APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2001; **15**: 710–716
DOI: 10.1002/aoc.221

Preparation and pyrolysis of a blended precursor possessing Ti—N and Al—N bonds

Fei Cheng,[1]† Yoshiyuki Sugahara[1,2]* and Kazuyuki Kuroda[1,2,3]
[1]Department of Applied Chemistry, School of Science and Engineering, Waseda University, Ohkubo-3, Shinjuku-ku, Tokyo 169–8555, Japan
[2]Research Laboratory for Energy, Environments, and Synthetic Materials, School of Science and Engineering, Waseda University, Ohkubo-3, Shinjuku-ku, Tokyo 169–8555, Japan
[3]Kagami Memorial Laboratory for Materials Science and Technology, Waseda University, Nishiwaseda-2, Shinjuku-ku, Tokyo 169–0051, Japan

The preparation and pyrolysis of a blended precursor possessing Ti—N and Al—N bonds were investigated. The precursor was prepared by mixing $(HAlN^{i}Pr)_n$, whose main component was a cage-type compound, and an aminolysis product of $Ti(NMe_2)_4$ with $MeHNCH_2CH_2NHMe$ with a molar ratio of Ti:Al = 2:1. IR analysis of the products pyrolyzed under NH_3–N_2 indicated that a large proportion of the organic groups in the precursor were removed by an amine-exchange reaction during the pyrolysis under NH_3; thus, the products contained only a small amount of carbon. On the contrary, a considerable amount of carbon was present in the product pyrolyzed under Ar. Composites consisting of AlN and an NaCl-type compound were obtained after pyrolysis of the precursor under both NH_3–N_2 and Ar. The composition of the NaCl-type compound depended significantly on the pyrolysis atmosphere. Copyright © 2001 John Wiley & Sons, Ltd.

Keywords: ceramic composite; aluminum nitride; titanium nitride; precursor; pyrolysis

Received 16 October 2000; accepted 11 April 2001

* Correspondence to: Y. Sugahara, Department of Applied Chemistry, Waseda University, Ohkubo-3, Shinjuku-ku, Tokyo 169–8555, Japan.
Email: ys6546@mn.waseda.ac.jp
† Current address: Department of Chemistry, The University of Hull, Cottingham Road, Hull HU6 7RZ, UK.
Contract/grant sponsor: Ministry of Education, Science, Sports, and Culture, Japan; Contract/grant number: 10650672.

1 INTRODUCTION

Ceramic composites consisting of two or more binary nitrides often exhibit improved properties compared with the single-component ceramics.[1,2] Ti–Al–N ceramic composites show higher thermal conductivity, higher strength and better light-shielding properties than single TiN and AlN phases.[3] In addition, the friction coefficients of the Ti–Al–N ceramic composites are smaller than those of TiN and AlN.[4] Because of their superior properties, Ti–Al–N ceramic composites are applied to heating materials and antifriction material.[3–5] Ti–Al–N ceramic composites are usually prepared by traditional powder processing using TiN and AlN powders as starting materials. The chemical vapor deposition (CVD) process has been applied to the preparation of TiN–AlN composite films recently,[6] but it is difficult to apply it to large-scale production and to coating preparation on substrates with complex shapes because of its large-equipment requirement.

Preparation of non-oxide ceramics *via* pyrolysis of inorganic and organometallic compounds has attracted considerable attention during the last two decades.[2,7,8] This chemical route provides an alternative method for the preparation of non-oxide ceramics with desirable shapes, but it is required that the precursors are soluble or fusible for such application.[2] Precursors for non-oxide ceramic composites with atomic-level or molecular-level homogeneity can be prepared, and several potential advantages for the preparation of ceramic composites, including improved control of overall composition, grain size, homogeneity, and lower processing temperatures, have been claimed for this chemical route.[9,10] So far, the emphasis has been placed on the preparation and pyrolysis of single-source molecular precursors that contain

heterogeneous linkages such as M–N–M′, since atomic-level homogeneity of the components in the initial precursor systems can be achieved through this approach.[9,11–13] Many non-oxide ceramic composites, such as Si–C–N, Si–B–C–N, and Si–Al–N, have been prepared by this single-source precursor approach.[9–11] To our knowledge, only titanium aluminum polyimide has been investigated as a single-source precursor for Ti–Al–N ceramic composites.[14]

