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Synthesis of titanium nitride by a spark-discharge method in liquid ammonia

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Titanium nitride powders were synthesized by the spark-discharge method in liquid ammonia at -78 to 130 °C and 3.5–10.5 kV discharge voltage using titanium pellets as the starting materials. Titanium nitride possessing nitrogen defect, TiN_{1-x} ($x \simeq 0.5$), was obtained as the main product, together with small amounts of α-Ti alloyed with nitrogen. The increase in temperature of the liquid ammonia resulted in an increase in the titanium nitride content in the product but a decrease in the powder production rate. By calcining the mixed powders of TiN_{1-x} and α-Ti in a nitrogen atmosphere around 1200 °C, stoichiometric TiN was obtained as single phase.

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1. Introduction

Because of the excellent high-temperature strength, thermal shock resistance, hardness and thermal conductivity, titanium nitride has received much attention for a variety of applications. Many studies have focused on the fabrication of powders with high purity, submicrometre particle size, a narrow particle-size distribution and minimal agglomeration, in order to improve the sinterability. Several methods have been commercially applied for fabricating titanium nitrides, including reacting metal powders with nitrogen and reacting metal chloride vapour with ammonia. These reactions usually require temperatures higher than 1000 °C, which result in the grain growth and hard agglomeration of the powders. The spark-discharge method, in which a spark discharge takes place at the contact points of pellets dipped in the liquid medium, is an attractive method to fabricate fine powder at low temperature. This method has been developed by Ishibashi *et al.* [1–3] and has been commercially operated for the synthesis of metal hydroxides and oxides such as $Al(OH)_3$, $Mg(OH)_2$, Al_2O_3, MgO and $MgAl_2O_4$ using water as the liquid medium. In previous papers, we reported that non-oxide ceramics such as AlN, TiN, Cr_2N, Al_4C_3, TiC, Fe_2C and Cr_7C_3 were able to be fabricated by the spark-discharge method using liquid ammonia and hydrocarbon as the liquid media [4, 5]. Kumar and Roy [6, 7] and Ono *et al.* [8] reported the fabrication of various non-oxide ceramic powders by the reactive-electrode submerged-arc (RESA) technique based on striking an arc between two metallic electrodes submerged in a dielectric liquid such as silicone oil, liquid nitrogen and liquid ammonia. It is speculated that the reaction of metal powder and the surrounding liquid in the spark-discharge process appeared to take place at much lower temperatures than those in the RESA process, because the reaction products of the Iwatani process are hydroxides and other hydrated phases, whereas in the RESA process, using water as the liquid medium, anhydrous phases are obtained. Tanaka *et al.* [9] also reported the synthesis of titanium nitride powder by a d.c. spark discharge at 20–45 V in liquid nitrogen using a rotating titanium disc electrode coupled with a titanium wire electrode. It seems that the spark discharge method using metal pellets as starting material possesses advantages, such as easy operation and preparing ceramic powders of uniform and repeatable character. However, the details of the reactions have not yet been clarified. In the present study, a series of tests was conducted to fabricate the titanium nitride powder by the spark-discharge method using liquid ammonia as the reaction medium.

2. Experimental procedure

Schematic illustrations of the apparatus for the spark discharge and the spark-discharge circuit are shown in Fig. 1. The spark-discharge reaction was conducted in an autoclave of 250 cm^3 internal volume, fabricated from SUS 304 type stainless steel. Polytetrafluoroethylene (Teflon) cell, 20 mm wide, 40 mm long and 30 mm deep, was inserted in the reaction vessel. Titanium plates, 20 mm × 40 mm × 1 mm were used for electrode, while titanium pellet, 2 mm diameter × 5 mm was used for the starting metal and liquid ammonia for the dielectric liquid medium. Trace amounts of water contained in liquid ammonia were removed using sodium metal. About 30 g titanium pellets were placed in the cell and then the vessel was evacuated and cooled by a dry ice-methanol solution prior to introducing 80 cm^3 liquid ammonia. After

