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Electrochemical synthesis of TiN precursors and their conversion to fine particles

Kenichiro Nakajima and Shiro Shimada

Division of Materials Science and Engineering, Graduate School of Engineering, Hokkaido University, Nishi-8, Kita-13, Kita-ku, Sapporo 060-8628, Japan

TiN precursors were synthesized at room temperature by galvanostatic electrolysis of a titanium plate and *n*-butylamine. The resulting liquid was black in color, and was converted to viscous liquid by polymerization, then to black solids by heat treatment at 200 °C in vacuum. The solid samples were characterized by IR and ^{1}H NMR measurements, suggesting formation of butylamidotitanium.

The black solids were pyrolyzed both in vacuum and under an ammonia atmosphere at 200 to 1000 °C. The samples were characterized by XRD, TEM, and chemical analysis. Fine TiN crystallites of up to 30 nm in size were produced with the retention of free carbon and/or hydrocarbons at 800 to 1000 °C in vacuum. These impurities were drastically reduced by increasing the TiN content by pyrolysis in ammonia. Two step pyrolysis, consisting of heating at 400 °C for 12 h and successively at a fixed temperature (600, 800 and 1000 °C) for 1 h, was found to be effective in reducing impurities and producing the TiN powders at temperatures as low as 600 °C.

Introduction

Titanium nitride (TiN) exhibits excellent chemical stability against chemical reaction, wear resistance, and high electrical conductivity and thermal stability. Fine TiN particles are an important starting source for fabricating sintered compact or thin films. Synthesis of fine TiN particles by reaction of titanium chloride, ammonia, nitrogen and hydrogen in the gas phase was reported by Kato *et al.*[1] The synthesis method using titanium chloride sometimes causes environmental and health problems because of the formation of chlorine and/or hydrogen chloride. These chlorides are sometimes retained in fine TiN particles, exerting a negative effect on the electrical properties. It is also reported that fine TiN powders may be prepared by pyrolysis of tetrakis(dialkylamido)titanium (TDAT).[2,3] TDAT is an important candidate source for making thin films, but is expensive which restricts its use for fabrication of thin films.[4–8]

Electrochemical synthesis provides a useful method of preparation of ceramic precursors in terms of a simple and easy technique, with no need for special apparatus, at room temperature, compared with conventional chemical reaction methods such as alkoxide and CVD methods. However, in the electrochemical synthesis of a ceramic precursor, it is not certain what reactions occur in the electrolytic cell, and inappropriate electrolysis results in the formation of undesired products. The electrochemical synthesis of zirconia gels and zirconia–alumina gels, and their thermal decomposition to zirconia and zirconia–alumina composites, have been reported.[9–11] The electrochemical synthesis and pyrolysis of several propylamido–metal compounds, including propylamidotitanium, have been reported by Rüssel *et al.*, who stated that propylamidotitanium is obtained by anodic dissolution of titanium with simultaneous cathodic reduction of propylamine at room temperature.[12,13] It is known that various dialkylamidotitaniums, including propylamidotitanium, convert to TiN.[2] Except for the high carbon content in the alkyl group of the amine, butylamidotitanium (BAT) is also suitable as a precursor of TiN because it is soluble in various organic solutions and transforms to a polymer.[14,15] The polymer is favorable for the preparation of thin films because of easy coating and handling, and it results in the production of ceramics with a high TiN content if the carbon can be removed by thermal decomposition. This paper describes the electrochemical synthesis and pyrolysis of BAT, with the aim of obtaining fine TiN particles.

Experimental

The experimental procedure is shown in Fig. 1. Acetonitrile was used as the solvent after distillation in argon in the presence of sodium lumps. Tetrabutylammonium bromide (TBAB), which had been kept for 24 h at 0.1 Pa after passing through liquid nitrogen, was used as the supporting electrolyte. TBAB (2 g) was dissolved in 50 ml of the acetonitrile solution. As-received *n*-butylamine solution (10 ml) was added to the dissolved solution while stirring. The solution was then put in an electrolytic cell with a three-necked flask, as shown in

