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

Fei Cheng[†], Yoshiyuki Sugahara[†*] and Kazuyuki Kuroda[†,§]

†*Department of Applied Chemistry, School of Science and Engineering*
Waseda University, Ohkubo-3, shinjuku-ku, Tokyo 169-8555, Japan
§*Kagami Memorial Laboratory for Materials Science and Technology*
Waseda University, Nishiwaseda-2, Shinjuku-ku, Tokyo 169-0051, Japan

Pyrolytic preparations of Ti-Al-N ceramics from three blended precursors were investigated. The precursors were prepared by stirring $(HAlN^iPr)_m$ and an aminolysis product of $Ti(NMe_2)_4$ with $MeHNCH_2CH_2NHMe$ 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 NH_3-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 Si_3N_4/BN and Si_3N_4/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 $(HAlN^iPr)_m$ and an aminolysis product of $Ti(NMe_2)_4$ with $MeHNCH_2CH_2NHMe$, 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 $(HAlN^iPr)_m$ was prepared based on a previous report.[18] Examinations of this $(HAlN^iPr)_m$ 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}.[18] The bands at 1165, 1139, 834 cm^{-1} and the bands at 1379, 1365 cm^{-1} were assigned to-CH(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 Ti(NMe$_2$)$_4$ with N,N'-dimethylethylenediamine with Ti(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 specturm 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 blanding 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 flack, 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$_2$O$_3$ 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°C/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°C/min under a He flow. The pyrolyzed products were analyzed by using XRD (Cu Kα; Mac Science MXP^3 diffractometer). The lattice parameters of the pyrolyzed products were calculated by the non-liner 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 $(HAlN^iPr)_m$ and the aminolysis product of Ti(NMe$_2$)$_4$ with MeHNCH$_2$CH$_2$NHMe. The ^1H NMR signals at 1.21 ppm due to the -CH$_3$ of the $(HAlN^iPr)_m$ 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 $(HAlN^iPr)_m$ 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 Ti(NMe$_2$)$_4$ with MeHNCH$_2$CH$_2$NHMe were essentially unchanged, indicating that the reactions between the $(HAlN^iPr)_m$ and the aminolysis product of Ti(NMe$_2$)$_4$ with MeHNCH$_2$CH$_2$NHMe were very limited. These results suggest that essentially no Ti-N-Al bonds are formed during blending the $(HAlN^iPr)_m$ and the aminolysis product of Ti(NMe$_2$)$_4$ with MeHNCH$_2$CH$_2$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%* Element analysis	7.9	10.2	12.3
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 [$W_{R(M)}$].
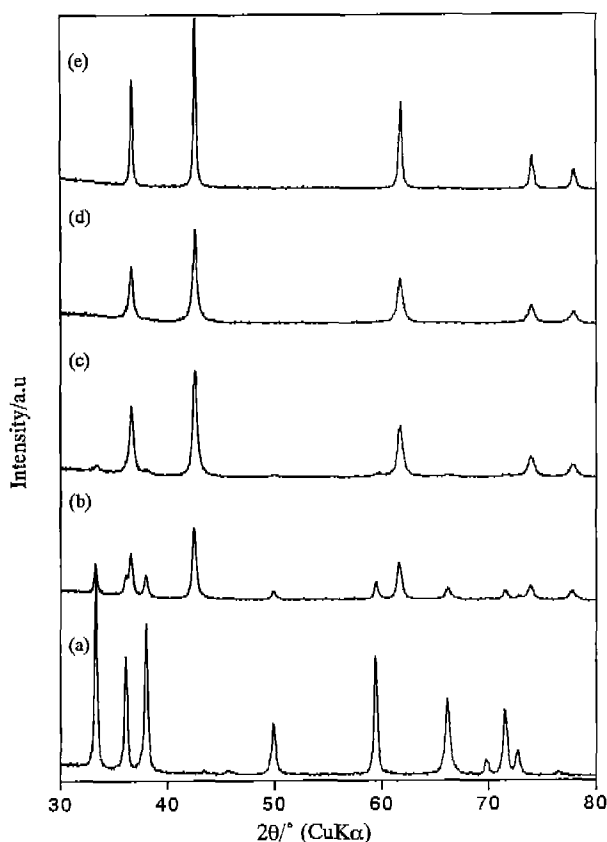$E_{L(M)}=[W_{P(M)}-YW_{R(M)}]/W_{P(M)}\times100$ Y: ceramics yield

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 ~500°C, and only 3% of mass loss was observed at the temperature range of ~500°C-900°C. This suggested that the decomposition of the organic groups should occur mainly at the temperature below ~500°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 be reported previously.[16,17]