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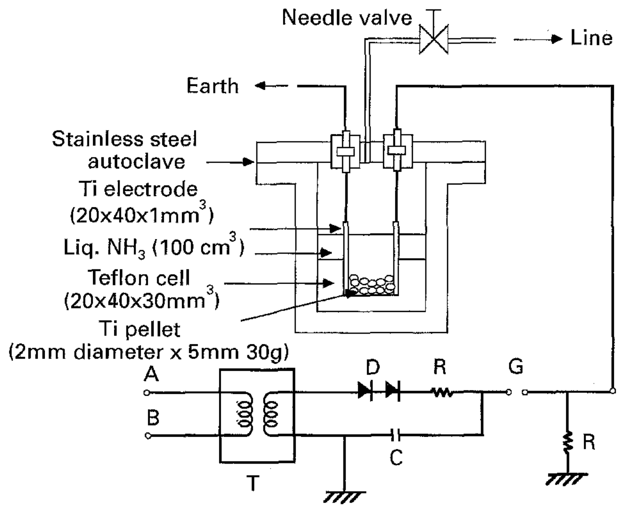

Figure 1 Schematic illustration of the apparatus and spark-discharge circuit. A, B, input, 100 V, 50 Hz; T, transformer, 170 VA, 100 V/15 kV; C, condenser, 0.1 μF; D, diode; R, resistance, 10 kΩ; G, gap.

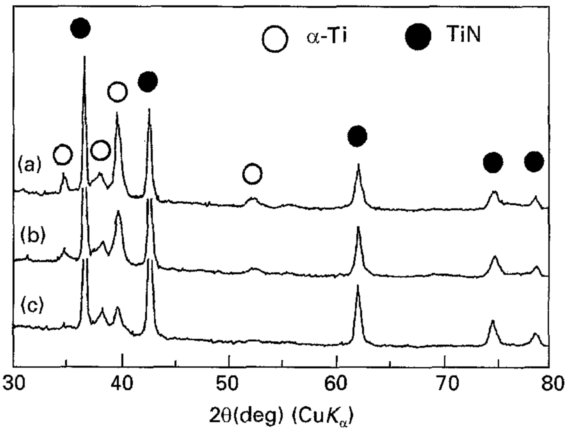

Figure 2 X-ray diffraction patterns of the powder fabricated by the spark-discharge reaction in liquid ammonia using titanium pellets at (a) − 78, (b) 0 and (c) 100 °C and 5 kV discharge voltage for 1 h.

raising the temperature of the vessel to the desired temperature using an oil bath, the spark-discharge reaction was started. An alternating current of 50 cycles was supplied as the primary electric source. Primary input voltage was adjusted to 50 V. Using a diode, a transformer of 170 VA and 100 V/15 kV, and a condenser of 0.1 μF, d.c. spark discharge at high discharge voltage, was generated. The discharge voltage was adjusted to 1.2–10.5 kV by controlling the gap width, *G*. The discharge current frequency was 1.25–5 s^{-1}. After completing the spark-discharge reaction, ammonia was evaporated prior to recovering the product powder in a nitrogen atmosphere using a glove box. The powders were characterized by X-ray diffraction analysis (XRD) using nickel-filtered CuK_α radiation, simultaneous thermogravimetry and differential thermal analysis (TG–DTA), scanning electron microscopy (SEM), centrifugal particle-size analysis. The titanium content in the powder was determined by gravimetry as TiO_2 after oxidizing the powder in air at 1200 °C for 2 h, and that of nitrogen was determined by alkalimetry after decomposing TiN by alkali fusion and absorbing the evolved ammonia with sulphuric acid as follows.

$$2TiN + 8NaOH \rightarrow 2TiO_2 + 4Na_2O + H_2 + 2NH_3 \tag{1}$$

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 \tag{2}$$

3. Results and discussion

3.1. Fabrication of titanium nitride

By the spark-discharge reactions in liquid ammonia using titanium pellet and electrodes at − 78 to 130 °C and 5 kV discharge voltage for 1 h, 1.14–0.08 g black powders were obtained. XRD profiles of the powders are shown in Fig. 2. The XRD peaks of the powders could be indexed as the mixture of TiN of the space group F*m*3*m* [10] and a small amount of α-Ti of the space group I4₁/*amd* [11]. There were two peaks around 40° which located at slightly lower angles than that corresponding to *d*(0 0 1) of pure α-Ti (ASTM 5-0682) [11]. From the phase diagram of the Ti–N system [12], it is seen that there are two phases of titanium, α-Ti and β-Ti, depending on the amount of nitrogen alloyed, above 800 °C. β-Ti can be alloyed at lower nitrogen concentrations than α-Ti, and transforms to α-Ti at low temperature. Therefore, the two peaks around 40° might be attributed to α-Ti alloyed with different amounts of nitrogen formed by rapid cooling after the spark-discharge reaction.