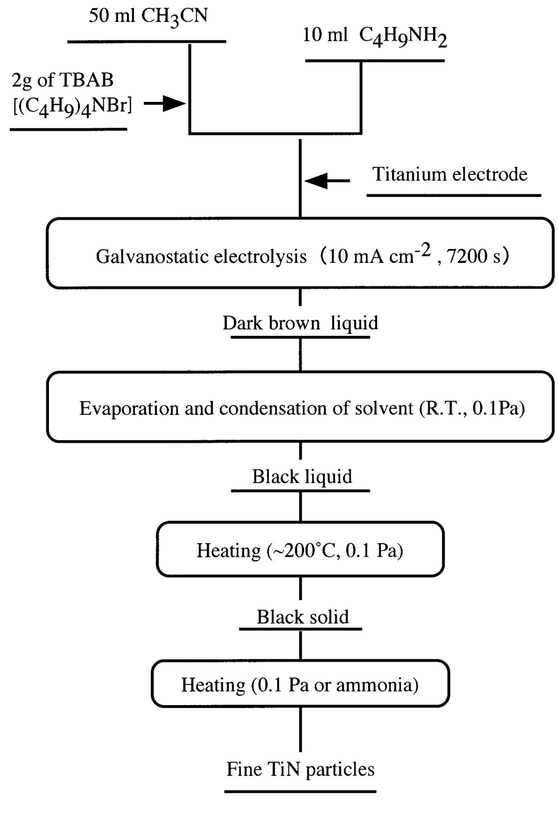

Fig. 1 Flow chart showing the experimental procedure

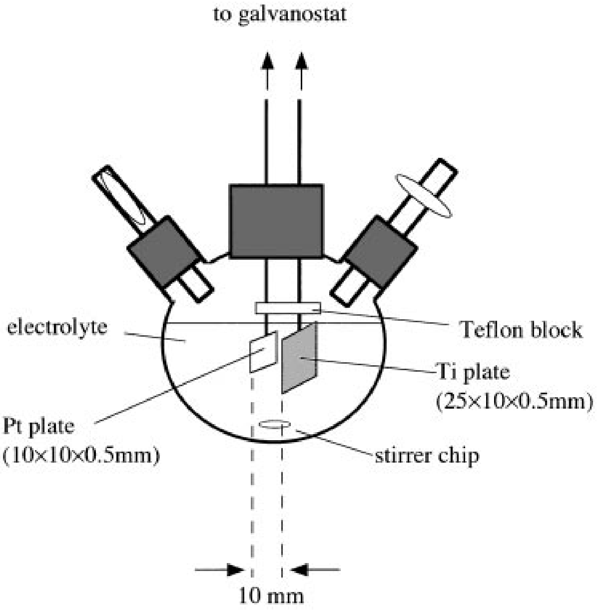

Fig. 2 The electrolytic cell

Fig. 2. The cell was placed in a glove box in a flowing argon atmosphere. A titanium plate (25 × 10 × 1 mm) polished by an abrasive sheet (#1200), followed by ultrasonic cleaning in acetone was used as the anode, and a platinum plate (10 × 10 × 0.5 mm) as the cathode. The distance between the anode and cathode was kept at 10 mm by fixing with a Teflon block. Galvanostatic electrolysis was carried out at a current density of 10 mA cm^{-2} for 7.2 × 10^3 s. During electrolysis, one neck of the three-necked flask was kept open to reduce the increasing inner pressure.

After the electrolysis, a dark brown liquid was produced and then condensed in vacuum (*ca.* 0.1 Pa) at room temperature. The resulting black liquid was characterized by IR spectroscopy. The liquid changed to black solids upon heating to 200 °C in vacuum (*ca.* 0.1 Pa). Powder X-ray diffraction (XRD) and Fourier transform IR spectroscopy (FTIR) of the solid were carried out. A part of the solid was dissolved in chloroform ($CDCl_3$) and then measured by ^{1}H NMR spectroscopy.

