Preparation of a Hybrid Preceramic Precursor for Al-Si-C-N Nanocomposites *via* a Molecular Building Block Approach

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The reaction between $(HAlNPr^i)_m$ ($Pr^i=CH(CH_3)_2$) and $[MeSi(H)NH]_n$ ($Me=CH_3$) led to hydrogen elimination to form a hybrid precursor. Thermogravimetry revealed that the ceramic yield of the hybrid precursor was much higher than those of $(HAlNPr^i)_m$ and $[MeSi(H)NH]_n$, which was ascribed to the hydrogen elimination condensation between the AlH groups in $(HAlNPr^i)_m$ and the NH groups in $[MeSi(H)NH]_n$ during precursor synthesis and pyrolysis. The pyrolyzed product under Ar was a mixture of β-SiC, β-Si_3N_4 and 2*H* wurtzite-type compound, and the particle sizes were in the range of 20-30 nm.

Ceramic-based nanocomposites have extensively been developed because of their possible tailored and improved properties.[1] Besides conventional methods based on powder technology, pyrolytic conversion of preceramic materials[2] is capable for the preparation of non-oxide ceramic composites.[3] Strategies for designing preceramic materials for non-oxide ceramic composites primarily aim at the homogeneous dispersion of components, since this homogeneity is expected to lead to the formation of fine crystalline materials after pyrolysis. If single-component precursors are miscible liquids, the mixing at a molecular level is expected to be easily achieved.[4-6] Another strategy is preparation of single-source precursors possessing heterogeneous linkages such as M-N-M'[7-11] and tailoring single-component polymeric precursors with monomeric or oligomeric species.[5,6,12-16]

A "molecular building block" approach has been applied for chemical processing of oxide ceramic materials for better control of conversion process of precursors, and a typical example of "molecular building block" is a cage-type silsesquioxane octamer ($[(MeO)SiO_{1.5}]_8$).[17] Since particle sizes in nanocomposites (typically 1-20 nm[1]) are similar to or larger than those of molecular building blocks, it is of interest to design preceramic materials via the molecular building block approach. As far as we know, a closely-related attempt in the non-oxide preceramics was reported only for a ring-type compound system, $(HBNH)_3$-$(Me_2SiNH)_3$.[13]

Poly(alkyliminoalane), $(HAlNR)_m$, is a series of well-studied compounds possessing an Al-N backbone, and some of $(HAlNR)_m$ are considered as attractive candidates for molecular building blocks because of their cage-type structures.[18] We have shown that $(HAlNPr^i)_m$, which is mainly composed of cage-type hexamer, can be converted into AlN.[19] Since AlH groups are capable for hydrogen elimination reactions with NH groups,[10] it appears possible to tailor $(HAlNPr^i)_m$ with appropriate species possessing NH groups.

Here we report the preparation of a hybrid preceramic precursor based on the molecular building block approach. A cage-type $(HAlNPr^i)_m$ was linked with ring-type $[MeSi(H)NH]_n$ to form a hybrid precursor. Pyrolysis behavior of the hybrid precursor was investigated using thermogravimetry (TG). The hybrid precursor was pyrolyzed in a tube furnace under Ar, and the pyrolyzed product was characterized by X-ray powder diffraction analysis (XRD), elemental analysis, and scanning electron microscopy (SEM).

All the procedures were performed under a protective nitrogen atmosphere using the standard Schlenk technique or a glove box. $(HAlNPr^i)_m$, $(MeAlNPr^i)_m$, $[MeSi(H)NH]_n$, and $(Me_2SiNH)_n$ were prepared by the methods reported previously.[18,20] Analytical data revealed that $(HAlNPr^i)_m$ and $(MeAlNPr^i)_m$ were present mainly as a cage-type hexamer. The NMR studies of $[MeSi(H)NH]_n$ and $(Me_2SiNH)_n$ indicated that the main species were cyclic tetramer and cyclic trimer, consistent with previous reports.[20,21]

The hybrid precursor was typically prepared as follows. As the atomic ratio of Al:Si was approximately 1:1, 2.9 g of solid $(RAlNPr^i)_m$ was added into 2.0 g of liquid $[MeSi(R')NH]_n$ (R=H, R'=H; R=H, R'=Me; R=Me, R'=H) in a Schlenk flask without using any solvent. The mixture was continuously stirred at room temperature until gas evolution ceased.

