr(NEt_2)_4$) and a doublet at 0.90 ppm (for Pr^iNH_2), some doublets and unresolved peaks are observed at 1.12-1.86 ppm. The

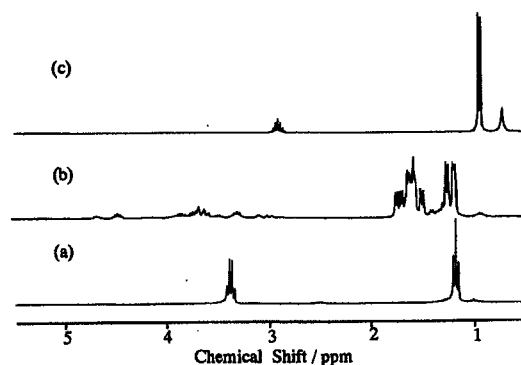
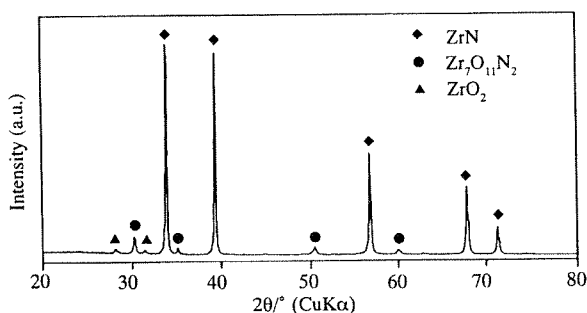


Figure 1. ¹H NMR spectra of (a) $Zr(NEt_2)_4$, (b) the precursor, and (c) Pr^iNH_2 (C_6D_6 , 270 MHz).

Table 1. Ceramic yield and characteristics of the product pyrolyzed under $\text{NH}_3\text{-N}_2$

Ceramic yield / mass% ^a	45.2
Elemental analysis / mass%	
Zr ^b	81.2
N ^c	11.6
C ^c	0.4
O ^c	3.1
Total	96.3
Empirical formula	$\text{ZrN}_{0.93}\text{C}_{0.03}\text{O}_{0.21}$
Lattice parameter / nm ^d	0.4576

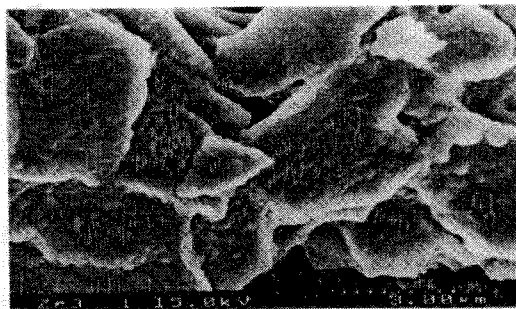
^a The ceramic yield (Y) was calculated from the masses of the precursor (M_p) and the pyrolyzed residue (M_r), $Y=(M_r/M_p)\times 100$. ^b The amount was determined by inductively coupled plasma emission spectroscopy. ^c The amounts were measured by using LECO TC-436 and CS-444LS instruments. ^d The lattice parameter was calculated by the non-linear least squared method.

**Figure 2.** XRD pattern of the product pyrolyzed under $\text{NH}_3\text{-N}_2$.

integrated intensity ratio of the signals at 1.12–1.86 ppm to those at 3.00–4.80 ppm is about 6, corresponding to the proton number ratio of CH_3 to CH in the $-\text{CH}(\text{CH}_3)_2$ group. All of these observations indicate that the aminolysis reaction of $\text{Zr}(\text{NEt}_2)_4$ with Pr^iNH_2 occurs and isopropyl groups with various environments are present in the precursor. Since no $\nu(\text{N-H})$ and $\delta(\text{N-H})$ bands were observed in the IR spectrum of the precursor, it is reasonable to consider that the nitrogen atoms in the NPr^i groups of the precursor are mainly present as $\text{Zr-N}(\text{Pr}^i)\text{-Zr}$ imido-bridges, which is different from the assumed environment of nitrogen in the polymeric compound $[\text{Zr}(\text{NR})(\text{NHR})_2]_n$ reported by Bartlett.¹⁴ In addition, although the presence of Et groups can not be confirmed in the ^1H NMR spectrum of the precursor due to overlapping of signals, a weak shoulder band assignable to $\nu_s(\text{CH}_2)$ mode of the ethyl groups at around 2829 cm^{-1} ¹⁹ was present in the IR spectrum obtained with a hexachloro-1,3-butadiene technique, suggesting that a small amount of NEt_2 groups remains in the precursor (The other three $\nu(\text{C-H})$ bands due to ethyl groups show wavenumbers similar to those of isopropyl groups).

Pyrolysis of the precursor under NH_3 flow at $600\text{ }^\circ\text{C}$ for 2 h and subsequently under N_2 at $1350\text{ }^\circ\text{C}$ for 8 h gave a yellow-gray residue with a ceramic yield of 45.2%. The characteristics of the product are shown in Table 1. The amount of carbon is very small (0.4 mass%), while 3.1% of oxygen, which was probably introduced during the pyrolysis, are present in the product.

The pyrolysis of the precursor under $\text{NH}_3\text{-N}_2$ leads to the formation of a well-crystallized NaCl-type compound (Figure 2). However, some weak peaks assignable to $\text{Zr}_7\text{O}_{11}\text{N}_2$ and ZrO_2 are also observed,²⁰ which is consistent with the presence of oxygen in the product. It has been reported that ZrN , ZrC and ZrO all possess NaCl-type structures with the lattice

**Figure 3.** Scanning electron micrograph of the product pyrolyzed under $\text{NH}_3\text{-N}_2$.

parameters of 0.4577, 0.4693 and 0.4620 nm, respectively.²⁰ ZrN can form solid solution with ZrC ,²¹ and the formation of a $\text{Zr}(\text{N,C,O})$ solid solution with an NaCl-type structure was also reported.²² However, the lattice parameter of the NaCl-type compound in the present study is 0.4576 nm, very close to that of ZrN , indicating that the crystallized NaCl-type compound should be cubic ZrN .