The solid obtained by heat treatment at 200 °C was heated at a rate of 10 K min^{-1} to a fixed temperature of 600, 800 or 1000 °C and held at that temperature for 1 h in both vacuum and static ammonia atmospheres. The solid sample was also calcined in two steps by heating at 400 °C for 12 h and successive heating to 600, 800 or 1000 °C. Thermogravimetry (TG) was carried out in argon and in an argon–ammonia mixture to trace the decomposition of the solid. XRD, X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) of the products after pyrolysis were performed. XPS spectra were corrected using 83.8 eV (Au 4f) of gold deposited on the TiN sample. The carbon, nitrogen, hydrogen and oxygen contents in the TiN samples were determined by chemical analysis based on the thermal conductivity method.

Results and Discussion

Electrochemical synthesis of BAT

Fig. 3 shows changes of cell voltage during galvanostatic electrolysis of *n*-butylamine and titanium metal. When electrolysis started at 30 V, gas evolution was observed at the platinum cathode. As the electrolysis proceeded, the electrolyte changed from a transparent to a brown liquid. The initial voltage (30 V) decreased to about 20 V in the first 300 s. This decrease may result from dissolution of titanium oxide which had been present at the surface of the titanium metal. After this decreased, the voltage increased linearly for 6 × 10^3 s, at which time the voltage increased sharply at the end of the electrolysis (6 × 10^3 s), which is due to thinning of the titanium metal by extensive dissolution. The electrolysis was terminated when the titanium metal fell to the bottom of the cell. After the electrolysis, the electrolyte became very dark brown. When the galvanostatic electrolysis was carried out at a larger current density (20 mA cm^{-2}), heat was generated, leading to incomplete electrolysis because of evaporation of the electrolyte. On the other hand, the addition of a large amount of TBAB could lower the voltage, but it became difficult to completely remove the TBAB from the product.

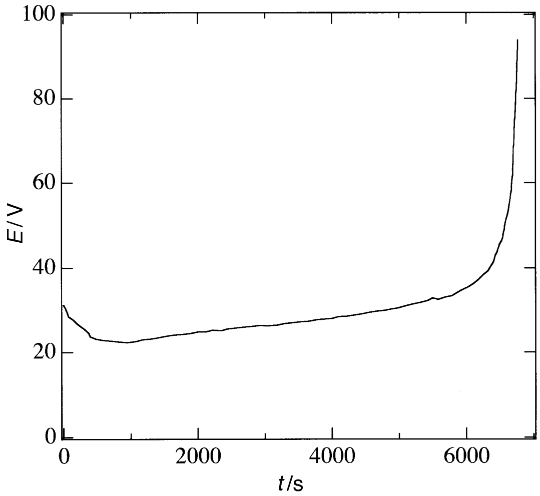

Fig. 3 Change of voltage during galvanostatic electrolysis of titanium nitride and *n*-butylamine

By referring to the mechanism suggested by Rüssel *et al.*,[12] the electrochemical formation of BAT was thought to occur as follows:

(i) anodic dissolution of titanium metal,

$$\mathrm{Ti} \rightarrow \mathrm{Ti}^{n+} + n\mathrm{e}^- \qquad (1)$$

(ii) cathodic reduction of *n*-butylamine at the cathode,

$$n\mathrm{C_4H_9NH_2} + n\mathrm{e}^- \rightarrow n\mathrm{C_4H_9NH}^- + n/2\mathrm{H_2}\uparrow \qquad (2)$$

where *n* is the charge of the metal ($n = 3$ or 4). The formation of hydrogen gas is supported by the evolution of a gas at the cathode. The anions and cations electrochemically produced by eqns. (1) and (2) are believed to form butylamidotitanium.

$$\mathrm{Ti}^{n+} + n(\mathrm{C_4H_9NH}^-) \rightarrow \mathrm{Ti(C_4H_9NH)}_n \qquad (3)$$

The dark brown liquid was condensed at room temperature in vacuum by evaporation of TBAB and acetonitrile. When the condensed liquid was heated in vacuum, it became black, viscous at 50 °C, and solidified at 200 °C. IR spectra of the solid obtained at 200 °C showed bands due to the N—H vibration at 3200 and 1600 cm^{-1} due to the presence of the amine group and the C—H vibrations at 2950 and 1380 cm^{-1} due to the alkyl group, indicating that the solid product contains alkylamido groups. The titanium–nitrogen bond of the TBAB monomer appearing[16] at 600–700 cm^{-1} could not be distinguished because of the high noise level. Fig. 4 shows the ^{1}H NMR spectrum of the solid products dissolved in $CDCl_3$ solution. This spectrum shows signals at δ 1.0, 1.6 and 3.3. It is reported that the position of the α-hydrogen signal varies, depending on the butylamidotitanium structure, appearing at δ 3.0–3.4 in butylamidotitanium.[16] It seems that the signal at δ 3.3 may be due to the α-hydrogen of the butylamidotitanium.