The lattice constants of titanium nitride, the contents of titanium and nitrogen, and crystallite size for the powders fabricated at 5 kV discharge voltage and various temperatures for 1 h, are shown in Table I. The lattice constants of titanium nitride fabricated by the spark-discharge reactions were 0.422 nm and were significantly smaller than that of stoichiometric TiN shown by JCPDS 38-1420 [10], indicating that the products were titanium nitride with nitrogen defects, TiN_{1-x}. According to the relationship between the lattice constant and composition for TiN_{1-x} [13], the chemical composition of titanium nitride obtained in the present reaction was determined as $TiN_{0.44}$–$TiN_{0.50}$ as shown in Table I. The nitrogen content in the product increased with increasing temperature of the liquid ammonia, indicating the increase of TiN_{1-x} content in the products. The total amounts of nitrogen and titanium content amounted to only 93–97 wt %. This might be due to the oxidation of the powders induced by oxygen and/or water vapour in air during handling of the powders. The crystallite size of titanium nitride determined by Scherrer's equation using XRD peaks of (1 1 1) and (2 0 0) monotonically increased from 23.1 to 26.0 m with increasing liquid ammonia temperature from − 78 to 130 °C.

The molar ratios of N/Ti in the powders and the powder production rates at various liquid ammonia temperatures and 5 kV discharge voltage are shown in Fig. 3. The molar ratio of N/Ti significantly increased with increasing liquid ammonia temperature, while the powder production rate greatly decreased.

TABLE I Lattice parameter, *a*, of titanium nitride, titanium and nitrogen contents, and crystallite size for the powders fabricated by the spark-discharge reaction in liquid ammonia using titanium pellets at 5 kV discharge voltage and various temperatures for 1 h

Temperature (°C)	*a* (nm)	Compound[a]	Chemical composition		Crystallite
			Ti (wt %)	N (wt %)	size (nm)
− 78	0.4216	$TiN_{0.44}$	87.8	5.6	23.1
0	0.4220	$TiN_{0.46}$	88.6	8.5	24.5
50	0.4218	$TiN_{0.44}$	87.1	9.0	25.3
100	0.4221	$TiN_{0.48}$	85.7	7.3	25.5
130	0.4222	$TiN_{0.50}$	86.2	10.6	26.0

[a] Determined according to the relationship between *a* and *x* in TiN_{1-x} [12].

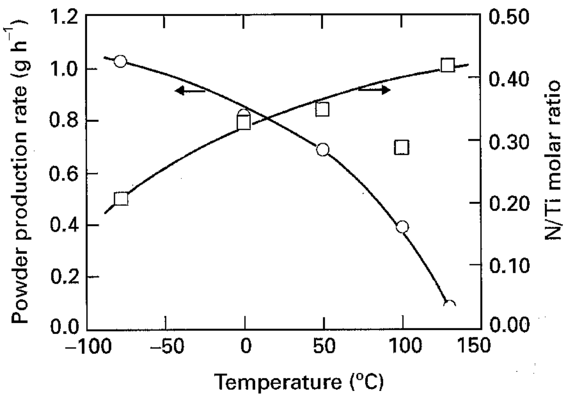

Figure 3 Molar ratio of N/Ti in the powder and powder production rate by the spark-discharge reaction in liquid ammonia using titanium pellets at 5 kV discharge voltage and various temperatures.

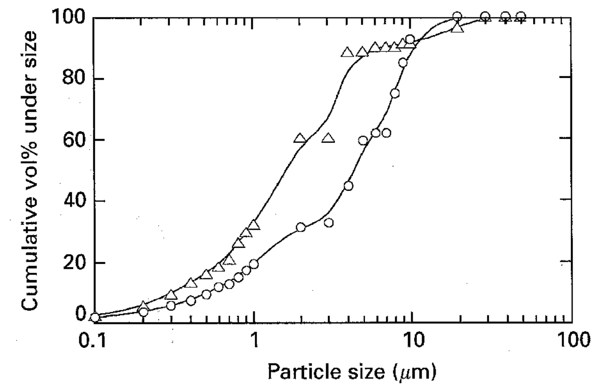

Figure 4 Particle-size distributions of the powders fabricated by the spark-discharge reaction in liquid ammonia using titanium pellets at 100 °C and (Δ) 3.5 and (○) 10.5 kV discharge voltages for 1 h.