The morphology of the product was investigated using SEM (Figure 3). Aggregated particles consisting of very minute particles with diameters of 50–300 nm are observed on the surface of the pyrolyzed product. The calculated mean crystallite diameter based on the XRD pattern using the Scherrer equation was 53 nm, consistent with the SEM observation.

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Synthesis of a Soluble Precursor Possessing an Nb–N Backbone Structure and Its Pyrolytic Conversion into Niobium-Based Ceramics

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Synthesis and pyrolysis of a soluble precursor possessing an Nb–N backbone structure were investigated. The precursor was prepared by aminolysis reaction of tetrakis(diethylamido)niobium with isopropylamine. The precursor was soluble in benzene, and had a polymeric structure possessing Nb–N–Nb imido-bridges. The precursor was pyrolyzed under $\text{NH}_3\text{--N}_2$ (at 600 °C for 2 h under NH_3 and subsequently at 1350 °C for 8 h under N_2) and Ar (at 1500 °C for 2 h) atmospheres. $\delta\text{-NbN}$ was obtained as a main crystalline phase after the pyrolysis of the precursor under $\text{NH}_3\text{--N}_2$, whereas pyrolysis of the precursor under Ar led to the formation of NbC as the only crystalline phase. More than 90% of niobium which was present in the precursor remained in both of the pyrolyzed products.

Niobium nitride has attracted considerable attention because of its desirable properties; these include hardness, thermal stability, and, particularly in the case of cubic form, superconductivity.¹ Niobium nitride has several phases: $\delta\text{-NbN}$, $\gamma\text{-NbN}$, $\varepsilon\text{-NbN}$, $\beta\text{-Nb}_2\text{N}$, and Nb_3N_4 . However, all of these phases except $\delta\text{-NbN}$ have hexagonal structures.^{2,3} The structure of $\delta\text{-NbN}$ is B1(NaCl)-type where the bonding character between Nb and N is metallic.¹ The $\delta\text{-NbN}$ is a superconductor with T_c of 17.3 K, and has been used in various devices such as dc-superconducting quantum interference devices, Josephson junctions, and switches for pulsed power applications.^{4,5} The conventional synthetic procedure of NbN is direct nitridation of Nb metal at high temperature and high N_2 pressure.^{1,3} Chemical vapor deposition (CVD) processes have also been widely investigated for the preparation of NbN films.^{2,6–8}

Pyrolytic conversion of precursors has been widely applied to the preparation of carbides and nitrides of various main group elements and transition metals, such as SiC, Si_3N_4 , BN, AlN, and TiN.^{9–12} Although this chemical route provides a method for the preparation of non-oxide ceramics with desirable shapes, such as coatings and fibers, it is required for such applications that the precursors are soluble or fusible.¹⁰ NbN has been prepared by direct ammonolysis of the niobium halides or niobium dialkylamides and subsequent pyrolysis of the resultant polymeric compounds.^{13–15} A NbN precursor has also been prepared recently by an electrochemical route in which metallic niobium was anodically dissolved in a liquid- NH_3 containing NH_4Br solution.^{16,17} However, since the precursors prepared by these techniques have highly cross-linked structures, they are insoluble in an

organic solvent such as pentane,¹⁵ pyridine,¹⁵ and acetonitrile.^{16,17} As far as we know, the synthesis and pyrolytic conversion of soluble NbN precursors have not been reported.

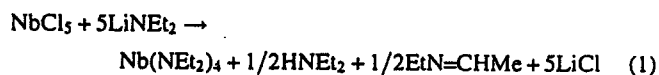
Aminolysis reactions of a number of transition metal dialkylamides of group 4 ($\text{M}(\text{NR}_2)_4$), typically $\text{Ti}(\text{NR}_2)_4$ ($\text{R} = \text{Me}$ or Et), with primary amine $\text{R}'\text{NH}_2$ have been extensively investigated.^{18–20} Since primary amines are bifunctional, the aminolysis reactions usually occur with the formation imido-bridge (M--N--M) structures in the aminolysis products. This chemical route provides a possible way to prepare soluble precursors because the formation of highly cross-linked structures can be suppressed by the introduction of organic groups into the aminolysis products. However, insoluble products will form if the steric hindrance of R' groups is too small.¹⁸ The reaction of $\text{Ti}(\text{NET}_2)_4$ with Pr^nNH_2 gave an insoluble $\text{Ti}(\text{NPr}^n)_2$, while the reaction with Bu^nNH_2 led to the formation of a soluble product with a proposed formula of $\text{Ti}_x(\text{NBu}^n)_{2x-2}(\text{NET}_2)_4$.¹⁸ A number of aminolysis products have been applied to the preparation of TiN or $\text{Ti}(\text{N,C})$.^{19–21} However, no aminolysis reactions of transition metal dialkylamides of group 5 with a primary amine and the pyrolytic conversion of the aminolysis products have been studied yet.

In this research, a precursor possessing an Nb–N backbone structure was prepared by an aminolysis reaction of tetrakis(diethylamido)niobium ($\text{Nb}(\text{NET}_2)_4$) using isopropylamine (Pr^iNH_2). Since isopropyl groups are branched, it is expected that the aminolysis reaction of $\text{Nb}(\text{NET}_2)_4$ will lead to the formation of a soluble product. Pyrolytic conversion of the precursor was investigated, and the pyrolyzed products were characterized by compositional analysis, X-ray powder diffraction (XRD) and scanning electron microscopy (SEM).

