

Preparation of Silicon Nitride–Titanium Nitride and Titanium–Titanium Nitride Composites from $(\text{CH}_3)_3\text{SiNHTiCl}_3$ -Coated Si_3N_4 and Ti Particles

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[(Trimethylsilyl)amino]titanium trichloride, $(\text{CH}_3)_3\text{SiNHTiCl}_3$, was isolated as a red-orange crystalline solid in 58% yield from the reaction of TiCl_4 with $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$ in 1:1 molar ratio in dichloromethane at -78°C . Pyrolysis of $(\text{CH}_3)_3\text{SiNHTiCl}_3$ at 600°C furnished titanium nitride. This precursor is suitable for the preparation of composites and was employed to prepare Si_3N_4 -TiN and Ti-TiN powders by adding Si_3N_4 particles or titanium powders to a solution of $(\text{CH}_3)_3\text{SiNHTiCl}_3$ in dichloromethane, drying and pyrolyzing the resulting solid. This precursor also has been used as a binder to prepare Si_3N_4 -TiN and Ti-TiN bodies. High-resolution transmission electron microscopic studies of the Si_3N_4 -TiN composite showed that titanium nitride is concentrated on the surface of the Si_3N_4 particles.

I. Introduction

PRE-CERAMIC precursor processing has received extensive attention in recent years for the preparation of diverse advanced materials. This route has been suggested to offer numerous advantages over conventional methods. Low-temperature syntheses, control of the purity, and ease of preparation of materials in the desired forms of fibers, coatings, and films can be achieved by preceramic precursor processing.¹ The chemistry of preceramic polymer pyrolysis routes for materials such as silicon nitride,¹ silicon carbide,^{1,2} and boron nitride³ has been reviewed recently.

Preceramic precursor routes for the preparation of group 4 metal nitrides, with emphasis on titanium nitride, involving the preparation of polymers from amido or alkoxy compounds of group 4 elements also have been reported. For example, Maya *et al.* described the ammonolysis of titanium or zirconium tetrakis(dialkylamides) to obtain insoluble polymers whose pyrolysis gave the respective nitrides.⁴ The soluble polymers obtained in the reactions of $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ with primary amines⁵ have been used by Seyferth and Mignani⁶ in the pyrolytic generation of TiN. A minor variation of this route which employs $\text{Ti}[\text{N}(\text{C}_3\text{H}_7)_2]_4$ instead of $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ was reported subsequently by Mackenzie *et al.*⁷ Jiang and Rhine⁸ synthesized polymers by reacting furfuryl alcohol with titanium alkoxides. These polymers required pyrolysis in an ammonia atmosphere

in the temperature range of 800 – 1200°C to form amorphous titanium nitride and calcining at 1200 – 1500°C for crystallization. A monomer, $\text{FTi}[\text{N}(\text{SiMe}_3)]_3$, also has been proposed to form titanium nitride on the basis of thermoanalytical studies.⁹

Our current interest is focused toward new routes to group 4 materials and composites at low temperatures.^{10,11} We recently described the photolytic decomposition of $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ on irradiation with $1.064\text{-}\mu\text{m}$ light from a pulsed Nd-YAG laser. The decomposition products were pyrolyzed to TiN at 1100°C . We also prepared TiN- Al_2O_3 , TiN- TiO_2 , and Si_3N_4 -TiN composites by this method requiring pyrolysis in the 800 – 1100°C range.¹¹ These materials are useful for automotive applications. For example, titanium nitride–silicon nitride composites have been suggested as structural materials because of their superior mechanical properties.¹² Titanium nitride electrodes have been shown to outperform metallic ones in “sodium heat engines” (SHE).¹³ It should be pointed out that these composites are traditionally prepared by mechanically mixing the components and sintering or hot pressing.¹⁴ Recently, TiO_2 has also been used to prepare TiN/ Si_3N_4 composites because of its ability to convert to TiN in the presence of N_2/H_2 at silicon nitriding temperature.¹⁵ Clearly, there is need for improved methods for preparation of composites with better distribution of components.

In this report, we describe the preparation of crystalline titanium nitride by the pyrolysis of [(trimethylsilyl)amino]titanium trichloride, $(\text{CH}_3)_3\text{SiNHTiCl}_3$, in ammonia at 600 – 800°C . The applications of this route are demonstrated by the preparation of Si_3N_4 -TiN and Ti-TiN composites with the titanium nitride component concentrated on the surface of the substrate particles. An application of preceramic polymers developed by Yajima *et al.*¹⁶ and, more recently, Seyferth and Czubarow¹⁷ employs them as binders in powder metallurgy and ceramic powder processing.¹⁸ We have also investigated the suitability of $(\text{CH}_3)_3\text{SiNHTiCl}_3$ as a binder and as an *in situ* source of TiN to prepare Si_3N_4 -TiN and Ti-TiN bodies.