When solid $(HAlNPr^i)_m$ and liquid $[MeSi(H)NH]_n$ were mixed, a white solid formed with the evolution of gas, which was identified as hydrogen by gas chromatography (GC); hence condensation due to hydrogen elimination should occur. The hybrid precursor was soluble in common organic solvents, and its IR spectrum can be interpreted essentially as an overlay of those of $(HAlNPr^i)_m$ and $[MeSi(H)NH]_n$, suggesting that the extent of the hydrogen elimination reaction should be very limited. On the other hand, when the hybrid precursor was pyrolyzed up to 200 °C, a part of the product became insoluble in benzene, indicating the formation of a cross-linked structure. The evolved gas during this pyrolysis (up to 200 °C) was collected using a liquid nitrogen trap, but no gases were detected by GC. Since hydrogen cannot be trapped at liquid nitrogen temperature, it is reasonable to conclude that further cross-linking reaction involving hydrogen elimination occurred.

The pyrolysis behavior of the $(HAlNPr^i)_m/[MeSi(H)NH]_n$ hybrid precursor (Figure 1a), as well as that of $(HAlNPr^i)_m$ (Figure 1d) and $[MeSi(H)NH]_n$ (Figure 1e), was investigated by using TG (Shimadzu TGA-50). The ceramic yield of the hybrid precursor up to 900 °C is

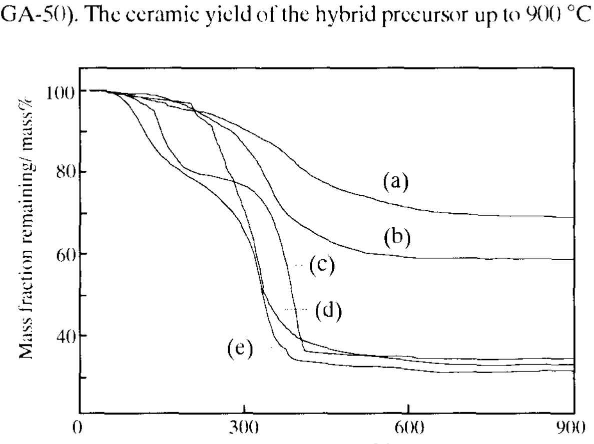


Figure 1. TG curves of (a) $(HAlNPr^i)_m/[MeSi(H)NH]_n$, (b) $(HAlNPr^i)_m/(Me_2SiNH)_n$, (c) $(MeAlNPr^i)_m/[MeSi(H)NH]_n$, (d) $(HAlNPr^i)_m$, and (e) $[MeSi(H)NH]_n$ at a rate of 10 °C/min under a He flow.

69%, which is much higher than those of $(\mathrm{HAlNPr}^i)_m$ (34%) and $[\mathrm{MeSi(H)NH}]_n$ (29%). Since the ceramic yields of $(\mathrm{HAlNPr}^i)_m$ and $[\mathrm{MeSi(H)NH}]_n$ are lower than their theoretical ones (48% for conversion of $(\mathrm{HAlNPr}^i)_m$ into AlN, and 61% and 68% for conversion of $[\mathrm{MeSi(H)NH}]_n$ into Si_3N_4 and SiC, respectively), Al- or Si-containing species should be lost during their pyrolyses because of volatilization and/or degradation. Corresponding large mass losses were observed for TG curves of $(\mathrm{HAlNPr}^i)_m$ (at ~240-320 °C) and $[\mathrm{MeSi(H)NH}]_n$ (at ~ 80-180 °C and ~ 260-380 °C). On the contrary, the TG curve of the hybrid precursor showed only a gradual mass loss up to 400 °C, at which $(\mathrm{HAlNPr}^i)_m$ and $[\mathrm{MeSi(H)NH}]_n$ showed large mass losses. Thus, the relatively high ceramic yield of the hybrid precursor should be ascribed to partial suppression of loss of Al- and Si-containing species, which should be due to the conversion into cross-linked structure during mixing and pyrolysis.