Experimental

All the procedures were performed under a protective nitrogen atmosphere using the standard Schlenk technique²² or in a glove box filled with nitrogen. The solvents, *n*-pentane and benzene, were freshly distilled over sodium/benzophenone prior to use. Diethylamine and isopropylamine were freshly distilled over potassium hydroxide prior to use. Niobium chloride (NbCl₅) was used as received.

1 Synthesis of Nb(NEt₂)₄. Tetrakis(diethylamido)niobium (Nb(NEt₂)₄) was prepared according to the following reaction based on the previous report:²³



Distillation of the obtained red viscous liquid gave a purple-brown viscous liquid product (bp 120 °C at 13.3 Pa). The IR spectrum (Fig. 1) of the distilled product shows the presence of a $\nu(\text{Nb-N})$ band at 583 cm⁻¹ (as shown by arrow) and two $\nu(\text{NC}_2)$ bands at 1001 and 1154 cm⁻¹, consistent with those in the previous report for Nb(NEt₂)₄.²⁴ Elemental analysis exhibits an empirical formula of NbN_{4.1}C_{16.0}H_{38.2} (Table 1), which approximately corresponds to Nb(NEt₂)₄. The mass spectrum of the product was consistent with a previous report for the formation of Nb(NEt₂)₄,²⁵ m/z (M⁺, EI), 381 (Nb(NEt₂)₄⁺, 20), 380 (Nb(NEt₂)₃[NEt(C₂H₄)]⁺, 32), 352 (Nb(NEt₂)₃(NEt)⁺, 43), 337 (Nb(NEt₂)₃(NCH₂)⁺, 43), 276 (Nb[NEt(CH=CH₂)₂(NEt)]⁺, 58), and 58 (EtNCH₃⁺, 100).

Table 1. Compositional Characteristics of the Nb(NEt₂)₄ and the Precursor

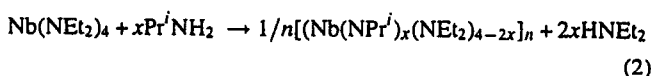
	Elemental analysis/mass%					Empirical formula
	Nb	N	C	H	Total	
Nb(NEt ₂) ₄	24.2	14.8	49.9	9.9	98.8	NbN _{4.0} C _{16.0} H _{38.2}
Precursor	35.5	14.2	37.6	8.1	95.4	NbN _{2.6} C _{8.1} H _{21.1}

However, although Nb(NEt₂)₄ does not show any signal in the NMR spectrum because of its paramagnetic property, the ¹H NMR spectrum of this viscous product showed the presence of small amounts of two diamagnetic compounds, tris(diethylamido)ethyl-imidoniobium (Et₂N)₃Nb(=NEt) and tris(diethylamido)azapentane-

2,3-diylniobium (Et₂N)₃Nb(EtNCHMe)²⁶ (The ¹H NMR data obtained in this study are shown in References). The presence

of (Et₂N)₃Nb(=NEt) and (Et₂N)₃Nb(EtNCHMe) as minor components in distilled Nb(NEt₂)₄ was also reported previously.^{7,26} Because only small amounts of (Et₂N)₃Nb(=NEt) and (Et₂N)₃Nb(EtNCHMe) were present in the viscous product according to the elemental analysis, we will hereafter refer to the viscous product simply as Nb(NEt₂)₄, which was used as a starting material of the precursor.

2 Synthesis of a Precursor. The polymeric precursor possessing an Nb-N backbone structure was prepared based on a previous report,²⁷ by the reaction of Nb(NEt₂)₄ with an excess of isopropylamine (Nb : Pr^{*i*}NH₂ = 1 : 5). An ideal reaction can be expressed by Eq. 2:



Nb(NEt₂)₄ was dissolved in 30 mL of benzene in a 100 mL three-necked flask, and Pr^{*i*}NH₂ in 20 mL of benzene was slowly dropped into the Nb(NEt₂)₄ solution at about 10 °C with stirring. The mixed solution was stirred for 2 h at 10 °C. Then the resultant solution was gradually heated, and finally refluxed at 78 °C for 16 h. A dark brown solid, which was completely soluble in benzene, was obtained after benzene was removed under reduced pressure.

3 Pyrolysis. The precursor was pyrolyzed in a tube furnace. About 0.5 g of precursor was placed in an Al₂O₃ boat, which was then introduced into an Al₂O₃ tube filled with Ar or NH₃. For pyrolysis under NH₃-N₂, the precursor was first heated at 600 °C

