Preparation of Si–Al–N–C Ceramic Composites by Pyrolysis of Blended Precursors

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ブレンド前駆体の熱分解による Si–Al–N–C セラミックコンポジットの作製

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Si–Al–N–C precursors have been prepared from perhydropolysilazane (PHPS) and cage-type poly(ethyliminoalane) [(HAINet)_n; PEIA, *n* is mainly 8] with different Si/Al molar ratios (Si/Al = 3, 1, 1/3). Spectroscopic analysis indicates that essentially no Si–N–Al linkages form, indicating that the precursors are blended polymers. TG analysis reveals that the ceramic yields of the blended precursors up to 900°C are higher than those of PHPS and (HAINet)_n, suggesting that cross-linking reactions occur during pyrolysis. Possible reactions are dehydrocoupling and radical reactions, as suggested by the results of solid-state nuclear magnetic resonance (NMR) spectroscopy. The results of solid-state NMR spectroscopy and X-ray diffraction (XRD) analysis indicate that the residue pyrolyzed at 1600°C contains mainly crystalline AlN, 2H-SiC and β-SiC.

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1. Introduction

Ceramic-based composites have been considered as attractive materials, since these composites generally have superior properties compared to single-component ceramics.¹⁾ Considerable attention has been given to an aluminum nitride (AlN)–silicon carbide (SiC) composite because this composite exhibits many attractive properties such as high hardness, toughness, excellent resistance to oxidation and corrosion, high thermal conductivity, high electrical resistance and low thermal expansion.^{2)–7)}

Pyrolytic organic-to-inorganic conversion of precursors, including inorganic and organometallic polymers, is a chemical route to non-oxide ceramics, such as nitrides and carbides of main group elements and transition metals, and ceramic-based composites.^{8)–14)} If precursors are fusible at relatively low temperatures or soluble in common organic solvents, this route can offer significant advantages for fabrication of ceramics and ceramic-based composites with desirable shapes, including coatings and fibers. Precursors can also be applied for powder processing, as sintering aids and binders. In addition, this process could lead to ceramic-based composites with homogeneous distribution of the component elements.

Precursors for composites are commonly single-source precursors, which typically possess heterogeneous M–N–M' and/or M–C–M' linkages.^{15),16)} The advantage of single-source precursors is the atomic-level homogeneity of their elemental compositions. In addition, a blended precursor approach to fabrication of composites can also be proposed. The blended precursors are usually prepared by simply mixing two single-component precursors.¹⁷⁾ If single-component precursors are miscible with each other or soluble in organic solvents, a molecular-level homogeneity can be achieved in blended precursors. A few studies have described the preparation of ceramic-based composites using the blended precursor approach.^{14),17)}

Perhydropolysilazane (PHPS) possessing Si–N backbones is a soluble precursor for Si–N–C-based materials that exhibits

a relatively high ceramic yield.¹⁸⁾ As soluble precursors exhibiting moderate ceramic yields for AlN, poly(alkyliminoalane)s [(HAINR)_n; PIAs, R = alkyl], cage-type oligomers possessing Al–N backbones, can be proposed.¹⁹⁾ We have prepared AlN by pyrolysis of cage-type PIAs, poly(ethyliminoalane) [(HAINet)_n; PEIA, *n* is mainly 8] and poly(isopropyliminoalane) [(HAINⁱPr)_n; PIPIA, *n* is mainly 6] and reported that the ceramic yield of PEIA was higher than that of PIPIA.^{20)–25)} Si–Al–N–C ceramic composites can therefore be obtained easily by pyrolysis of a precursor that is prepared by blending PHPS and PEIA.

Here we report the preparation of Si–Al–N–C ceramic composites by pyrolysis of blended precursors that were synthesized simply by mixing PHPS with PEIA and that possess essentially no Si–N–Al linkages. We focus on the pyrolytic organic-to-inorganic conversion of the blended precursors, investigated by solid-state nuclear magnetic resonance (NMR) spectroscopy and X-ray diffraction (XRD) analysis.