On the other hand, molecular-level homogeneity can also be achieved by blending two or more single-component precursors, if they are miscible liquids or solids soluble in organic solvents.[9,11] The obvious benefit of this blending approach over the single-source precursor route is that the desirable compositions of the composite precursors can be easily achieved by adjusting the ratios of the single-component precursors through very simple syntheses.[9] However, only a few studies have been reported on the preparation of ceramic composites by this blending approach.[9,11,15,16]

We have previously reported preliminary results on the preparation of Ti–Al–N ceramic composites from a blend of a cage-type compound $(HA1N^{i}Pr)_n$ and an aminolysis product of $Ti(NMe_2)_4$ with $MeHNCH_2CH_2NHMe$.[17] In this paper, we focus on the structure of the precursor and pyrolysis behavior, as well as on the effect of the pyrolysis atmosphere on the resulting pyrolyzed products.

2 EXPERIMENTAL

2.1 Synthesis of the precursor

All the procedures were performed under a protective nitrogen atmosphere using a standard Schlenk technique[18] or a glove box filled with nitrogen. All the organic solvents and amines were freshly distilled by using appropriate drying agents before use.

$(HA1N^{i}Pr)_n$ was prepared based on a previous report.[19] Nuclear magnetic resonance spectroscopy (NMR; ^{1}H, ^{13}C, and ^{27}Al) revealed that $(HA1N^{i}Pr)_n$ was present mainly as the cage-type hexamer.[19] In addition, weak signals due to the tetramer were observed in the ^{1}H and ^{13}C NMR spectra.[19] The IR spectrum showed the presence of a ν(Al—H) stretching band at 1860 cm^{-1}.[19] The bands at 1165, 1139 and 834 cm^{-1} and those at 1379 and 1365 cm^{-1} were assigned to —$CH(CH_3)_2$ skeletal bands and bending band respectively.[20]

The precursor possessing Ti—N bonds was prepared by the reaction of $Ti(NMe_2)_4$ with *N*,*N*′-dimethylethylenediamine with $Ti(NMe_2)_4$:diamine = 1:2 based on a previous report.[21] Examinations of the black oily product by ^{1}H and ^{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 three bands assignable to Ti—N stretching bands at 556, 590 and 650 cm^{-1}. In addition, the presence of an N—H stretching band at 3290 cm^{-1} suggested that the product contained a small amount of unreacted —N(H)Me groups.[20,22]

The blended precursor was prepared as follows. After the precursor possessing Ti—N bonds was dissolved in 30 ml of benzene in a 100 ml three-necked flask, $(HA1N^{i}Pr)_n$ was added with a molar ratio of Ti:Al = 2:1. The mixed solution was stirred for 1 h to ensure homogeneity. Removal of benzene gave an orange–brown highly waxy liquid.

2.2 Pyrolysis of the precursor

The blended precursor was pyrolyzed in a tube furnace. About 0.5 g of the precursor was placed in a BN boat, which was then introduced into an Al_2O_3 or SiO_2 tube filled with Ar or NH_3. For the pyrolysis under Ar, the precursor was heated at 1500 °C for 2 h with a flow rate of 100 ml min^{-1}. For the pyrolysis under NH_3 at 200, 400 and 600 °C, the precursor was heated at the desired temperature under NH_3 (30 ml min^{-1}) for 3 h and then cooled to room temperature. For the pyrolysis under NH_3–N_2, the precursor was first heated at 600 °C for 3 h under NH_3 (30 ml min^{-1}), and 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^{-1}). The heating and cooling rates were 5 °C min^{-1}.

2.3 Analysis of the precursor and the pyrolyzed products

The precursors were characterized by using infra red (IR) spectroscopy (Perkin–Elmer FTIR-1640) and NMR (^{1}H and ^{13}C; JEOL JNM-270X). Thermogravimetry (TG) of the blended precursor was carried out using a Shimadzu TGA-50 thermobalance at a heating rate of 10 °C min^{-1} under an He flow. The pyrolyzed products were analyzed by using IR and X-ray diffraction (XRD) analysis (Mac Science MXP^3 diffractometer with Cu K_α-radiation). The lattice parameters of the