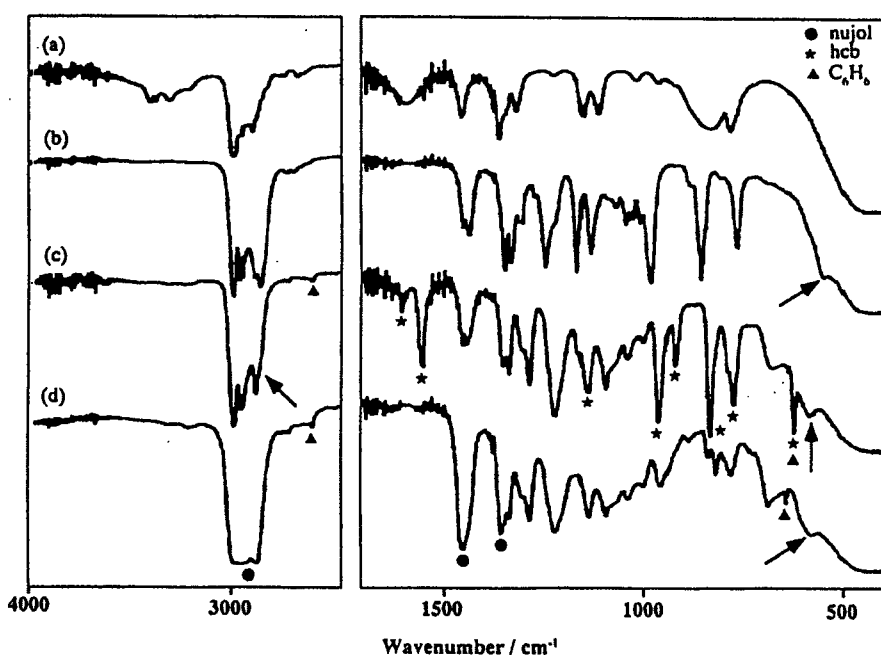


Fig. 1. IR spectra of (a) Pr^{*i*}NH₂, (b) Nb(NEt₂)₄, (c) precursor (hcb technique), and (d) precursor (nujol technique). The meaning of the arrows is prescribed in the text.

for 2 h under NH_3 with a flow rate of 30 mL min^{-1} , and cooled to room temperature. Then, the resultant product was heated again at 1350°C for 8 h under N_2 (100 mL min^{-1}). For pyrolysis under Ar, the precursor was heated at 1500°C for 2 h with a flow rate of 100 mL min^{-1} .

4 Analyses. The precursor was characterized by infra-red spectroscopy (IR, Perkin-Elmer FTIR-1640, with nujol technique and hexachloro-1,3-butadiene (hcb) technique). The amounts of nitrogen, carbon, and hydrogen in the precursor were measured by using a Perkin-Elmer PE2400 instrument. The pyrolysis behavior of the $\text{Nb}(\text{NEt}_2)_4$ and the precursor was investigated by thermogravimetry-mass spectrometry (TG-MS) (Shimadzu TGA-50 thermobalance coupled with a Shimadzu QP1100EX quadrupole mass spectrometer via a stainless capillary). In order to identify the evolved gases clearly, $\text{Nb}(\text{NEt}_2)_4$ and the precursor were pyrolyzed using a tube furnace under a He flow; the evolved gases trapped using liquid nitrogen in a certain temperature range were identified by gas chromatography-mass spectrometry (GC-MS) (Hewlett-Packard Model 5890 Series II Gas Chromatograph coupled with a 5971A Mass Selective Detector; the separation was performed on a capillary column (Chrompack Pora Plot Q, for the gases from $\text{Nb}(\text{NEt}_2)_4$) or a capillary column (GL Science TC-5, for the gases from the precursor)). The pyrolyzed products were analyzed by X-ray powder diffraction (XRD, $\text{Cu K}\alpha$; Mac Science MXP³). The lattice parameters of the pyrolyzed products were calculated by the non-linear least-squares method. The amounts of nitrogen, oxygen and carbon in the pyrolyzed products were measured by using LECO TC-436 and CS-444LS instruments. The amounts of niobium in the precursor and the pyrolyzed products were determined by inductively coupled plasma emission spectroscopy (ICP, Nippon Jarrell Ash ICAP-575 II), after the samples were dissolved with a mixed solution of 10 mL of HF, 5 mL of H_2SO_4 , and 5 mL of HNO_3 at 200°C for 2 h. The morphology of the pyrolyzed products was investigated by scanning electron microscopy (SEM, Hitachi S4500-S).

Results and Discussion

1 Preparation of a Soluble Precursor via Aminolysis of $\text{Nb}(\text{NEt}_2)_4$. The IR spectrum of the precursor, as well as those of the $\text{Nb}(\text{NEt}_2)_4$ and isopropylamine, are shown in Fig. 1. The IR spectrum of $\text{Nb}(\text{NEt}_2)_4$ shows four strong (C-H) bands at 2963, 2926, 2865, and 2834 cm^{-1} , which are assigned to $\nu_{\text{as}}(\text{CH}_3)$, $\nu_{\text{as}}(\text{CH}_2)$, $\nu_s(\text{CH}_3)$, and $\nu_s(\text{CH}_2)$ modes of the ethyl groups respectively (Fig. 1b).²⁸ On the other hand, the IR spectrum of the precursor (Fig. 1c) shows three strong (C-H) bands assignable to $\nu_{\text{as}}(\text{CH}_3)$, $\nu(\text{CH})$, and $\nu_s(\text{CH}_3)$ modes of isopropyl group at 2960, 2908, and 2861 cm^{-1} , respectively; only a weak shoulder band assignable to $\nu_s(\text{CH}_2)$ modes of ethyl groups is present at around 2832 cm^{-1} (as shown by the arrow).²⁸ In addition, in the spectrum of the precursor, the bands at 1155 and 1111 cm^{-1} due to $-\text{CH}(\text{CH}_3)_2$ skeletal bands²⁸ are clearly observed. All of these observations indicate that a large portion of the NEt_2 (and NEt) groups in the starting material has been substituted with NPr^i groups. Besides, in the IR spectrum of the precursor (Fig. 1c), the $\nu(\text{Nb}-\text{N})$ band of $\text{Nb}(\text{NEt}_2)_4$ (at 583 cm^{-1} as shown by arrow in Fig. 1b) disappears, and a new band assignable to $\nu(\text{Nb}-\text{N})$ appears at 613 cm^{-1} (as shown by the arrow). Because no band is observed at the

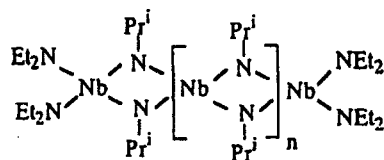
typical frequency region of $\nu(\text{N}-\text{H})$ ($3300\text{--}3500 \text{ cm}^{-1}$)²⁸ in the spectrum of the precursor, Nb-N-Nb imido-bridges should have formed.