II. Experimental Procedure

Standard inert atmosphere techniques were used in the synthesis and handling of $(\text{CH}_3)_3\text{SiNHTiCl}_3$.¹⁹ Dichloromethane was stored over phosphorus pentoxide and distilled before use. Commercial titanium tetrachloride and hexamethyldisilazane were purified by distillation. Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN).

(1) Preparation of $(\text{CH}_3)_3\text{SiNHTiCl}_3$

A 250-mL three-necked flask fitted with a condenser was charged with TiCl_4 (6.9 g, 36.3 mmol) and CH_2Cl_2 (100 mL)

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and cooled to -78°C . To this solution, $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$ (5.87 g, 36.3 mmol) was added slowly by syringe with stirring. After the addition was completed, the reaction mixture was warmed slowly to room temperature. An orange precipitate formed (1.0 g), which was filtered. Its analysis (C, 9.32; H, 3.35; N, 5.15; Ti, 22.25; in one example) was not reproducible from reaction to reaction, precluding identification.

The filtrate was concentrated and cooled to -20°C , yielding 5.16 g (58%) of red-orange crystals. Anal. Calcd for $\text{C}_3\text{Cl}_3\text{H}_{10}\text{NSiTi}$: C, 14.8; H, 4.16; N, 5.8; Ti, 19.7. Found: C, 15.1; H, 4.2; N, 6.7; Ti, 19.1. IR[†] (KBr pellet, cm^{-1}): 3196 (m, b, $\nu(\text{NH})$), 2975 (ms, $\nu_{\text{as}}(\text{CH})$ of $\text{Me}(\text{Si}(\text{N}))$), 2900 (w, $\nu_{\text{s}}(\text{CH})$ of $\text{Me}(\text{Si})$), 1406 (m, $\delta_{\text{as}}(\text{Me}(\text{Si}))$), 1252 (s, $\delta_{\text{s}}(\text{C}-\text{Si})$ of $\text{Me}(\text{Si})$), 848 (vs, $\rho(\text{C}-\text{Si})$ of $\text{Me}(\text{Si})$), 805 (vs, $\nu(\text{Si}-\text{N}-\text{Ti})$), 763 (s, $\rho(\text{Me}(\text{Si}))$), 667 ($\nu_{\text{as}}(\text{SiC}_3)$), 462 (w, $\nu(\text{Ti}-\text{Cl})$). ¹H NMR[‡] (CDCl_3): δ 0.42. ¹³C NMR: δ (1.98). The compound turned dark at 110°C without melting in a sealed capillary and did not melt even on being heated to 250°C .

(2) Pyrolysis of $(\text{CH}_3)_3\text{SiNHTiCl}_3$

The sample (2.0 g) was placed in a quartz tube connected to a system to maintain a dynamic nitrogen atmosphere. The temperature of the furnace was raised at a rate of $5^{\circ}\text{C}/\text{min}$ to 800°C and maintained at that temperature for 5 h. A black residue (0.68 g) was obtained whose X-ray powder diffraction[§] pattern matched that of titanium nitride. The elemental analysis for impurity elements: Si, 1.12; Cl, 3.86; C, 0.33.

In another experiment, pyrolysis of a 2.0-g sample of $(\text{CH}_3)_3\text{SiNHTiCl}_3$ was carried out in a dynamic ammonia atmosphere, heating to 600°C at $5^{\circ}\text{C}/\text{min}$ and holding at 600°C for 4 h. A golden-brown material (0.42 g) was obtained which