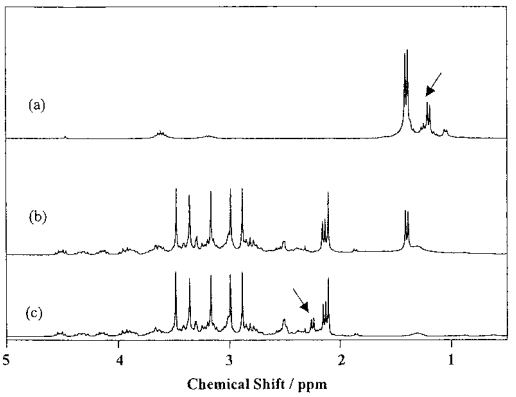

Figure 1 ^{1}H NMR spectra of (a) $(HA1N^iPr)_n$, (b) the blended precursor, and (c) the aminolysis product of $Ti(NMe_2)_4$ with $MeHNCH_2CH_2NHMe$ (C_6D_6, 270 MHz).

pyrolyzed products were calculated by the non-linear least-squares method using silicon as an internal standard. The amounts of nitrogen, oxygen and carbon in the pyrolyzed products were measured 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 (ICP) emission spectrometry (Nippon Jarrell Ash ICAP-575 II).

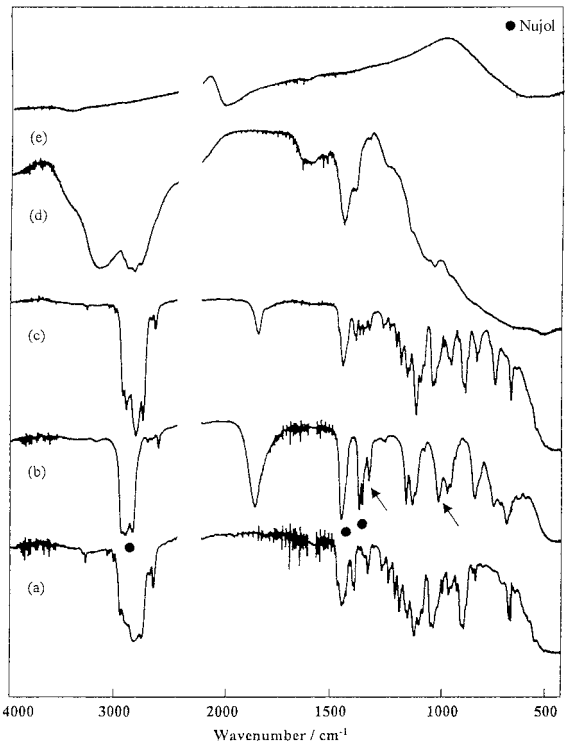

Figure 2 IR spectra of (a) the aminolysis product of $Ti(NMe_2)_4$ with $MeHNCH_2CH_2NHMe$, (b) $(HA1N^iPr)_n$, (c) the blended precursor, (d) the product pyrolyzed under NH_3 at 200 °C, and (e) the product pyrolyzed under NH_3 at 400 °C. Spectra (a) and (c) were obtained by the neat technique; spectrum (b) was obtained by the Nujol technique; spectra (d) and (e) were obtained by the KBr technique.

3 RESULTS AND DISCUSSION

3.1 Characterization of the blended precursor

The ^{1}H NMR spectrum of the blended precursor, as well as those of $(HA1N^iPr)_n$ and the aminolysis product of $Ti(NMe_2)_4$ with $MeHNCH_2CH_2NHMe$, is shown in Fig. 1. The ^{1}H NMR spectrum of the blended precursor shows that the signals at 1.21 ppm (as shown by the arrow) due to —CH_3 of $(HA1N^iPr)_4$ disappear, but the signals due to $(HA1N^iPr)_6$ are clearly observed. Similarly, the profile of the signals of the methyl groups of the aminolysis product of $Ti(NMe_2)_4$ with $MeHNCH_2CH_2NHMe$ is essentially unchanged, except for the disappearance of a very weak doublet at 2.25 ppm (as shown by the arrow). The ^{13}C NMR spectrum of the blended precursor (not shown) can also be interpreted essentially as an overlay of those of $(HA1N^iPr)_n$ and the aminolysis product of $Ti(NMe_2)_4$ with $MeHNCH_2CH_2NHMe$, except for the disappearance of the two singlets at 28.9 and 45.8 ppm, which can be assigned to the —$CH(CH_3)_2$ groups of $(HA1N^iPr)_4$.

The IR spectra (Fig. 2) show that the characteristic peaks of $(HA1N^iPr)_n$ and the aminolysis product of $Ti(NMe_2)_4$ with $MeHNCH_2CH_2NHMe$ are all present in the IR spectrum of the blended precursor, although the bands at 1004 and 1316 cm^{-1} (as shown by the arrow) assignable to $(HA1N^iPr)_n$ disappear.