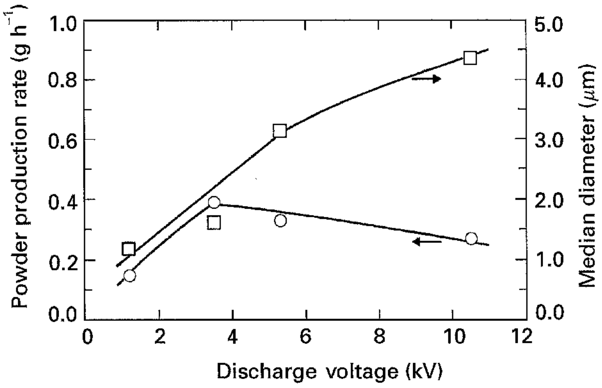

Figure 5 Powder production rate and mean particle size for the powders fabricated by the spark-discharge reaction in liquid ammonia using titanium pellets at 100 °C and various discharge voltages.

The spark provides a zone of extremely high temperature, resulting in the vaporization of the liquid medium and fusion and/or vaporization of the metal around the contact points. It is suspected that the formation of a fine powder from the pellet is promoted by the bombardment accompanied by the vaporization of the liquid medium with rapid and large volume expansion.

Therefore, the decrease of the powder formation rate with increasing temperature seemed to be due to the decrease of the bombardment stress, because the density of the liquid ammonia should decrease with increasing temperature.

The particle-size distributions of powders fabricated at 100 °C and 3.5 and 10.5 kV discharge voltage are shown in Fig. 4. The powders consisted of particles less than 10 μm in size. The particle size seemed to decrease with decreasing discharge voltage.

The effects of discharge voltage on the mean diameter of the particles and the powder production rate were tested at 100 °C by changing the gap width, *G*, in the spark-discharge circuit. The results are shown in Fig. 5. The mean diameter of the particles monotonically increased with increasing discharge voltage. On the other hand, the powder production rate increased with increasing discharge voltage up to 3.5 kV, and then decreased, indicating there is an optimum discharge voltage for the synthesis of titanium nitride powder. This might be due to the increase of the bombardment stress at the spark point and the decrease of spark frequency with increasing discharge voltage.

The scanning electron micrographs of the powders and the surface of the titanium electrode prepared at 10.5 kV discharge voltage and 100 °C are shown in Fig. 6a and b, respectively. The particles obtained were spherical shell fragments. Most of the particles were 1–5 μm diameter. Figure 7b indicates that titanium was fused and large cracks and holes were formed at the spark point. Therefore, the spark seemed to