The elemental analysis results of the precursor are shown in Table 1. The N:C:H molar ratio of the precursor is 1:3.1:8.1, close to that of NPr^i group (1:3:7), indicating that a large portion of the NEt_2 groups (1:4:10) in $\text{Nb}(\text{NEt}_2)_4$ has been substituted with NPr^i groups. The N/Nb molar ratio decreases from 4 for the $\text{Nb}(\text{NEt}_2)_4$ to 2.6 for the precursor, which is consistent with the IR results showing that the nitrogen atoms in the NPr^i groups are present as Nb-N-Nb imido-bridges. The empirical formula of $\text{NbN}_{2.6}\text{C}_{8.1}\text{H}_{21.1}$ indicates that, besides the NPr^i groups, a small amount of NEt_2 groups should remain in the precursor (assuming that N and C belong to either NPr^i or NEt_2 groups), also consistent with the IR results. Bradley et al.¹⁸ reported that the aminolysis of $\text{Ti}(\text{NEt}_2)_4$ with *n*-butylamine led to the formation of a soluble polymer due to the presence of a small amount of NEt_2 groups as chain stoppers. Hence, it is also probable that the presence of a small amount of NEt_2 groups as chain stoppers led to the formation of a soluble polymer with a postulated structure as shown in Scheme 1.

2 Pyrolysis of the Precursor. The pyrolysis behavior of the precursor was investigated by using TG-MS. The pyrolysis behavior of $\text{Nb}(\text{NEt}_2)_4$ was also studied for comparison. The TG curves and the temperature profiles of the selected fragments are shown in Fig. 2. The ceramic yields of $\text{Nb}(\text{NEt}_2)_4$ and the precursor up to 900°C are 37 and 57% respectively, indicating the advantage of the polymeric structure of the precursor.

In the TG curve of the $\text{Nb}(\text{NEt}_2)_4$, a sharp mass loss is observed in the temperature range of ca. $160\text{--}280^\circ\text{C}$. Gas (in the trap-tube), liquid (near the outlet of the tube furnace and in the trap-tube), and a small amount of yellow solid (near the outlet of the tube furnace) were obtained during the pyrolysis of the $\text{Nb}(\text{NEt}_2)_4$ using a tube furnace in the corresponding temperature range (ca. $160\text{--}280^\circ\text{C}$). GC-MS (for gas) and $^1\text{H NMR}$ (for liquid) analyses showed that C_2H_4 , C_2H_6 , C_3H_6 , C_4H_8 , CH_3CN , and HNEt_2 were the main species evolved. ICP analysis showed that the condensed yellow solid contained Nb.

The temperature profiles for the pyrolysis of the $\text{Nb}(\text{NEt}_2)_4$ show that fragments at m/z 58 (arising from HNEt_2), m/z 27 (arising from C_2H_4 and C_2H_6) and m/z 41 (arising from higher hydrocarbons (C_nH_{2n} and $\text{C}_n\text{H}_{2n+2}$, $n \geq 3$; e.g., C_3H_6 , C_4H_8 , and C_4H_{10}) and CH_3CN) are clearly detected in the temperature range of ca. $160\text{--}280^\circ\text{C}$ (Fig. 2a). Et_2NH and C_2H_4 were reported as the major evolution gases during the pyrolysis of $\text{Nb}(\text{NEt}_2)_4$ at 220°C .²⁹ The main py-



Scheme 1. The postulated structure of the precursor.

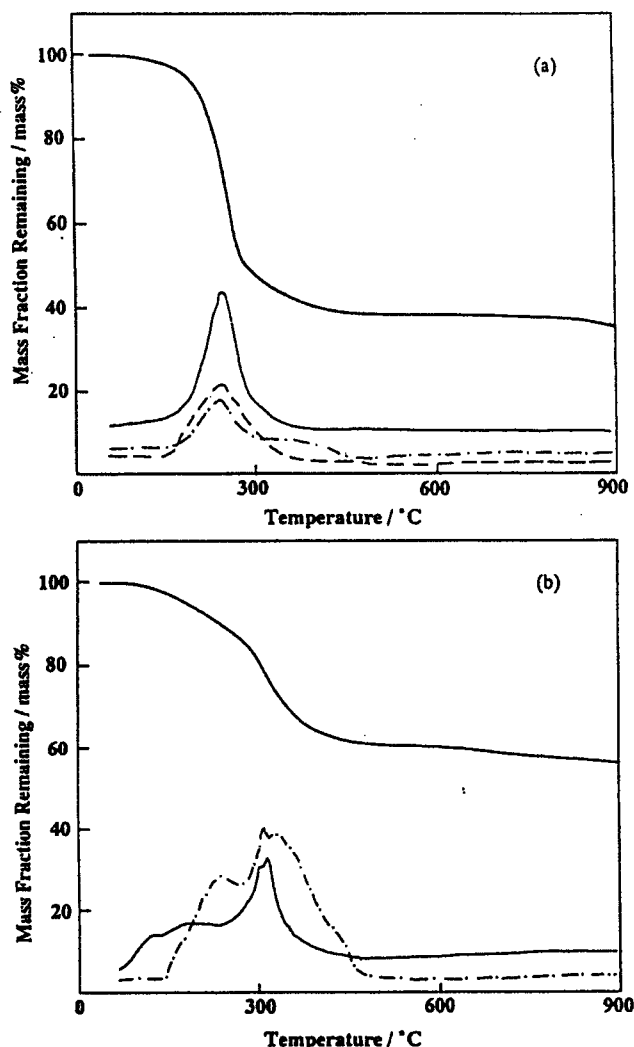
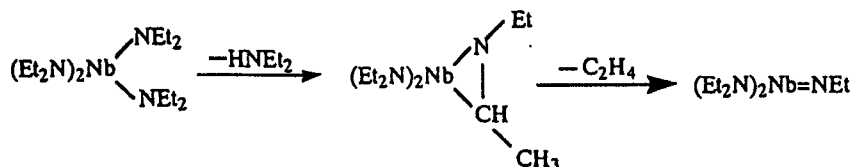