Thus, based on the NMR and IR results, it can be considered that, although some reactions occur, the reactions between $(HA1N^iPr)_n$ and the aminolysis product of $Ti(NMe_2)_4$ with $MeHNCH_2CH_2NHMe$ are very limited. ICP analysis showed that the Ti:Al molar ratio of the precursor was 2.06:1, confirming the preservation of the metal ratio.

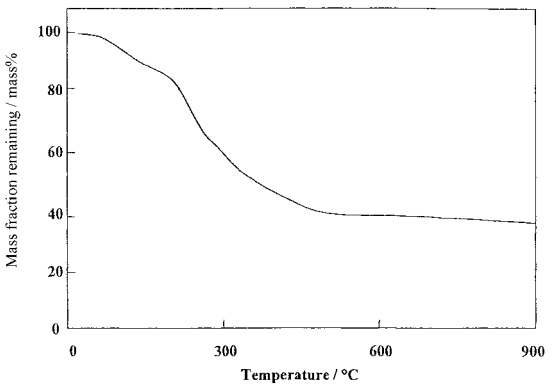

Figure 3 TG curve of the precursor under He at a heating rate of 10 °C/min^{-1}.

3.2 Pyrolysis behavior of the blended precursor

The pyrolysis behavior of the blended precursor under an He flow was investigated using TG. The TG curve of the precursor up to 900 °C shows a three-step mass loss in the following temperature ranges; from room temperature to ~200 °C, ~200 to ~500 °C and from ~500 °C upwards (Fig. 3). The mass losses for these steps are 15%, 42% and 3% respectively, indicating that the decomposition of the organic groups should occur mainly below ~500 °C. The residue at 900 °C was black, and the ceramic yield was 40%, that is greater than the theoretical yield (29%) for the complete conversion of titanium and aluminum in the precursor into TiN and AlN. These results suggest that a considerable amount of carbon arising from the organic groups should be present in the residue, possibly as free carbon and carbide.

The pyrolysis behavior of the blended precursor under NH_3 was investigated on the basis of both the ceramic yields on pyrolysis and IR analysis of the residues. Compared with the IR spectrum of the blended precursor, the intensities of the bands due to the C—H stretching vibration (2760 to 2960 cm^{-1})[23] decrease remarkably in the IR spectrum of the residue pyrolyzed at 200 °C under NH_3 (Fig. 2). In addition, a new strong broad band in the region 3000–3500 cm^{-1} (N—H stretching) and a new weak broad band at 1550–1635 cm^{-1} (N—H deformation) appear.[23] Unlike TG analysis under He (15 mass% of mass loss up to 200 °C), 47 mass% of the precursor was lost after the pyrolysis under NH_3 at 200 °C. All of these results indicate that a large proportion of the organic groups were removed by amine-exchange reactions between the precursor and NH_3.[24] The disappearance of the band at 1860 cm^{-1} indicates that no Al—H groups are present in the residue, possibly due to its reaction with NH_3:

$$\equiv Al—H + NH_3 \xrightarrow{-H_2} \equiv Al—NH_2$$

After the pyrolysis at 400 °C under NH_3, a black residue was obtained with a ceramic yield of 41%. In the IR spectrum of the residue (Fig. 2), the C—H stretching bands in the region from 2760 to 2960 cm^{-1} disappear completely, probably due to the further amine-exchange reaction and the decomposition of the organic groups. The disappearance of the N—H vibration bands suggests that condensation reactions involving NH and NH_2 groups leading to the formation of a highly cross-linked structure should occur.[25] In addition, a new broad band at 2044 cm^{-1} that could be ascribed to the stretching vibration of the C≡N group is observed in the spectrum.[26,27] This band was also present in the IR spectrum of the residue pyrolyzed under NH_3 at 600 °C (not shown). The XRD analysis showed that the residue pyrolyzed at 600 °C was amorphous (not shown).