Hydrogen elimination is possible by the following two reactions;
1) condensation between $(\mathrm{HAlNPr}^i)_m$ and $[\mathrm{MeSi(H)NH}]_n$:

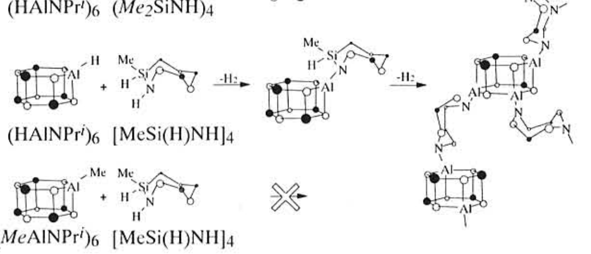
$$\equiv\mathrm{Al{-}H} + \mathrm{H{-}N{=}} \longrightarrow \equiv\mathrm{Al{-}N{=}}$$

and
2) condensation involving $[\mathrm{MeSi(H)NH}]_n$ only:

$$\equiv\mathrm{Si{-}H} + \mathrm{H{-}N{=}} \longrightarrow \equiv\mathrm{Si{-}N{=}}\ .$$

In order to clarify the condensation mechanism, we prepared additional two hybrid precursors using $(Me\mathrm{AlNPr}^i)_m$ (possessing no AlH groups) and $(Me_2\mathrm{SiNH})_n$ (possessing no SiH groups); $(Me\mathrm{AlNPr}^i)_m/[\mathrm{MeSi(H)NH}]_n$ and $(\mathrm{HAlNPr}^i)_m/(Me_2\mathrm{SiNH})_n$ hybrid precursors were prepared. The pyrolytic processes are very different between these two hybrid precursors (Figure 1). The $(\mathrm{HAlNPr}^i)_m/(Me_2\mathrm{SiNH})_n$ hybrid precursor (Figure 1b) showed a relatively high ceramic yield (58%) up to 900 °C, and its TG curve is similar to that of $(\mathrm{HAlNPr}^i)_m/[\mathrm{MeSi(H)NH}]_n$ (Figure 1a), suggesting a similar pyrolytic process. On the contrary, the ceramic yield of $(Me\mathrm{AlNPr}^i)_m/[\mathrm{MeSi(H)NH}]_n$ is very low (34%). Its TG curve (Figure 1c) is not similar to those of the other two hybrid precursors, and a two-step mass loss occurs up to ~ 400 °C. Hence, volatilization/degradation during pyrolysis was not effectively suppressed. Thus, we conclude that the condensation between the AlH groups and the NH groups plays a key role for the conversion of the hybrid precursors into cross-linking structures (Scheme 1).

When the $(\mathrm{HAlNPr}^i)_m/[\mathrm{MeSi(H)NH}]_n$ hybrid precursor was pyrolyzed in a tube furnace at 1600 °C under Ar (ceramic yield: 46%), the black residue, whose composition was $\mathrm{AlSi_{1.41}C_{1.55}N_{1.01}O_{0.12}}$ (Al, 24.4%; Si, 35.8%; C, 16.8%; N, 12.8%; O, 1.8%), was obtained. The XRD pattern (monochromated CuKα radiation) of the residue showed the peaks of β-SiC and the *2H* wurtzite-type compound and weak peaks due to β-Si_3N_4. The XRD peaks of the *2H* wurtzite-type compound were too broad to allow closer inspection of the XRD pattern; thus, we cannot determine whether the XRD peaks due to the *2H* wurtzite-type compound is ascribed to a AlN/SiC solid solution or a mixture of the endmembers (AlN and *2H* SiC). SEM observation (Hitachi S4500-S) reveals that the residue (Figure 2) consists of very fine particles with diameters of 20-30 nm. It should be noted that the particles were very uniform in sizes, indicating that all the phases possess similar particle sizes.



Scheme 1. Proposed reaction mechanisms of the precursors for the conversion into cross-linked structures (●: the Al-H or Al-Me groups, ○: the N-Pr^i groups, ○: the Si(H)Me or $\mathrm{SiMe_2}$ groups, and •: the N-H groups).

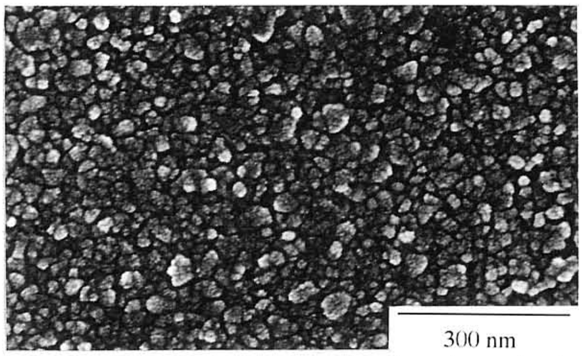


Figure 2. A scanning electron micrograph of the product pyrolyzed at 1600 °C under Ar.

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