Fig. 2. TG-MS analysis of $\text{Nb}(\text{NEt}_2)_4$ and the precursor under He. (a) The TG curve of $\text{Nb}(\text{NEt}_2)_4$; the fragment at $m/z = 58$ arising from HNEt_2 (—); the fragment at $m/z = 27$ arising from C_2H_4 and C_2H_6 (— —); the fragment at $m/z = 41$ arising from higher hydrocarbons (C_nH_{2n} and $\text{C}_n\text{H}_{2n+2}$, $n \geq 3$) and CH_3CN (- - -). (b) The TG curve of the precursor; the fragment at $m/z = 44$ arising from Pr^iNH_2 (—); the fragment at $m/z = 41$ arising from hydrocarbons (C_nH_{2n} and $\text{C}_n\text{H}_{2n+2}$, $n \geq 3$) and CH_3CN (- - -).

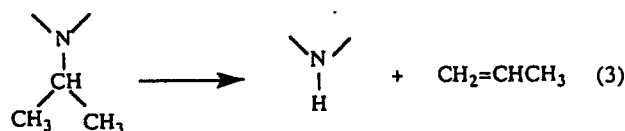
pyrolysis processes probably involve the elimination of the NEt_2 groups through the transfer of hydrogen atom from an NEt_2 group to another one, leading the subsequent formation of a three-membered metallacycle intermediate containing a Nb—C bond (see Scheme 2). Then C_2H_4 was released from the three-membered metallacycle intermediate via the Nb—C bond cleavage. The formation of such a three-mem-



Scheme 2. The main pyrolysis processes for the pyrolysis of $\text{Nb}(\text{NEt}_2)_4$ in the temperature range of ca. 160—ca. 280 °C.

bered metallacycle compound has been reported previously for the pyrolysis of diethylamido complexes of Nb, Ta, V, and Ti.^{25,30–32}

On the other hand, a large mass loss is observed at the temperature below ca. 500 °C in the TG curve of the precursor (Fig. 2b). C_3H_6 , C_4H_8 , CH_3CN , and Pr^iNH_2 were the main species evolved during the pyrolysis of the precursor using the tube furnace below 500 °C. The temperature profiles of the fragments at m/z 44 (arising from Pr^iNH_2) and m/z 41 (arising from hydrocarbons (C_nH_{2n} and $\text{C}_n\text{H}_{2n+2}$, $n \geq 3$; e.g., C_3H_6 , C_4H_8 , and C_4H_{10} and acetonitrile CH_3CN) are shown in Fig. 2b. The fragment at m/z 44 in the temperature range of ca. 250—ca. 350 °C shows that Pr^iNH_2 evolved at this relatively high temperature range. (The evolution of Pr^iNH_2 near room temperature is probably due to the hydrolysis of the precursor with a small amount of water in the TG-MS equipment. The precursor is more air-sensitive than $\text{Nb}(\text{NEt}_2)_4$). Laine et al. have reported that the pyrolysis of a TiN precursor with Ti—N(Pr^i)—Ti imido-bridges led to the evolution of C_3H_6 through the direct cleavage of the C—N bond with transfer of β -hydrogen to the nitrogen atom (reaction 3).²⁰ Since the present precursor possesses M—N(Pr^i)—M imido-bridges which are very similar to that reported by Laine et al., C_3H_6 , one of the main evolved species, most likely arises from the direct cleavage of the C—N bond via reaction 3, which is different from the formation mechanism of C_2H_4 from $\text{Nb}(\text{NEt}_2)_4$ via the metallacycle intermediate.



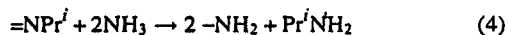
Pyrolysis of the precursor under NH_3 flow at 600 °C for 2 h, and subsequently under N_2 at 1350 °C for 8 h gave a yellow-gray residue, while a lavender-gray residue was obtained after the pyrolysis under Ar flow at 1500 °C for 2 h. Table 2 shows the ceramic yields, compositional characteristics and the lattice parameters of the pyrolyzed products. The ceramic yields of the precursor are 39.2 and 38.0% for the pyrolyses under NH_3 — N_2 and Ar flow, respectively. Based on the ceramic yields, the amount of niobium in the precursor, and those in the pyrolyzed products, it can be estimated that 92.7 and 91.1% of the niobium present in the precursor remain in the products pyrolyzed under NH_3 — N_2 and Ar, respectively. This should be ascribed to the fact that the precursor possesses double niobium—nitrogen bridges as shown in Scheme 1, which makes the degradation of the precursor into smaller volatile Nb-containing species difficult.