2. Experimental

All the manipulations were performed under a protective nitrogen atmosphere using the standard Schlenk technique or a nitrogen-filled glove box.²⁶⁾ Toluene (Kanto Chemical) and *p*-xylene (Wako Pure Chemical Industries) were distilled over sodium and benzophenone under a nitrogen atmosphere. PHPS (Clariant Japan, N-N310, with an average molecular mass of 974) was used as received. The preparation procedure for PEIA was described elsewhere.²⁰⁾

2.1 Preparation of the blended precursors

The blended precursors were prepared from PHPS and PEIA with different Si/Al ratios (Si/Al = 3, 1, 1/3, hereinafter abbreviated as SA31, SA11 and SA13, respectively). The preparation of the blended precursor (SA11) is described below as a representative example, since the other precursors were prepared in a similar manner. The reaction was conducted in a two-necked round-bottomed flask equipped with a gas inlet tube and a glass stopper. The apparatus was charged with

PEIA (2.15 g) and *p*-xylene. PHPS (1.38 g) in *p*-xylene was added to this solution by means of a stainless cannula. After stirring at 30°C for one hour, *p*-xylene was removed from this solution by trap-to-trap distillation under reduced pressure to yield a white soluble solid.

2.2 Pyrolysis of the blended precursors

For pyrolysis at 200–400°C, **SA11** was placed on a BN boat in a quartz tube under an argon atmosphere and pyrolyzed at the desired temperature with no holding time. The heating and cooling rate was 5°C/min. For pyrolysis at 1600°C, **SA11** was placed on a BN boat in an alumina tube under an argon atmosphere. The heating rate was 10°C/min from room temperature to 200°C and 5°C/min from 200 to 1600°C. The temperature was maintained at 1600°C for 2 h, and the pyrolyzed residue was then cooled to room temperature at 5°C/min.

2.3 Characterization of the blended precursors and the pyrolyzed residues

The blended precursors were characterized by nuclear magnetic resonance (NMR) spectroscopy (JEOL, JNM-Lambda 500). The ^{27}Al NMR (130.20 MHz) spectra of the precursors were recorded on the same apparatus using $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ (0 ppm) as an external standard. Thermogravimetry (TG, Perkin-Elmer, TGA-7) was performed at a heating rate of 10°C/min under flowing argon up to 900°C.

The pyrolyzed residues were characterized by solid-state NMR spectroscopy (JEOL, NM-GSX 400) and X-ray diffraction (XRD, Rigaku, Rint-2500) analysis. For the residues pyrolyzed at 200–400°C, the solid-state ^{29}Si NMR (79.43 MHz) spectra of the pyrolyzed residues were obtained with cross polarization and magic angle spinning (CP/MAS) techniques. The residues were packed in sample tubes in a nitrogen-filled glove box, and kept under nitrogen flow during the measurements. Five hundred scans were accumulated with a pulse delay of 5 s and a spinning rate of 7 kHz. For the residue pyrolyzed at 1600°C, the solid-state ^{27}Al and ^{29}Si NMR spectra of the pyrolyzed residue were recorded on the same instrument with the MAS technique only. Five hundred scans were accumulated with a pulse delay of 100 s (^{29}Si) or 1 s (^{27}Al) and a spinning rate of 7 kHz (^{29}Si) or 9 kHz (^{27}Al). The XRD pattern of the pyrolyzed residue was obtained using monochromated Cu K α radiation.

3. Results and discussions

3.1 Preparation of soluble Si-Al-N-C precursors by a blending technique

The ^{27}Al NMR spectra of the blended precursors show one signal centered at 135 ppm assignable to the H_2AlN_3 environment.¹⁹⁾ These chemical shifts in the ^{27}Al NMR spectra of the blended precursors are very similar to that of PEIA. It should be noted that no other signals are observed in the ^{27}Al NMR spectra.