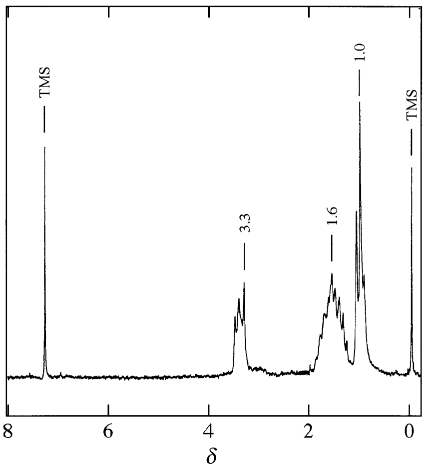

Fig. 4 ^{1}H NMR spectrum of the solid obtained at 200 °C

The results of chemical analysis showed the amounts of nitrogen, carbon and hydrogen in the solid obtained at 200 °C to be 14 ± 1, 41 ± 3 and 7 ± 1 mass%, respectively; the amount of titanium was calculated as the residue to be 38 ± 5 mass%. The composition calculated from these values was $TiN_1C_4H_8$. Since the monomers of $Ti[NH(C_4H_9)]_4$ and $Ti[NH(C_4H_9)]_3$ have the compositions $TiN_4C_{16}H_{40}$ and $TiN_3C_{12}H_{30}$, respectively, the solid obtained at 200 °C contained smaller amounts of carbon, hydrogen and nitrogen than the monomer, and also possessed N—H bonds. It is suggested that the solid was polymerized by heating at 200 °C.

Conversion of BAT to fine TiN particles

Fig. 5 shows the TG curves of the samples heated in flowing argon and in an argon–ammonia mixture. It is seen that the mass loss occurs in two temperature ranges of 50 to 500 °C and 500 to 1000 °C in pure argon. The first step proceeds slowly with a large mass loss in the wide temperature range, which is probably attributable to evolution of organic gases and CH_3CN remaining in the sample. The second step accompanying a relatively small mass loss may be evolution of hydrocarbon gases. The decomposition of the solid is terminated around 1100 °C in argon at which about 70 mass% of the solid was lost. In a mixed atmosphere of argon and ammonia, the decomposition of the solid proceeds in two steps, similarly to that in argon, but the mass loss is terminated at 1000 °C. It was found from XRD that TiN is formed below 1000 °C as described below. This indicates that the addition of ammonia is effective in promoting BAT decomposition to TiN. Although the total mass loss was almost the same in both cases, the product obtained from a mixed atmosphere of ammonia and argon is more pure than that obtained from pure argon, as described below.

Fig. 6 shows the C 1s XPS spectra of the TiN samples obtained in both vacuum and ammonia atmospheres at 800 °C. Vacuum pyrolysis produces two peaks at 284 and 289 eV, assigned as free carbon and alkylamine, respectively.[17,18] No peak at 282 eV corresponding to TiC was recognized in either sample. When the sample was heated in ammonia, the peak at 289 eV (alkylamine) disappeared, but the peak due to free carbon is still observed. From the XPS data, it is understood that an ammonia atmosphere is very effective in reducing the alkylamine remaining in the TiN sample. As shown in Fig. 7(a), the spectrum of N 1s in the vacuum-heated sample obtained at 800 °C shows two broad peaks around 396 and 400 eV, corresponding to TiN and alkylamine, respectively.[17,18] When heated in ammonia, the alkylamine peak at 400 eV is greatly decreased, in contrast to an increase of the TiN peak at 396 eV. These results indicate that the nitrogen content in the TiN sample obtained in ammonia was increased with a considerable decrease of alkylamine. The O 1s and Ti 2p XPS spectra showed that TiO_2 covered the surface of the samples. As Ar sputtering progressed, the XPS spectra of O 1s and Ti 2p were gradually changed with sputtering time, probably because of reduction of these species, which made the assignment of these spectra difficult.