After the pyrolysis under Ar flow, a considerable amount

Table 2. Ceramic Yields and Characteristics of the Products Pyrolyzed under $\text{NH}_3\text{-N}_2$ (at 600 °C for 2 h under NH_3 , and then at 1350 °C for 8 h under N_2) and Ar (at 1500 °C for 2 h)

Atmosphere	$\text{NH}_3\text{-N}_2$	Ar
Ceramic yield/mass%	39.2	38.0
Loss of niobium/%	7.3	8.9
Elemental analysis/mass%		
Nb	83.9	85.1
N	11.2	0.1
C	0.8	16.2
O	3.4	0.3
Total	99.3	101.6
Empirical formula	$\text{NbN}_{0.89}\text{C}_{0.08}\text{O}_{0.23}$	$\text{NbN}_{0.01}\text{C}_{1.47}\text{O}_{0.02}$
Lattice parameter/nm	0.4394	0.4472

of carbon remains in the residue, and the amount of nitrogen is very small (0.1 mass%). In contrast, a considerable amount of nitrogen (11.2 mass%) and a very small amount of carbon (0.8 mass%) are present in the product pyrolyzed under $\text{NH}_3\text{-N}_2$. The removal of carbon is probably due to the effective amine-exchange reaction during the pyrolysis under NH_3 , i.e., two -NH_2 groups displace one =NPr^i group in the precursor and isopropyl amine is liberated.



Removal of carbon during the pyrolysis under NH_3 due to amine exchange reactions has been reported for other systems such as AlN precursors³³ and TiN precursors.³⁴ It should also be noted that 3.4% of oxygen, which was probably introduced during the pyrolysis, is present in the product pyrolyzed under $\text{NH}_3\text{-N}_2$. The pyrolysis of the precursor under $\text{NH}_3\text{-N}_2$ results in the formation of a NaCl-type compound, but the presence of some weak peaks, which can be assigned to NbO_2 ,³⁵ accounts for the presence of oxygen (Fig. 3a). It has been reported that NbN, NbC, and NbO all possess NaCl-type structures with the lattice parameters of 0.4393,³⁶ 0.4470,³⁷ and 0.4211 nm,³⁸ respectively. Besides, niobium oxynitride $\text{NbN}_x\text{O}_{1-x}$ also possesses a NaCl-type structure, and the lattice parameter of $\text{NbN}_x\text{O}_{1-x}$ decreases with the incorporation of oxygen in the lattice; for example $\text{NbN}_{0.9}\text{O}_{0.1}$ has the lattice parameter of 0.438 nm.³⁹ The observed lattice parameter of the NaCl-type compound is 0.4394 nm, which is very close to that of $\delta\text{-NbN}$ (0.4393 nm). Thus, if all the oxygen was present as NbO_2 , the pyrolyzed product should be a mixture of 0.89NbN and 0.11 NbO_2 based on the empirical formula of $\text{NbN}_{0.89}\text{C}_{0.08}\text{O}_{0.23}$.

The pyrolysis of the precursor under Ar leads to the formation of a well-crystallized single-phase NaCl-type compound (Fig. 3b). The observed lattice parameter is 0.4472 nm, which is very close to that of NbC (0.4470 nm) rather than that of NbN (0.4393 nm). The composition of the product (Table 2) also reveals that the ratios of N/Nb and O/Nb are 0.01 and 0.02 respectively. Thus, the crystallized NaCl-type compound should be cubic NbC. The C/Nb ratio of 1.47 (Table 2) suggests that a considerable amount of carbon is present as free carbon. The presence of a large amount

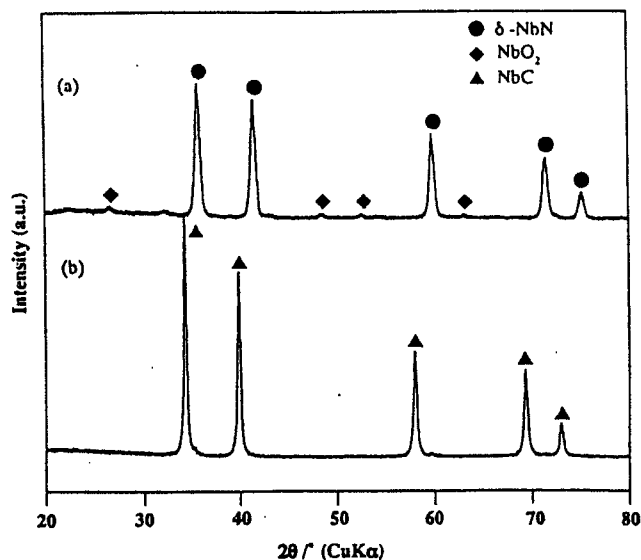


Fig. 3. XRD patterns of the products pyrolyzed under (a) $\text{NH}_3\text{-N}_2$ (at 600 °C for 2 h under NH_3 , and subsequently at 1350 °C for 8 h under N_2) and (b) under Ar (at 1500 °C for 2 h).

of carbon in the residues pyrolyzed under Ar has also been reported during the pyrolysis of titanium precursors prepared with the aminolysis of $\text{Ti}(\text{NR}_2)_4$.^{19,34}

It is interesting that most of the nitrogen is lost during the pyrolysis under Ar at 1500 °C, although the precursor possesses the initial N/Nb ratio of 2.6. The precursor has also been pyrolyzed at lower temperatures in order to obtain further information about the loss of nitrogen. The compositions of the products are shown in Table 3. After the pyrolysis at 600 °C under Ar, 60.5% of the nitrogen is lost, and very broad peaks ascribable to a NaCl-type compound were observed in the XRD pattern of the residue (not shown). The ceramic yield was 54.5%, close to the ceramic yield of 57% obtained from the TG curve of the precursor (Fig. 2a). Nitrogen is lost mainly as Pr^iNH_2 and CH_3CN below ca. 600 °C according to the aforementioned TG-MS analysis results. After the pyrolysis at 1000 °C, a poorly crystalline NaCl-type compound was detected by XRD (not shown).