Pyrolysis of the blended precursors under NH₃ flow at 600°C for 3 h and subsequently under N₂ 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 NH₃, 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 NH₃ 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 NH₃ 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
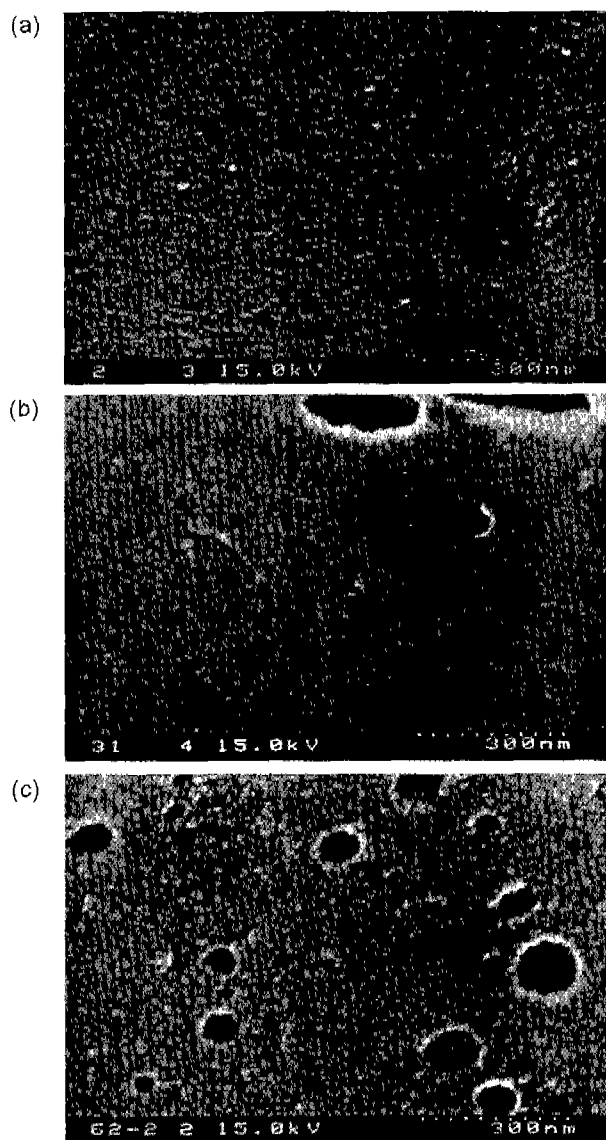
(a)

(b)

(c)

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=0.310-0.3114 nm, c=0.496-0.4986 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°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 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 $(HAlN^iPr)_m$ and an aminolysis product of $Ti(NMe_2)_4$ with $MeHNCH_2CH_2$-NHMe homogeneously, and their pyrolytic conversion behavior was investigated. Pyrolysis of the precursors under NH_3-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 the precursor with Ti:Al=5:1 was pyrolyzed. 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.

References

1. K. K. Chawla, Ceramic Matrix Composites, Chapman &

Hall, London, 1993.

2. S. Komarncni, "Nanocomposites," *J. Mater. Chem.*, **2**, 1219 (1992).

3. C. K.Narula, "Ceramic Precursor Technology and Its Applications," Marcel Dekker, New York, 1995.

4. R. T. Paine, J. F. Janik and M. Fan, "Some Recent Developments in Precursor Routes to Ceramic Nanocomposites," *Polyhedron*, **13**, 1225-1232 (1994).

5. O. L. Dozhdikova, Yu, P. Zarichnyak, A. V. Zuev, S. O. Krylov, S. S. Ordanyan and E. K. Stepanenko, "Anomalies of the Concentration Dependence of Thermal Conductivity of Sintered Compositites of Ultrafine Titanium Nitride-Aluminum Nitride Powders," *Poroshk. Metall. (Kiev)*, **5**, 74 (1992).

6. A. D. Pansayuk, L. I. Struk, A. I. Yuga, L. F. Kolesnichenko, I. P. Neshpor and O. I. Fushchich, "Tribological Properties of Nonmetallic Nitride-based Composites," *Poroshk. Metall., (Kiev)*, **8**, 76-81 (1990).

7. J. P. Mathers, T. E. Forester and W. P. Wood, "Sol-Gel Preparation of Non-oxide Abrasives," *Am. Ceram. Soc. Bull.*, **68**, 1330-1332 (1989).

8. Y. J. Liu, H. J. Kim, Y. Egashira, H. Kimura and H. Komiyama, Using Simultaneous Deposition and Rapid Growth of Produce Nanostructured Composite Films of AlN/TiN by Chemical Vapor Deposition," *J. Am. Ceram. Soc.*, **79**, 1335-1342 (1996).