3.3 Effect of atmospheres on the pyrolyzed products

Pyrolysis of the precursor under Ar at 1500 °C for

Table 1 Ceramic yields and characteristics of the products pyrolyzed under NH_3–N_2 (at 600 °C for 3 h under NH_3, and then at 1350 °C for 8 h under N_2) and Ar (at 1500 °C for 2 h)

Atmosphere	NH_3–N_2	Ar
Ceramic yield/mass%	29.0	31.8
Loss of Ti[a]/mass%	3.7	18.1
Loss of Al[a]/mass%	5.2	9.3
Element analysis		
Ti/mass% (molar ratio)	56.0 (1)	43.5 (1)
Al/mass% (molar ratio)	15.0 (0.48)	13.1 (0.53)
N/mass% (molar ratio)	15.5 (0.94)	6.4 (0.51)
C/mass% (molar ratio)	6.3 (0.45)	30.0 (2.75)
O/mass% (molar ratio)	2.2 (0.12)	1.7 (0.11)
Total/mass%	95.0	94.7
Lattice parameter[b]/nm	0.4249	0.4319

[a] The loss of metal $E_{L(M)}$ (M = Ti or Al) during the pyrolysis was calculated from the amount of the metal in the precursor $W_{P(M)}$ and that in the pryolyzed residue $W_{R(M)}$: $E_{L(M)} = [W_{P(M)} - YW_{R(M)}]/W_{P(M)} \times 100$; Y: the ceramic yield.
[b] The lattice parameter is for NaCl-type compounds.

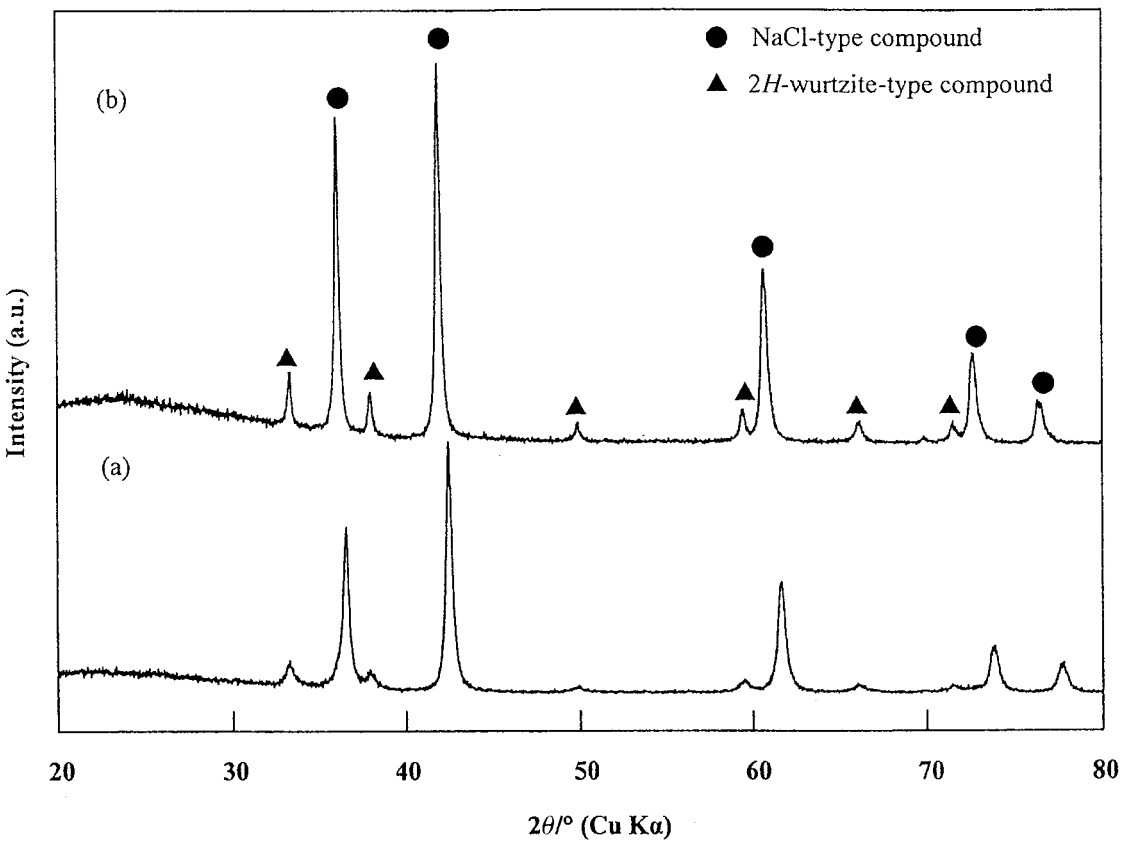

Figure 4 XRD patterns of the products pyrolyzed under (a) NH_3–N_2 (at 600 °C for 3 h under NH_3–N_2 and at 1350 °C for 8 h under N_2) and (b) Ar (at 1500 °C for 2 h).