Fig. 8(**A**) and (**B**) show the XRD patterns of products obtained by one step heating of BAT to 200, 600, 800 and 1000 °C in vacuum and in pure ammonia, respectively. It is found that there is no big difference in the XRD patterns of the products obtained at any of the temperatures in either atmosphere. The XRD patterns of the solids at 200 °C show a broad peak around $2\theta = 22°$ [Fig. 8(a)]; this peak might be due to the presence of BAT. When the solid was heated to 600 °C, very broad peaks appeared around 42° and 62° [Fig. 8(b) and (b′)]. At 800 °C, the broad peaks increase with the appearance of an additional peak at 36° [Fig. 8(c) and

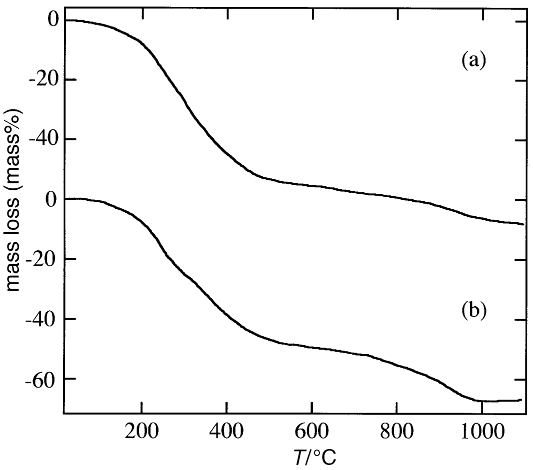

Fig. 5 TG curves of the solid (a) in flowing argon (100 ml min^{-1}) and (b) in a flowing mixture of argon (50 ml min^{-1}) and ammonia (50 ml min^{-1})

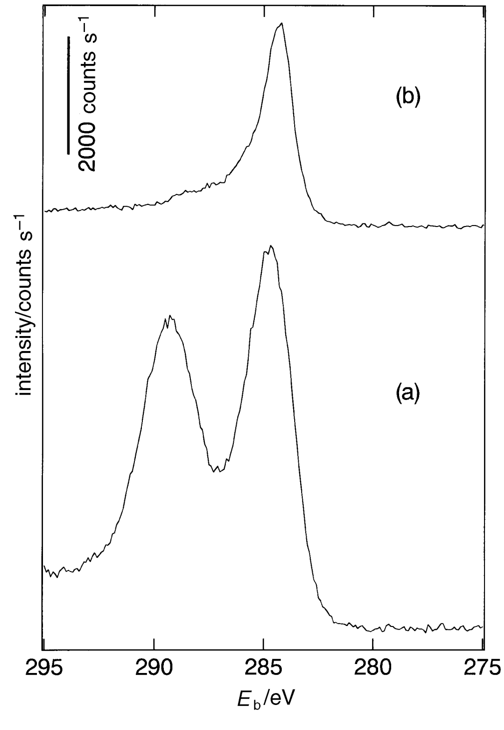

Fig. 6 C 1s XPS spectra of the samples obtained at 800 °C in (a) vacuum and (b) ammonia