The structures of the blended precursors are discussed below. PHPS has reactive SiH and NH bonds, and PEIA has reactive AlH bonds. In the preparation of aluminum-modified polysilazanes, NH bonds and AlH bonds can undergo dehydrocoupling to form new Al-N bonds.²⁷⁾ In our previous work, we found that the precursor for Al-Si-N-C ceramic composites possessed Al-N-Si linkages formed *via* dehydrocoupling between the NH bonds in cyclosilazane $[\text{Me}(\text{H})\text{SiNH}]_m$ and the AlH bonds in a cage-type oligomer $(\text{HAlN}^i\text{Pr})_n$.^{28),29)} The ^{27}Al NMR spectrum of this precursor exhibited a broad signal at 100 ppm^{28),29)} assignable to the AlN_4 environment,³⁰⁾ which was formed by dehydrocoupling between the NH bonds and the AlH bonds in the H_2AlN_3 environment. Since only the H_2AlN_3 resonance at 135 ppm is

Fig. 1. Solid-state ^{27}Al NMR spectra of **SA11** pyrolyzed at 1600°C. The signals marked by asterisks are spinning side bands.

Fig. 2. Solid-state ^{29}Si NMR spectra of **SA11** pyrolyzed at (A) 1600°C and (B) 1000°C.

observed and no AlN_4 resonance at 100 ppm is observed in the ^{27}Al NMR spectra of the blended precursors, dehydrocoupling between the NH bonds in PHPS and the AlH bonds in PEIA occurs only to a very limited extent; essentially no Al-N-Si linkages are formed during the preparation of the blended precursors. In the preparation of precursors possessing Al-N-Si linkages, at least one of the starting compounds must be a compound with a relatively low molecular mass such as tetrakis(methylaminosilane); $\text{Si}(\text{NHCH}_3)_4$, cyclosilazane, Lewis-base adduct of alane $(\text{H}_3\text{Al}\cdot\text{NMe}_3)$,^{27)–29)} while both PHPS and PEIA are compounds with a relatively high molecular mass or oligomeric compounds. Thus, it is reasonable to assume that the occurrence of dehydrocoupling is limited during the preparation of precursors because of the steric hindrance.

3.2 Characterizations of the residue pyrolyzed at 1600°C

Figure 1 shows the solid-state ^{27}Al NMR spectrum of **SA11** pyrolyzed at 1600°C. The solid-state ^{27}Al NMR spectrum exhibits one signal at 110 ppm, which is assignable to the AlN_4 environment.³¹⁾ It is worth noting that this signal corresponds to the chemical shift for AlN_4 .³¹⁾ **Figure 2** shows the solid-state ^{29}Si NMR spectrum of the residues pyrolyzed of **SA11**. The solid-state ^{29}Si NMR spectrum of **SA11** pyrolyzed at 1600°C (**Fig. 2A**) exhibits two signals at -16 and -20 ppm and two shoulders centered at ~ -14 ppm and ~ -23 ppm, which are

Fig. 3. XRD pattern of SA11 pyrolyzed at 1600°C.

attributable to the SiC_4 environments.^{32)–35)} The SiC_4 resonances at -16 ppm seem to be close to the reported chemical shifts for $\beta\text{-SiC}$.³²⁾ In terms of the resonances of the SiC_4 environments in $\alpha\text{-SiC}$, which has various polytypes (e.g., $2H$, $4H$, $6H$, $15R$, etc.), the signal positions depend on the crystal structures. The ^{29}Si NMR spectrum of $2H\text{-SiC}$ exhibited only one signal at -20 ppm.³³⁾ In the ^{29}Si NMR spectra of $6H$ and $15R$ polytypes, three SiC_4 resonances were observed at ~ -14.5 ppm, ~ -20.5 ppm and ~ -24.5 ppm.^{33)–35)} The intensity ratios (high to low frequency) were $1 : 1 : 1$ ($6H$) and $1 : 2 : 2$ ($15R$). In the spectrum of $4H$ polytypes, two SiC_4 resonances were observed at -19.7 ppm and -22.5 ppm and the intensity ratio was $1 : 1$.³³⁾ In the spectrum of SA11 pyrolyzed at 1600°C , an intense SiC_4 resonance is observed at -20 ppm, and the signal at -20 ppm can therefore be attributed to the SiC_4 environment in $2H\text{-SiC}$. The presence of shoulders at ~ -14 ppm and ~ -23 ppm suggests that the residue could contain small amounts of $4H$, $6H$ and/or $15R$ polytypes.