2 h gave a black solid, whereas a brown solid was obtained after pyrolysis under NH_3 at 600 °C for 3 h and subsequently under N_2 at 1350 °C for 8 h.

The ceramic yields, compositional characteristics and the lattice parameters of the products are shown in Table 1. The ceramic yields are 31.8% and 29.0% for the pyrolyses of the precursor under Ar and NH_3–N_2 respectively. The losses of titanium and aluminum after pyrolysis under Ar are 18.1% and 9.3% respectively, whereas only 3.7% of titanium and 5.1% of aluminum are lost during the pyrolysis under NH_3–N_2. The low metal losses during the pyrolysis under NH_3–N_2 make the Ti:Al molar ratio of the products (2.08:1) very close to that of the precursor (2.06:1), and may be ascribed to the formation of the highly cross-linked structures during the pyrolysis under NH_3 at temperature below 400 °C, as described above.

After the pyrolysis under Ar, about 30% of carbon and 6% of nitrogen are present in the residue. The molar ratio of C to (Ti + Al) is greater than unity (Table 1). Even if we assume that all of the titanium and aluminum are bound to carbon to form TiC and Al_4C_3, C/(Ti+Al) should be less than unity, indicating that a considerable amount of free carbon is present in the residue. On the other hand, pyrolysis of the precursor under NH_3–N_2 gives a residue with about 15% of nitrogen and 6% of carbon. The lower degree of carbon contamination can be ascribed to the amine-exchange reaction during the pyrolysis under NH_3 flow, as shown in Section 3.2.

The XRD patterns of these two pyrolyzed products are shown in Fig. 4. Both the XRD patterns show that the resultant products are ceramic composites containing a 2*H*-wurtzite-type compound exhibiting weak peaks and a well-crystallized NaCl-type compound. Based on the

XRD characterization of the pyrolyzed residues from similar precursors with larger aluminum contents, the 2*H*-wurtzite type compounds should be essentially pure AlN.[17] The lattice parameter of the NaCl-type compound in the product pyrolyzed under NH_3–N_2 is 0.4248 nm, which is similar to that of TiN (0.4242 nm).[28] However, the empirical formula of the product is $TiAl_{0.48}N_{0.94}C_{0.45}O_{0.12}$, indicating that the N/Ti ratio in the NaCl-type compound is 0.46, assuming that all the aluminum atoms form AlN; hence, the NaCl-type phase should be Ti(N,C,O).[17] On the contrary, the lattice parameter of the product pyrolyzed under Ar is 0.4318 nm, which is closer to that of TiC (0.4327 nm)[29] than to that of TiN. The empirical formula of the product is $TiAl_{0.53}N_{0.51}C_{2.75}O_{0.11}$, suggesting that essentially all the nitrogen atoms are present as AlN, and the NaCl-type phase should be the solid solution whose composition is close to Ti(C,O).[30] All of these results indicate that the pyrolysis atmosphere significantly affects the compositions of the NaCl-type compounds.

The surface of the product pyrolyzed under NH_3–N_2 consists mainly of particles with diameters of 20–40 nm, based on scanning electron microscope analysis.[17] On the other hand, slightly larger particles with diameters of 30–100 nm were observed on the surface of the product pyrolyzed under Ar. Thus, the pyrolysis atmosphere also affects the particle sizes of the products to a certain extent.

4 CONCLUSIONS

A soluble blended precursor was prepared simply by mixing $(HAlN^iPr)_n$ and the aminolysis product of $Ti(NMe_2)_4$ with $MeHNCH_2CH_2NHMe$ homogeneously (Ti:Al = 2:1). The pyrolysis of the precursor under Ar led to the presence of a large amount of carbon derived from the organic groups in the resultant product. The carbon content was reduced significantly *via* the pyrolysis under NH_3, because a large proportion of the organic groups in the precursor were removed, probably *via* the amine-exchange reaction. Furthermore, although the precursor possessed only molecular homogeneity, the Ti:Al molar ratio of the blended precursor was preserved during the pyrolysis under NH_3–N_2 because of the formation of the highly cross-linked structure during the pyrolysis under NH_3.