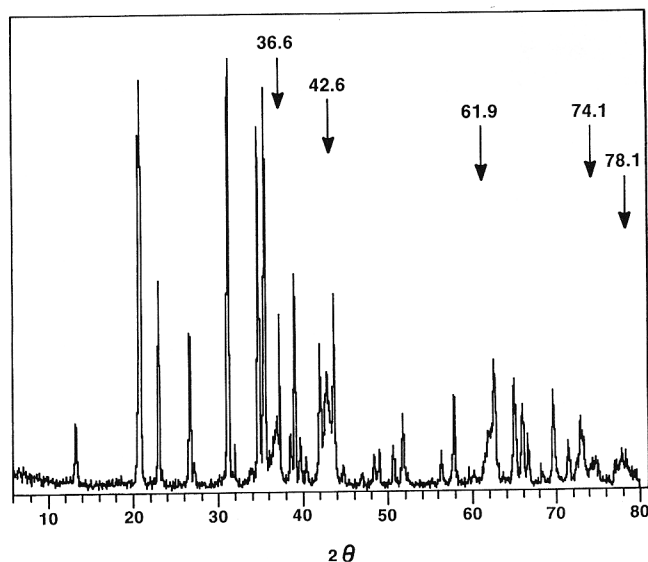


Fig. 2. X-ray powder diffraction pattern of Si_3N_4 -TiN composite powder.

showed broad peaks in its X-ray powder diffraction pattern. Further firing at 800°C for 4 h improved crystallinity and, at 1000°C for 4 h, reduced the carbon content (0.12% as determined by elemental analysis).

(3) Preparation of Silicon Nitride-Titanium Nitride Composites

Dichloromethane was condensed into a mixture of Si_3N_4 powder (2.0 g, particle size less than $1.0\ \mu\text{m}$, CERAC) and $(\text{CH}_3)_3\text{SiNHTiCl}_3$ (1.57 g). The mixture, a slurry of Si_3N_4 in a solution of $(\text{CH}_3)_3\text{SiNHTiCl}_3$, was warmed to room temperature with stirring and the solvent was removed under vacuum with vigorous stirring. The residue was pyrolyzed to 800°C at $5^{\circ}\text{C}/\text{min}$ in an ammonia atmosphere with a 4 h hold at 800°C . The yield was 2.35 g.

In a second experiment, a flask was charged with Si_3N_4 powder (CERAC) (10 g), $(\text{CH}_3)_3\text{SiNHTiCl}_3$ (3.91 g), and dichloromethane ($\sim 40\ \text{mL}$). The solvent was removed with vigorous stirring under vacuum to obtain a free-flowing powder. A portion of this powder was pressed into a green body of size $3.51\ \text{cm} \times 1.2\ \text{cm} \times 0.5\ \text{cm}$ following the procedure described elsewhere.¹⁷ The green body was placed in a furnace and the temperature was raised to 200°C in argon (hold 2 h), 600°C in ammonia (hold 2 h), and 1500°C in argon (hold 2 h). The X-ray powder diffraction pattern showed lines due to β - Si_3N_4 , α - Si_3N_4 , Si, and TiN. The bulk density of the composite was $1.71\ \text{g}/\text{cm}^3$. The silicon in the composite body originated from the decomposition of silicon nitride (a sample of CERAC Si_3N_4 showed lines due to β - Si_3N_4 , α - Si_3N_4 , and Si after heating at 1500°C in argon).

(4) Preparation of Titanium-Titanium Nitride Composites

Titanium powder (8.0 g) was added to a solution of $(\text{CH}_3)_3\text{SiNHTiCl}_3$ (2.0 g) in 50 mL of dichloromethane and the solvent was removed under vacuum with vigorous stirring. A portion of the resulting powder was heated in argon at 200°C followed by heating in ammonia at 800°C . The X-ray powder diffraction pattern of the powder showed peaks for titanium and titanium nitride.

The powder also was used to fabricate a green body as described above which was heated at 200°C in argon (hold 2 h), followed by heating at $5^{\circ}\text{C}/\text{min}$ in ammonia at 600°C (hold 2 h) and argon at 1000°C (hold 2 h). The X-ray powder diffraction pattern of the resulting body showed peaks due to Ti and Ti_2N . The bulk density of the composite was $2.2\ \text{g}/\text{cm}^3$.