9. G. Pouskouleli, "Metallorganic Compounds as Preceramic Materials 1. Non-oxide Ceramics," *Ceram. Int.*, **15**, 213-239 (1989).

10. M. Peuckert, T. Vaahs and M. Brück, "Ceramics from Organometallic Polymers," *Adv. Mater.*, **2**, 398-403 (1990).

11. J. Bill and F. Aldinger, "Precursor-Derived Covalent Ceramics," *Adv. Mater.*, **7**, 775-787 (1995).

12. L. V. Interrante, W. J. Hurley, Jr., W. R. Schmidt, D. Kwon, R. H. Doremus, P. S. Marchetti and G. E. Maciel, "Preparation of Nanocrystalline Composites by Pyrolysis of Organometallic Precursors" in "Advanced Composite Materials-Ceramic Transactions vol. 19," ed by M. D. Sacks, American Ceramic Society, Westerville. Ohio (1991). pp. 3-17.

13. R. Jaschek and C. Rüssel, "Titanium Nitride and Titanium Aluminum Nitride Coatings on Silica Glass, Prepared by Pyrolysis of a Polymeric Precursor Film," *J. Non-Cryst. Solids*, **135**, 236-242 (1991).

14. D. Seyferth, G. Brodt and B. Boury, "Polymeric Aluminasi-

lazane Precursors for Aluminosilicon nitride," *J. Mater. Sci. Lett.*, **13**, 348-349 (1996).

15. J. Hapke and G. Ziegler, "Synthesis and Pyrolysis of Liquid Organometallic Precursors for Advanced Si-Ti-C-N Composites," *Adv. Mater.*, **7**, 380-384 (1995).

16. Y. Saito, S. Koyama, Y. Sugahara and K. Kuroda, "Characterization of Aluminum Nitride from a Precursor Poly (isopropyliminoalane)," *J. Ceram. Soc. Jpn.*, **104**, 143-145 (1996).

17. S. Koyama, D. lizuka, Y. Sugahara and K. Kuroda, "Pyrolytic Conversion of Precursors Prepared in Ti(NMe$_2$)$_4$-diamine," *Appl. Organometal. Chem.*, **12**, 787-797 (1998).

18. M. Cesari and S. Cucinella, in "The Chemistry of Inorganic Homo- and Heterocycles," ed. by I. Haiduc and D. B. Sowerby, Academic Press, London, 1987, pp. 167-190.

19. K. Kiss-Eröss, Analytical Infrared Spectroscopy, in "Comprehensive Analytical Chemistry, vol. 5," ed. by G. Svehla, American Elsevier Publishing Company, Inc., New York, 1976.

20. D. Seyferth and G. Mignani, "Preparation of Titanium Nitride and Titanium Carbonitride by the Preceramic Polymer Route," *J. Mater. Sci. Lett.*, **7**, 487-488 (1988).

21. Z. Jiang and L. V. Interrante, "N, N'-Bis(triethylaluminio) ethylenediamine- and N, N'-Bis(trimethylaluminio) ethlenediamine-Derived Organometallic Precursors to Alumium Nitride: Syntheses, Structures and Pyrolyses, *Chem. Mater.*, **2**, 439-446 (1990).

22. H. J. Beattie and F. L. Versnyder, in Transaction American Society for Metals, ed. by R. T. Bayless, American Society for Metals, Cleveland, Ohio, 1953, p. 397.

23. G. Neumann, R. Kieffer and P. Ettmayer, "The System TiC-TiN-TiO," *Monatsh, Chem.*, **103**, 1130-1137 (1972).

24. O. Knoteck and T. Leyendecker, "On the Structure of (Ti, Al)N-PVD Coatings," *J. Solid State Chem.*, **70**, 318-322 (1987).

25. J. R. Roos, J. P. Celis and E. Vancoille, "Interrelationship between Processing, Coating Properties and Founctional Properties of Steered Arc Physically Vapour Deposited (Ti, Al)N and (Ti, Nb)N Coatings," *Thin Solid Films*, **193/194**, 547-556 (1990).

26. I. B. Cutler, P. D. Miller, W. Rafaniello, H. K. Park, D. P. Thompson and K. H. Jack, "New Materials in the Si-Al-O-N and related systems," *Nature*, **275**, 434-435 (1978).

27. G. A. Slack, "Nonmetallic Crystals with high Thermal Conductivity," *J. Phys. Chem. Solids*, **34**, 321-325 (1973).