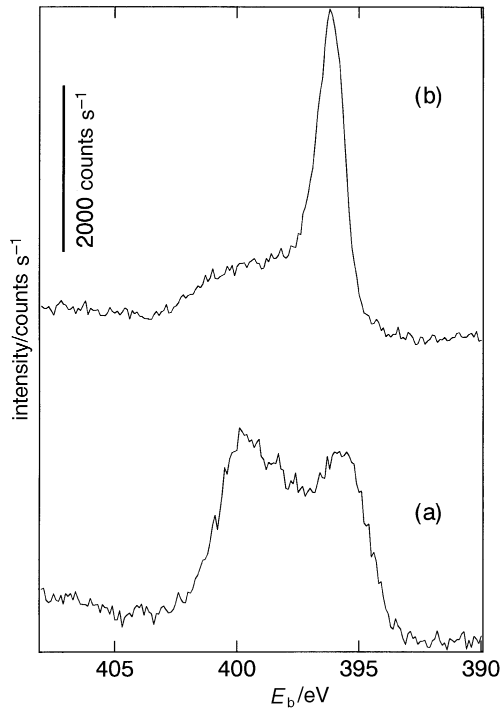

Fig. 7 N 1s XPS spectra of the samples at 800 °C in (a) vacuum and (b) ammonia

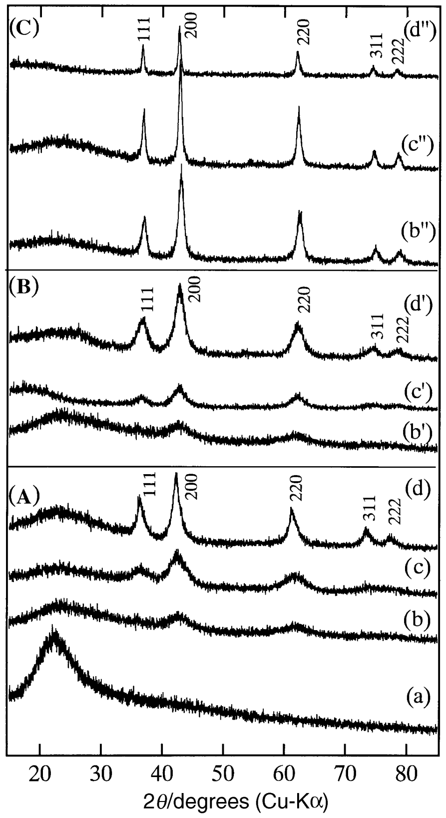

Fig. 8 XRD patterns of the samples heated by one step calcination **(A)** in vacuum, **(B)** in ammonia and by two step calcinations **(C)** in ammonia; (a) the solid obtained at 200 °C, (b–b″) the sample heated to 600 °C, (c–c″) 800 °C and (d–d″) 1000 °C

(c′)]. These three peaks were identified as TiN.[19] The broad peaks reflect the formation of small crystallites of TiN. At the higher temperature of 1000 °C, the TiN peaks become strong, probably resulting from enhanced growth of TiN crystallites [Fig. 8(d) and (d′)]. Table 1 shows the results of elemental analysis of the samples obtained at 1000 °C. The products obtained at 1000 °C in vacuum were deep brown in color and contained 10 ± 3 mass% of oxygen, 16 ± 1 mass% of carbon and < 1 mass% of hydrogen. The lattice constant of the sample was smaller ($a_0 = 0.4214 \pm 0.001$ nm) than that of pure TiN ($a_0 = 0.4242 \pm 0.001$ nm). The products obtained at 1000 °C in ammonia were gold in color, and showed the reduction of carbon and hydrogen to 0 and 0.2 mass% in contrast to increase of nitrogen to 13 ± 1 mass%. It is known that the lattice constant of TiN decreases with the lowering of the nitrogen content,[20] but the lattice constant was also small ($a_0 = 0.4225$ nm).The small lattice constant of the samples heated in both vacuum and ammonia are due to the fact that the samples form a solid solution of TiN and TiO rather than having deficiency of nitrogen.

As described above, the presence of ammonia drastically decreased the amount of free carbon and alkylamine, resulting in the increase of the nitrogen content in TiN. Such an effect of ammonia is often observed in the formation of TiN thin films.[3–8] It is supposed that this effect is due to the occurrence of a transamination reaction by substitution of alkylamido for ammonia,[21] eliminating butylamine and a considerable amount of free carbon remaining in the sample. Since a considerable evolution of organic gas occurred at 400 °C, as seen from the TG curves, two step pyrolysis by heating at 400 °C for 12 h and successive heating at a fixed temperature (600, 800 or 1000 °C) was attempted. The XRD patterns of the products calcined by the two step heating are shown in Fig. 8(**C**). It is seen that the TiN is already well crystallized at 600 °C, compared with one step heating. With increasing temperature, the TiN peaks gradually become sharp. The elemental analysis showed that the samples obtained at 600 to 1000 °C contain 16 ± 1 mass% nitrogen, 2 ± 2 mass% carbon, and 0.5 ± 0.2 mass% of hydrogen. The carbon content was reduced to by about 50% by two step calcination in ammonia. The lattice constants of the samples obtained at 600, 800 and 1000 °C were measured to be $a_0 = 0.424 \pm 0.01$, 0.421 ± 0.001, and 0.423 ± 0.002 nm, respectively, becoming slightly larger with increasing temperature, compared with the one step calcination.