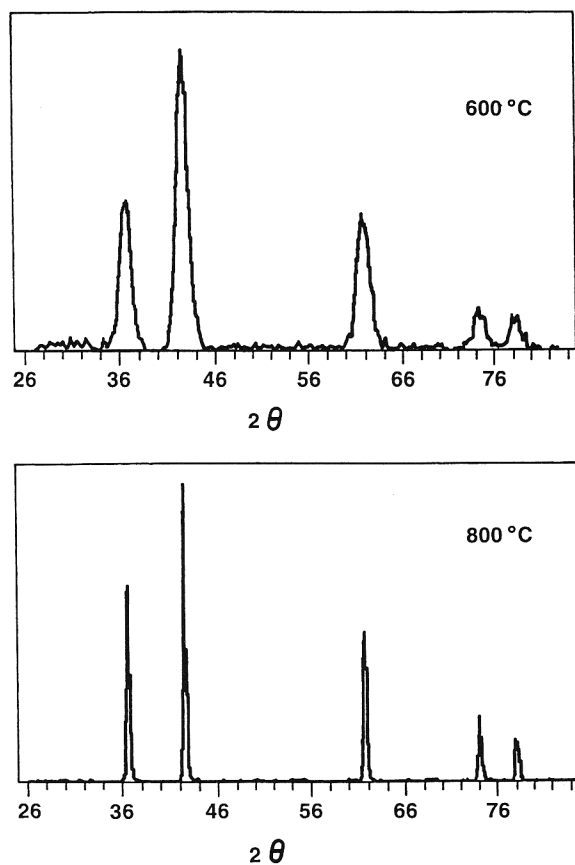


Fig. 1. X-ray powder diffraction patterns of products of pyrolysis (in an NH_3 atmosphere) of [(trimethylsilyl)amino]titanium trichloride.

[†]Galaxy Series FTIR 5000 Spectrometer, Mattson Instruments, Inc., Madison, WI.

[‡]WM-360 NMR Spectrometer, Bruker.

[§]PAD V XRD, Scintag, Santa Clara, CA.

III. Results and Discussion

The reactions of TiCl_4 with $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$ were investigated by Andrianov *et al.*²⁰ and Bürger and Wannagat²¹ under different reaction conditions. Andrianov *et al.* proposed formation of "NHTiCl₂" in the absence of solvents while Bürger and Wannagat isolated $[(\text{CH}_3)_3\text{Si}]_2\text{NH}\cdot 2\text{TiCl}_4$ and $(\text{CH}_3)_3\text{SiNHTiCl}_3$ by varying the reaction conditions and characterized them by elemental analysis.

We have reinvestigated this chemistry and found that "NHTiCl₂" is not formed under the conditions described by Andrianov *et al.*²⁰ We also found that $\text{Me}_3\text{SiNHTiCl}_3$ can be prepared in high yield by the addition of $[(\text{CH}_3)_3\text{Si}]_2\text{NH}$ to a dichloromethane solution of TiCl_4 at -78°C . Red-orange crystals of $\text{Me}_3\text{SiNHTiCl}_3$ were isolated in 58% yield upon appropriate workup.



The infrared spectrum of the product showed $\nu(\text{Si-N-Ti})$ ²¹ at 825 cm^{-1} in addition to expected absorptions for $(\text{CH}_3)_3\text{Si}$ ²² and TiCl_3 ²³ groups. The presence of $\nu(\text{Ti-Cl})$ (terminal) at 462 cm^{-1} suggests a tetrahedral environment for titanium which is possible only if $(\text{CH}_3)_3\text{SiNHTiCl}_3$ is monomeric. $(\text{CH}_3)_3\text{SiNHTiCl}_3$ is stable over several months in an inert atmosphere and is soluble in aprotic organic solvents.

Thermogravimetric analysis⁸ (in argon at $20^\circ\text{C}/\text{min}$) of $(\text{CH}_3)_3\text{SiNHTiCl}_3$ showed a weight loss of 44% in the 120–200°C range. Further heating resulted in a gradual weight loss of 11% in the 220–550°C range and of 7% in the 550–600°C region. The following course can be proposed for the decomposition of $(\text{CH}_3)_3\text{SiNHTiCl}_3$ based on the TGA results:



The first step suggested in the decomposition involves a weight loss of 45%, which is in good agreement with the weight loss observed in the 120–200°C range. The next two steps require a total weight loss of 29.5%. However, the observed weight loss is only 18%, which suggests that the pyrolysis of $(\text{CH}_3)_3\text{SiNHTiCl}_3$ in argon furnishes contaminated TiN. Silicon and chlorine contamination has been previously observed in the pyrolysis of $\text{Me}_3\text{SiAlCl}_2$.²⁴

The pyrolysis of $(\text{CH}_3)_3\text{SiNHTiCl}_3$ in nitrogen to 800°C left a black powder. The X-ray powder diffraction (XRD) pattern of this black powder showed only crystalline titanium nitride (JCPD No. 38,1420) to be present.²⁵ Thus, any contaminants probably are amorphous. Elemental analysis showed the presence of 1.12% Si, 3.86% Cl, and 0.33% carbon in the sample. This supports our inference from TGA data.