Figure 3 shows the XRD pattern of SA11 pyrolyzed at 1600°C . In the XRD pattern of the residue, the overlapping reflections are assignable to AlN, $\alpha\text{-SiC}$ and $\beta\text{-SiC}$, which are identified by the aforementioned results for the solid-state NMR. It is therefore concluded that the residue of SA11 pyrolyzed at 1600°C mainly possesses crystalline AlN, $2H\text{-SiC}$ and $\beta\text{-SiC}$. The minor crystalline phases in the residue may be $4H$, $6H$ and/or $15R$ polytypes.

With pyrolysis of PHPS, which possesses the Si–N backbone, the Si_3N_4 formation generally occurs.^{18),36)–40)} The solid-state ^{29}Si NMR spectrum of SA11 pyrolyzed at 1000°C (Fig. 2B) exhibits a broad signal at ~ -44 ppm, which is assignable to the SiN_4 environment,³⁰⁾ and no Si_3N_4 reflection is observed in the XRD pattern of SA11 pyrolyzed at 1000°C . These results suggest the presence of amorphous Si_3N_4 in the residue pyrolyzed at 1000°C . As described above, the results for the solid-state ^{29}Si NMR spectrum and XRD pattern indicate the presence of crystalline SiC in the residue pyrolyzed at 1600°C . Based on thermodynamic considerations, the transformation from Si_3N_4 into SiC can occur above 1440°C via the following reaction:⁴¹⁾

Thus, it is suggested that the formation of crystalline SiC is due to this reaction, and that the residue pyrolyzed at 1000°C appears to contain amorphous Si_3N_4 and free carbon.

3.3 Pyrolytic behavior of the blended precursors

Figure 4 shows the TG curves of the blended precursors, PHPS and PEIA. The ceramic yields of SA31, SA11 and SA13, up to 900°C under an Ar atmosphere are 87.5, 80.3 and

Fig. 4. TG curves of (A) SA31, (B) SA11, (C) SA13, (D) PHPS and (E) PEIA.

Fig. 5. Solid-state ^{29}Si NMR spectra of SA11 pyrolyzed at (A) 200°C , (B) 300°C and (C) 400°C .

76.0 mass%, respectively. These ceramic yields are higher than those of PHPS (75.3 mass%) and PEIA (61.1 mass%), although essentially no Al–N–Si linkage between the two starting precursors is formed during the preparation of the blended precursors. This observation seems to suggest that cross-linking reactions progress during pyrolysis.

Spectroscopic characterizations of the residues pyrolyzed at $200\text{--}400^\circ\text{C}$ (SA11) were therefore carried out in order to investigate the pyrolytic process of the blended precursors in detail. Figure 5 shows the solid-state ^{29}Si NMR spectra of the

Scheme 1. Possible reactions during pyrolysis of poly(ethyliminoalane) (PEIA).

residue pyrolyzed at 200–400 $^\circ\text{C}$. The residue at 200 $^\circ\text{C}$ exhibits one broad signal at ~ -37 ppm, assignable to the $\text{N}_3\text{SiH}/\text{N}_2\text{SiH}_2$ environments.^{42),43)} As the temperature increases, shoulders appear at ~ -44 ppm and at ~ -20 ppm. These shoulders are attributable to the SiN_4 ³⁰⁾ and $\text{N}_2\text{Si}(\text{H})\text{C}(sp^3)$ environments,^{44)–47)} respectively. In the ^{29}Si NMR spectrum at 400 $^\circ\text{C}$, the $\text{N}_2\text{Si}(\text{H})\text{C}(sp^3)$ resonance is clearly observed.