The samples obtained at 800 and 1000 °C in both vacuum and ammonia by one step calcination were examined by TEM (Fig. 9). Electron diffraction showed that the samples calcined at 800 °C in vacuum gave weak rings of TiN and that those at 1000 °C in vacuum and those at 800 and 1000 °C in ammonia produced distinct rings of TiN with the occasional appearance of spots. It is seen that TiN crystallites obtained at 800 °C in vacuum are very small, being only a few nm in size [Fig. 9(a)]. The crystallites at 1000 °C were relatively uniform and increased to about 10 nm in size [Fig. 9(b)]. The presence of ammonia produced crystallites less than 10 nm in size at 800 °C [Fig. 9(c)]. Some crystallites were grown to 30 nm sizes by the ammonia treatment at 1000 °C [Fig. 9(d)].

Table 1 Elemental analysis of the products obtained by the thermal decomposition of butylamidotitanium to 1000 °C

atmosphere	N (mass%)	O (mass%)	C (mass%)	H (mass%)	Ti[a] (mass%)
vacumm	10 ± 3	11 ± 2	16 ± 1	< 1	62 ± 6
ammonia (one step)	13 ± 1	8 ± 2	0	0.2	80 ± 2
ammonia (two step)	16 ± 1	4 ± 1	0	0.5 ± 0.2	80 ± 2

[a] Calculated from the residual masses.

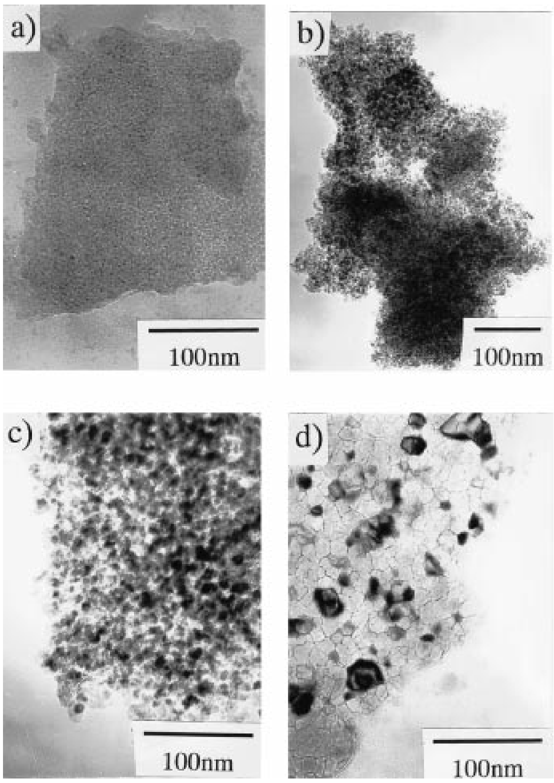

Fig. 9 TEM bright field image of the samples heated to (a) 800 °C, (b) 1000 °C in vacuum and (c) 800, (d) 1000 °C in ammonia by one step calcination

Conclusion

Galvanostatic electrolysis of titanium metal and *n*-butylamine produced a black liquid at room temperature. Heat-treatment of the liquid at 200 °C in vacuum gave a black solid. The IR and ^{1}H NMR spectra of the solid suggested the formation of butylamidotitanium.

When the solid was heated in vacuum, a lot of carbon and/or hydrocarbons remained in the TiN samples. By pyrolysis in ammonia, the carbon and/or hydrocarbon were drastically reduced, but the lattice constants of TiN were still smaller than that of pure TiN. It was found that two step pyrolysis in ammonia was effective in reducing the amount of carbon and/or hydrocarbon. The lattice constants of the two step calcined samples in ammonia were slightly increased compared with that of pure TiN. TEM observation showed that fine TiN crystallites of up to 30 nm in size were formed by pyrolysis of the solid in vacuum and ammonia at 800 and 1000 °C.

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