The pyrolysis of $(\text{CH}_3)_3\text{SiNHTiCl}_3$ in an ammonia atmosphere to 600°C furnished a golden material which could be ground to a dark-olive-brown powder. The peaks due to TiN in the XRD pattern of the powder were somewhat broad, suggesting a small particle size (Fig. 1). After the samples had been heated at 800°C , the resulting powder showed sharp peaks in its XRD pattern (Fig. 1). Transmission electron micrographs (TEM) showed the particle size to be in the 40–200 nm range. Energy dispersive spectra (EDS) of several particles showed $K\alpha$ peaks for titanium and nitrogen but no peaks for silicon or chlorine. Only a small amount of carbon (0.12%) was found by elemental analysis. These data show that titanium nitride is fairly pure. The titanium nitride yield was 80% based on titanium in $(\text{CH}_3)_3\text{SiNHTiCl}_3$.

In principle, $(\text{CH}_3)_3\text{SiNHTiCl}_3$ can be deposited on the surface of any substrate from its solution and fired to prepare TiN on the substrate. To demonstrate this, we deposited $(\text{CH}_3)_3\text{SiNHTiCl}_3$ on commercial Si_3N_4 and titanium powders and fired the samples in an ammonia atmosphere to prepare Si_3N_4 -TiN and Ti-TiN composites. The X-ray powder diffraction pattern of the Si_3N_4 -TiN powder showed diffraction peaks for α - and β - Si_3N_4 and TiN (Fig. 2) and that of the Ti-TiN sample showed peaks due to titanium and titanium nitride. The particle size of the TiN component in Si_3N_4 -TiN is 300–500 Å as estimated from the Scherrer equation. This procedure is expected to concentrate the TiN component on the surface of the silicon nitride particles. To find support for this, the Si_3N_4 -TiN samples were examined by high-resolution electron microscopy (HREM).¹¹ The atomic structure of particles of thickness less than 10 nm can be resolved directly without the need to thin the sample. Figure 3(a) shows a single Si_3N_4 particle decorated with numerous smaller structures of size range 5–20 nm. The observed size range is consistent with the X-ray diffraction results above, which display peak broadening. The small particles were found to occur on the SiN surface as per Fig. 3(b). The inset to Fig. 3(b) represents the Fourier

⁸TA7 Thermogravimetric Analyzer, Perkin-Elmer, Eden Prairie, MN.

¹¹4000EX HREM, JEOL, Peabody, MA.

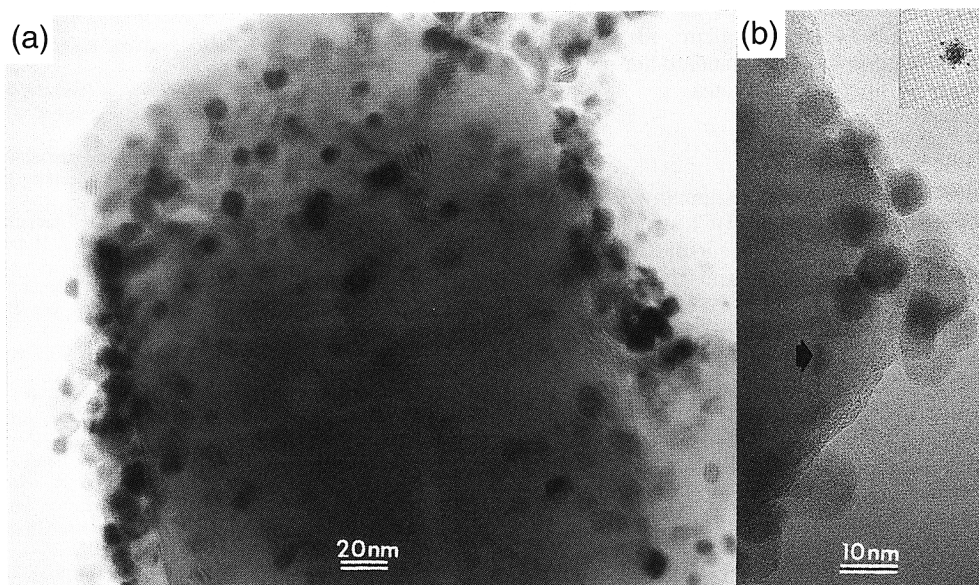


Fig. 3. High-resolution electron micrograph of TiN-Si₃N₄ powders.