Acknowledgements This work was supported financially in part by the Grant-in Aid for Scientific Research (no. 10650672) from the Ministry of Education, Science, Sports, and Culture, Japan.

REFERENCES

1. Komarneni S. *J. Mater. Chem.* 1992; **2**: 1219.
2. Narula CK. *Ceramic Precursor Technology and Its Applications*. Marcel Dekker: New York, 1995.
3. Dozhdikova OL, Zarichnyak YuP, Zuev AV, Krylov SO, Ordan'yan SS, Stepanenko EK. *Poroshk. Metall. (Kiev)* 1992; 70.
4. Pansayuk AD, Struk LI, Yuga AI, Kolesnichenko LF, Neshpor IP, Fushchich OI. *Poroshk. Metall. (Kiev)* 1990; 76.
5. Mathers JP, Forester TE, Wood WP. *Am. Ceram. Soc. Bull.* 1989; **68**: 1330.
6. Liu YJ, Kim HJ, Egashira Y, Kimura H, Komiyama Y. *J. Am. Ceram. Soc.* 1996; **79**: 1335.
7. Pouskouleli G. *Ceram. Int.* 1989; **15**: 213.
8. Peuckert M, Vaahs T, Baück M. *Adv. Mater.* 1990; **2**: 398.
9. Paine RT, Janik JF, Fan M. *Polyhedron* 1994; **13**: 1225.
10. Bill J, Aldinger F. *Adv. Mater.* 1995; **7**: 775.
11. Interrante LV, Hurley Jr WJ, Schmidt WR, Kwon D, Doremus RH, Marchetti PS, Maciel GE. Preparation of nanocrystalline composites by pyrolysis of organometallic precursors. In *Advanced Composite Materials–Ceramic Transactions*, vol. 19, Sacks MD (ed). American Ceramic Society: Westerville, OH, 1991; 3–17.
12. Seyferth D, Brodt G, Boury B. *J. Mater. Sci. Lett.* 1996; **15**: 348.
13. Hapke J, Ziegler G. *Adv. Mater.* 1995; **7**: 380.
14. Jaschek R, Rüssel C. *J. Non-Cryst. Solids* 1991; **135**: 236.
15. Interrante LV, Schmidt WR, Shaikh SN, Gercia R, Marchetti PS, Maciel GE. Silicon carbide–aluminum nitride solid solutions by pyrolysis of organometallics. In *Chemical Processing of Advanced Materials*, Hench LL, West JK. (eds). John Wiley and Sons: New York, 1992; 777–789.
16. Bao X, Edirisinghe MJ. *Composites Part A* 1999; **30**: 601.
17. Cheng F, Sugahara Y, Kuroda K. *Korean J. Ceram.* 2000; **6**: 32.
18. Schriver DF, Drezdzon MA. *The Manipulation of Air-Sensitive Compounds*, 2nd edn. Wiley–Interscience: New York, 1986.
19. Cucinella S, Dozzi G, Mazzei A, Salvatori T. *J. Organomet. Chem.* 1975; **90**: 257.
20. Kiss-Eröss K. Analytical infrared spectroscopy. In *Comprehensive Analytical Chemistry*, vol. 5, Svehla G (ed.). Elsevier: New York, 1976.
21. Seyferth D, Mignani G. *J. Mater. Sci. Lett.* 1988; **7**: 487.
22. Koyama S, Iizuka D, Sugahara Y, Kuroda K. *Appl. Organomet. Chem.* 1998; **12**: 787.
23. Silverstein RM, Bassler CG, Morrill TC. *Spectrometric Identification of Organic Compounds*. John Wiley & Sons; New York, 1974.

24. Jiang Z, Interrante LV. *Chem. Mater.* 1990; **2**: 439.
25. Dubois LH. *Polyhedron* 1994; **13**: 1329.
26. Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B*, 5th edn. John Wiley & Sons; New York, 1997.
27. Kim JY, Sriram MA, McMichael PH, Kumta PN, Phillips BL, Risbud SH. *J. Phys. Chem. B* 1997; **101**: 4689.
28. Powder diffraction data file, 38–1420, JCPDS International Center for Diffraction Data, Swathmore, PA, 1988.
29. Powder diffraction data file, 32–1383, JCPDS International Center for Diffraction Data, Swathmore, PA, 1988.
30. Neumann G, Kieffer R, Ettmayer P. *Monatsh. Chem.* 1972; **103**: 1130.