Based on these observations, the possible pyrolysis mechanism can be discussed. During pyrolysis of PEIA below $\sim 300^\circ\text{C}$, the heterolytic cleavage of an Al–N bond in PEIA seems to occur to form nitrogen terminals ($=\text{N}:$). The nitrogen terminals subsequently attack the ethyl groups in PEIA to lead to the formation of new NH bonds (Scheme 1A).²⁵⁾ This reaction can occur continuously because of regeneration of the nitrogen terminals. From $\sim 300^\circ\text{C}$ to $\sim 650^\circ\text{C}$, new NH bonds should form *via* the concerted β -elimination mechanism (Scheme 1B).^{25),48)} Since the SiN_4 resonance is observed at ~ -44 ppm in the ^{29}Si NMR spectrum of the residue pyrolyzed at 400 $^\circ\text{C}$, the SiH bonds in PHPS moiety appear to react with the NH bonds to form new Si–N bonds. In the pyrolysis of aluminum- or boron-modified polysilazane, dehydrocoupling between the SiH and the NH bonds occurred to form new Si–N bonds in this temperature range.^{49)–51)} It is therefore assumed that a possible reaction during pyrolysis up to 400 $^\circ\text{C}$ is dehydrocoupling between the SiH bonds in PHPS moiety and the NH bonds in PHPS moiety and/or the newly-formed NH bonds in PEIA moiety:

The formation of ethylene during pyrolysis of PEIA from $\sim 300^\circ\text{C}$ to $\sim 650^\circ\text{C}$ upon the homolytic cleavage of C–N bonds in $=\text{N}^\cdot\text{Et}$ groups involves the formation of radicals ($=\text{N}^\cdot$, $\text{R}^\cdot$) and the subsequent β -elimination of a hydrogen radical ($\text{H}^\cdot$) (Scheme 1C).^{25),52)} The radicals ($\text{R}^\cdot$) can react with SiH bonds to form silicon radicals ($\text{Si}^\cdot$) *via* hydrogen abstraction.^{53),54)} (Scheme 2A) In the ^{29}Si NMR spectra of the residues pyrolyzed at 300–400 $^\circ\text{C}$, $\text{N}_2\text{Si}(\text{H})\text{C}(sp^3)$ resonances are observed at -20 ppm, suggesting the presence of new Si–C bonds. For the formation of new Si–C bonds, a possible mechanism that involves a reaction between the silicon radicals ($\text{Si}^\cdot$) and ethylene (Scheme 2B) can be proposed.^{53),54)} Based on these results, possible reactions occurring during pyrolysis are dehydrocoupling between the SiH and NH bonds and radical reactions.

4. Conclusions

Soluble blended precursors for Si–Al–N–C ceramic composites have been prepared from perhydropolysilazane (PHPS) and poly(ethyliminoalane) (PEIA). The ceramic yields of the blended precursors up to 900 $^\circ\text{C}$ are higher than those of the starting precursors, a result which can be ascribed to cross-

Scheme 2. Possible mechanism of the formation of Si–C bonds ($\text{R} = \text{Et}$).

linking reactions, possibly including dehydrocoupling and radical reactions during pyrolysis. The solid-state NMR spectra and XRD pattern indicate that the residue pyrolyzed at 1600 $^\circ\text{C}$ contains mainly crystalline AlN, 2H–SiC and β -SiC. These results suggest that the precursors prepared by blending PHPS and PEIA can be considered to serve as precursors for Si–Al–N–C ceramic composites.

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