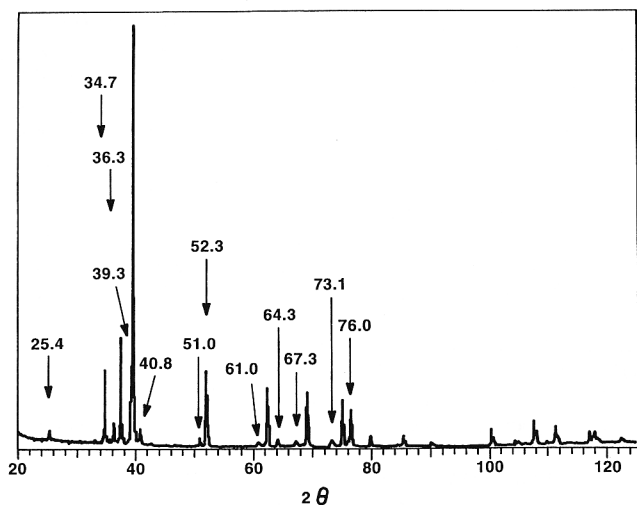


Fig. 4. X-ray powder diffraction pattern of Ti-Ti₂N composite body.

power spectrum of one such particle in a zone axis orientation (indicated by an arrow).²⁶ The aspect ratio of this pattern closely matches that of a face-centered cubic structure, looking along a (011) type zone axis. Measurements of the reciprocal lattice vectors of this pattern were calibrated with reference to similar measurements of the [011] zone axis power spectrum from a silicon standard. The results indicate interplanar spacings of 0.236 and 0.202 nm, which compare favorably with the {111} and {002} spacings of TiN (0.245 and 0.212 nm, respectively).²⁷ Since atomic structure images arise from areas within 5–10 nm of the free surface, these particles must reside in this region. These results clearly show that the titanium nitride component of the composites is concentrated near the surface.

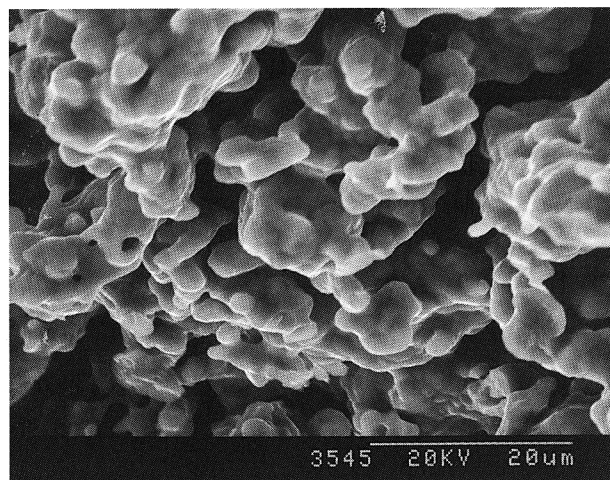
The fabrication of Si₃N₄-TiN and Ti-TiN bodies was carried out by the procedure described by Czubarow and Seyferth.¹⁷ The X-ray powder diffraction of the Si₃N₄-TiN composite body was similar to the one obtained for the powder described above except that the diffraction peaks due to TiN are sharp, suggesting sintering of the fine particles. Additional peaks due to elemental silicon also are present.

The X-ray powder diffraction pattern of the Ti-TiN body showed diffraction peaks due to elemental titanium and nitrogen-deficient titanium nitride, Ti₂N (Fig. 4). The formation of Ti₂N is due to reaction of TiN with Ti metal. The SEM of the body showed high porosity (Fig. 5). The bulk densities of Si₃N₄-TiN and Ti-TiN bodies prepared by using (CH₃)₃SiNHTiCl₃ as binder were 1.71 and 2.2 g/cm³, respectively. Further experiments are in progress using standard hot-pressing methods to improve the densities of composites.