Table 3. Compositional Characteristics of the Products Pyrolyzed under Ar

Temperature/°C	600	1000
Ceramic yield/mass%	54.5	47.5
Loss of nitrogen ^{a)} /%	60.5	96.3
Elemental analysis/mass%		
Nb	61.3	68.9
N	10.3	1.1
C	23.6	21.5
O	1.8	2.2
Total	96.8	98.8
Empirical formula	$\text{NbN}_{1.11}\text{C}_{2.98}\text{O}_{0.18}$	$\text{NbN}_{0.19}\text{C}_{2.28}\text{O}_{0.18}$

a) The loss of nitrogen [$E_{\text{L}(\text{N})}$] during the pyrolysis was calculated from the amounts of nitrogen in the precursor [$W_{\text{P}(\text{N})}$] and in the pyrolyzed residues [$W_{\text{R}(\text{N})}$]: $E_{\text{L}(\text{N})} = [W_{\text{P}(\text{N})} - YW_{\text{R}(\text{N})}] / W_{\text{P}(\text{N})} \times 100$. Y: ceramic yield.

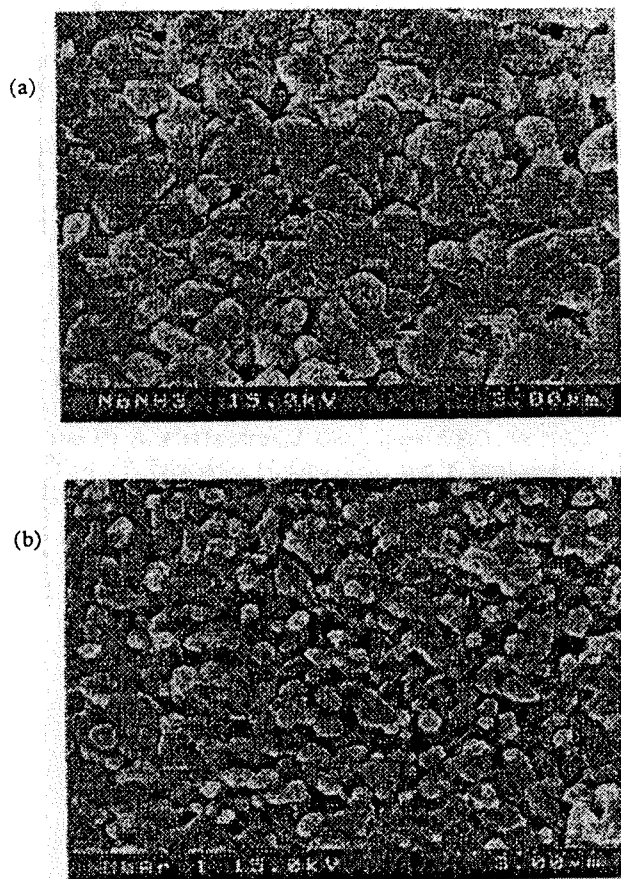


Fig. 4. Scanning electron micrographs of the products pyrolyzed (a) under $\text{NH}_3\text{-N}_2$ (at 600°C for 2 h under NH_3 , and then at 1350°C for 8 h under N_2) and (b) under Ar (at 1500°C for 2 h).

The loss of 96.3% of nitrogen indicates a further loss of nitrogen at $600\text{--}1000^\circ\text{C}$. The loss of nitrogen during the crystallization from an amorphous phase has also been reported for titanium precursors prepared by the aminolysis of $\text{Ti}(\text{NMe}_2)_4$.^{20,34}

Scanning electron micrographs of the pyrolyzed products are shown in Fig. 4. Particles with diameters of $0.4\text{--}1.0\ \mu\text{m}$ are observed on the surface of the product pyrolyzed under $\text{NH}_3\text{-N}_2$. Particles with diameters of $0.1\text{--}0.5\ \mu\text{m}$ are observed on the surface of the product pyrolyzed under Ar.

Summary.

The precursor possessing a Nb-N backbone structure was prepared by aminolysis reaction of tetrakis(diethylamido)-niobium with isopropylamine. IR and elemental analysis showed that the precursor was a polymer which contained the Nb-N-Nb imido-bridge structures. The precursor was soluble in benzene. TG-MS analysis and tube pyrolysis showed that the large mass loss, with the evolution of C_3H_6 , C_4H_8 , CH_3CN , and Pr^iNH_2 as main species, occurred at a temperature below ca. 500°C during pyrolysis of the precursor under He. The yellow-gray residue with the ceramic yield of 39.2% was obtained after pyrolysis of the precursor under $\text{NH}_3\text{-N}_2$ (at 600°C for 2 h under NH_3 and then at 1350°C

$^\circ\text{C}$ for 8 h under N_2), and the XRD analysis indicated that the main crystalline phase was $\delta\text{-NbN}$. On the other hand, pyrolysis of the precursor under Ar at 1500°C for 2 h led to the formation of a lavender-gray residue with the ceramic yield of 38.0%. XRD analysis of the product indicated that NbC was the only crystalline phase. More than 90% of niobium present in the precursor remained in both of the pyrolyzed products. SEM examination showed that the diameters of the particles obtained by pyrolysis under $\text{NH}_3\text{-N}_2$ and Ar were $0.4\text{--}1.0$ and $0.1\text{--}0.5\ \mu\text{m}$, respectively.

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39 Powder Diffraction Data File, 25-1360, JCPDS International Center for Diffraction Data, Swathmore, PA, 1988.