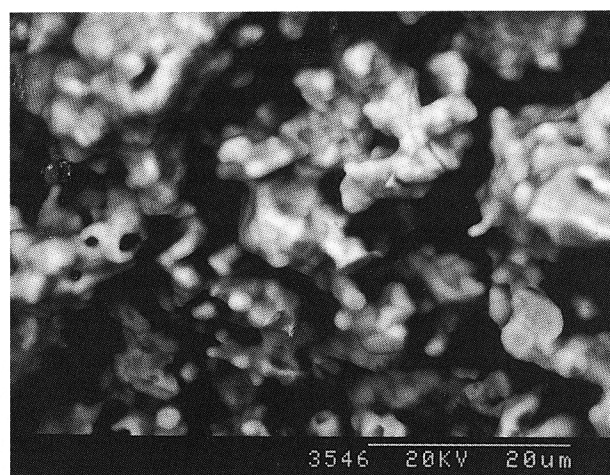
IV. Conclusions

Reaction of titanium tetrachloride with hexamethyldisilazane in dichloromethane furnished (CH₃)₃SiNHTiCl₃ which is soluble in common organic solvents. This precursor formed titanium nitride on pyrolysis in an ammonia atmosphere at 600°C. Si₃N₄-TiN and Ti-TiN composites with TiN content concentrated on the surface of the substrate particles were prepared by depositing (CH₃)₃SiNHTiCl₃ on Si₃N₄ or Ti particles followed by pyrolysis. Thus, this method offers a low-temperature route to titanium nitride and a convenient preparation of composites with the TiN content concentrated on the surface. (CH₃)₃SiNHTiCl₃ also can be used as a binder in the fabrication of ceramic or metal-matrix composite bodies.

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(a)



(b)

Fig. 5. Scanning electron micrographs of Ti-Ti₂N body.

References

- K. J. Wynne and R. W. Rice, "Ceramics via Polymer Pyrolysis," *Annu. Rev. Mater. Sci.*, **14**, 297–334 (1984).
- R. M. Laine, "Preceramic Polymer Routes to Silicon Carbide," *Chem. Mater.*, **5**, 260–79 (1993).
- R. T. Paine and C. K. Narula, "Synthetic Routes to Boron Nitride," *Chem. Rev.*, **90**, 73–92 (1990).
- G. M. Brown and L. Maya, "Ammonolysis Products of the Dialkylamides of Titanium, Zirconium, and Niobium as Precursors to Metal Nitrides," *J. Am. Ceram. Soc.*, **71**, 78–82 (1988).
- D. C. Bradley and E. G. Torrible, "Metallo-Organic Compounds Containing Metal-Nitrogen Bonds, Part IV. Some Bis(primary amino)titanium Compounds," *Can. J. Chem.*, **41**, 134–38 (1963).
- D. Seyferth and G. Mignani, "Preparation of Titanium Nitride and Titanium Carbonitride by the Preceramic Polymer Route," *J. Mater. Sci. Lett.*, **7**, 487–88 (1988).
- H. Zheng, K. Oka, and J. D. Mackenzie, "Preparation of Titanium Carbonitride Coatings by the Sol-Gel Process," *Mater. Res. Soc. Symp. Proc.*, **271**, 893–98 (1992).
- Z. Jiang and W. E. Rhine, "Preparation of TiN and TiC from Polymer Precursor," *Chem. Mater.*, **3**, 1132–37 (1991).
- F. Laurent, C. Daures, L. Valade, R. Choukroun, J.-P. Legros, and P. Cassoux, "Organometallic Precursors to Vanadium and Titanium Carbonitride," *Mater. Res. Soc. Symp. Proc.*, **271**, 875–80 (1992).
- (a) C. K. Narula, "Preparation of Titanium Nitride from Organometallic Precursors," U.S. Pat. No. 5 087 593, 1992. (b) C. K. Narula and G. M. Crosbie, "Preparation of TiN Containing Refractory Material Composites," U.S. Pat. No. 5 350 719, 1992. (c) C. K. Narula, "New Routes to Group IVa Metal Nitrides," *Mater. Res. Soc. Symp. Proc.*, **271**, 881–86 (1992).
- (a) M. M. Maricq and C. K. Narula, "1.064 μm Multiphoton Laser Induced Fluorescence and Dissociation of Tetrakis(dimethylamino)titanium(IV)," *Chem. Phys. Lett.*, **187**, 220–26 (1991). (b) C. K. Narula, M. M. Maricq, B. G. Demczyk, I. T. Salmeen, and W. H. Weber, "Composite Particles by Nd-YAG

Laser Decomposition of $[(\text{CH}_3)_2\text{N}]_4\text{Ti}$ to TiN-Coat TiO_2 , Al_2O_3 , or Si_3N_4 Powders," *J. Am. Ceram. Soc.*, **76** [11] 2727-33 (1993).

¹²R. L. Allor, G. M. Crosbie, E. L. Cartwright, and R. K. Govila, "Silicon Nitride Based Ceramic Composites"; pp. 555-62 in Proceedings of the Sixth Annual ASM/ESD Advanced Composites Conference (Detroit, MI, 1990). ASM International, Metals Park, OH, 1990.

¹³T. K. Hunt, N. Weber, and T. Cole, "High Efficiency Thermoelectric Conversion with β -Alumina Electrolytes, The Sodium Heat Engine," *Solid State Ionics*, **5**, 263-66 (1981).

¹⁴C. Martin, B. Cales, P. Vivier, and P. Mathien, "Electric Discharge Machinable Ceramic Composites," *Mater. Sci. Eng.*, **A109**, 351-56 (1989).

¹⁵C. J. Shin and J.-M. Yang, "Feasibility Study of Developing an *in-situ* TiN-Reinforced Si_3N_4 Composite," *Scr. Metall. Mater.*, **24**, 2419-24 (1990).

¹⁶S. Yajima, T. Shishido, and H. Kayano, "Heat-Resistant Iron-Chromium Alloy with Poly(carbosilane) as Binder," *Nature (London)*, **264**, 237-38 (1976).

¹⁷D. Seyferth and P. Czubarow, "Application of Preceramic Polymers in Powder Metallurgy: Their Use as Low-Loss Binders and for the *in Situ* Formation of Dispersed Ceramic Phases in the Metal Matrix," *Chem. Mater.*, **6**, 10-12 (1994).

¹⁸(a) J. Semen and J. G. Loop, "A Preceramic Polymer Route to Molded Silicon Carbide Ceramic Parts," *Ceram. Eng. Sci. Proc.*, **12**, 1967 (1991).

(b) A. Luckacs III, "Reaction Injection Molding of Ceramics Using a Ceramic Precursor as Binder," U.S. Pat. No. 5 190 709, 1993; *Chem. Abstr.*, **118**, 259, 866 (1993).

¹⁹D. F. Shriver, *The Manipulation of Air-Sensitive Compounds*. McGraw-Hill, New York, 1967.

²⁰K. A. Andrianov, V. V. Astakhin, D. A. Kuchkin, and I. V. Sukhanova, "Reaction of Hexamethyldisilazane with Al and Ti Halides—Synthesis of Trialkylhalosilanes," *Zh. Obshch. Khim.*, **31**, 3410-11 (1961); *Chem. Abstr.*, **57**, 852f (1962).

²¹H. Bürger and U. Wannagat, "Über Titan-Stickstoff-Verbindungen. 2. Mitt.: Silylsubstituierte Titanamide," *Monatsh. Chem.*, **94**, 761-71 (1963).

²²J. Goubeau and J. J.-Barberá, "Tris(trimethylsilyl)amin," *Z. Anorg. Allg. Chem.*, **303** [5-6] 217-26 (1960).

²³(a) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; p. 133. Wiley, New York, 1986. (b) N. N. Alcock, M. P. Butler, and G. R. Willey, "Catane-di- μ -chloro-bis- μ -(trimethylsilylamino)-di[chlorotitanium (IV)]: Preparation, Properties, and Crystal Structure," *J. Chem. Soc., Dalton Trans.*, 707-13 (1976). (c) R. Schlichenmaier und J. Strähle, "Synthese, Eigenschaften und Struktur von Octamerem Titanimidchlorid $[\text{Ti}(\text{NSiMe}_3)_2\text{Cl}_2]_8$," *Z. Anorg. Allg. Chem.*, **619**, 1526-29 (1993).

²⁴R. Riedel, G. Petzow, and U. Klingebiel, "Characterization of AlN Powder Produced by the Reaction of AlCl_3 with Hexamethyldisilazane," *J. Mater. Sci. Lett.*, **9**, 222-24 (1990).

²⁵(a) A. E. Palty, H. Margolin, and J. P. Nielsen, "Titanium-Nitrogen and Titanium-Boron Systems," *Trans. Am. Soc. Met.*, **46**, 312-28 (1954); *Chem. Abstr.*, **48**, 6361a (1954). (b) P. Ehrlich, "Über die binären Systeme des Titans mit den Elementen Stickstoff, Kohlenstoff, Bor und Beryllium," *Z. Anorg. Allg. Chem.*, **259**, 1-48 (1949).

²⁶J. Cowley, *Diffraction Physics*, 2nd rev. ed.; pp. 35-49. North-Holland Physics Publishing Co., New York, 1984.

²⁷P. Villars and L. D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, 2nd ed., Vol. 4. ASM International, Materials Park, OH, 1991. □