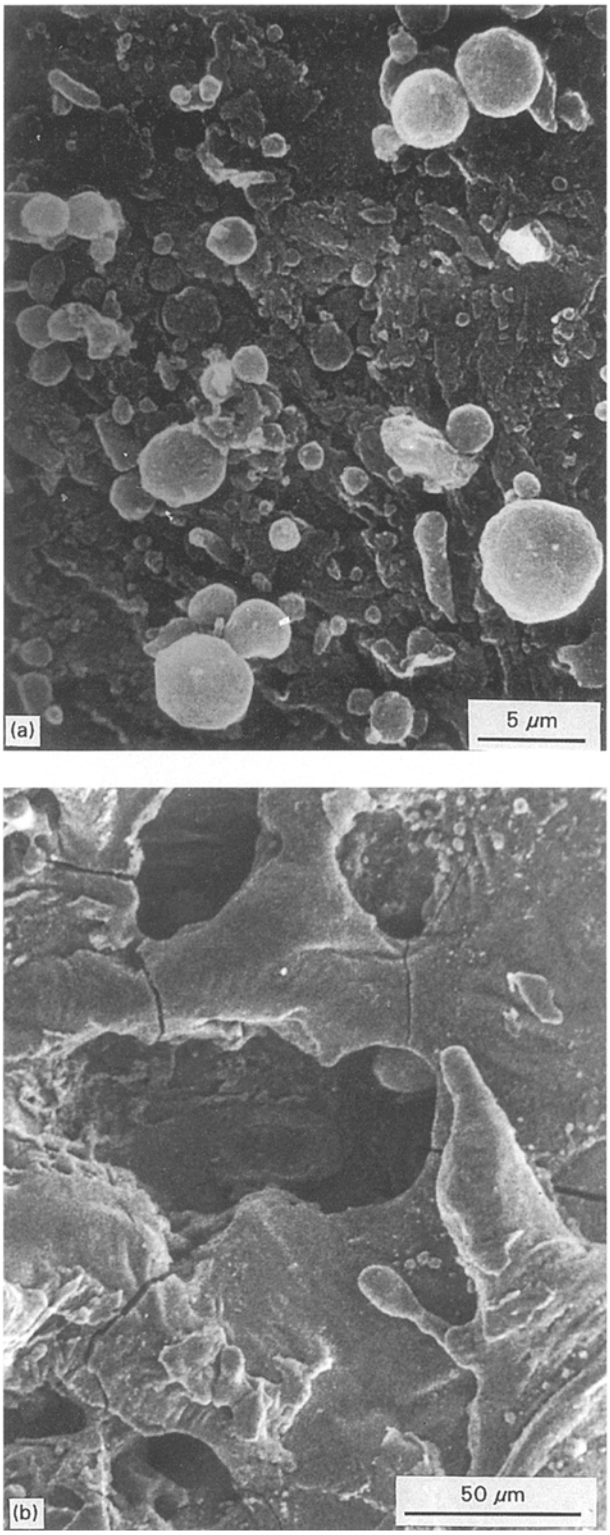

Figure 6 Scanning electron micrographs of (a) the powders and (b) the surface of the titanium electrode prepared by the spark-discharge reaction in liquid ammonia using titanium pellets at 100 °C and 10.5 kV discharge voltage.

provide a high temperature above the melting point of titanium, 1725 °C, resulting in vaporization of surrounding ammonia and elimination of the small parts on the pellet to cause their reaction. The cracks might be formed by the thermal shock when the metal heated by a spark is quenched by the surrounding liquid ammonia.

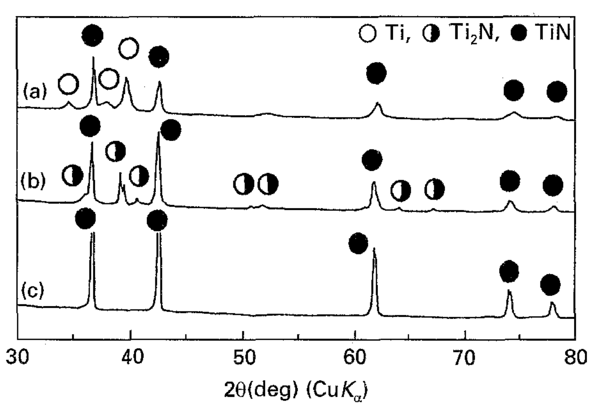

Figure 7 X-ray diffraction profiles of the powders (a) as-prepared by the spark-discharge reaction in liquid ammonia using titanium pellets at − 78 °C and 5 kV discharge voltage for 1 h, and calcined in a nitrogen atmosphere at (b) 900 and (c) 1100 °C for 2 h.

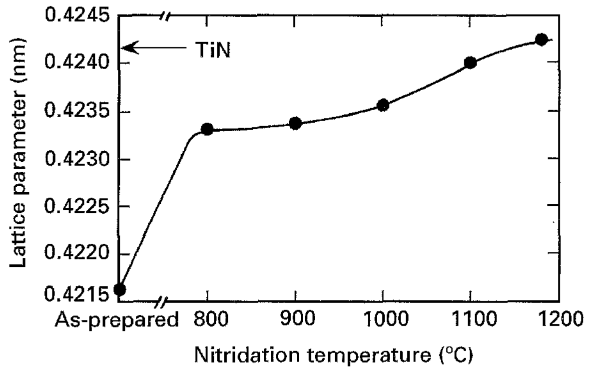

Figure 8 Lattice constants of titanium nitride as-prepared by the spark-discharge reaction in liquid ammonia using titanium pellets at − 78 °C and 5 kV discharge voltage for 1 h and calcined in a nitrogen atmosphere at various temperatures for 2 h.

3.2. Nitridation of the mixed powders of TiN_{1-x} and α-Ti

The mixed powders of TiN_{1-x} and α-Ti obtained by the spark-discharge reaction at − 78 °C and 5 kV discharge voltage were calcined in a nitrogen-gas atmosphere at 900 and 1100 °C for 2 h in order to nitride the coexisting α-Ti. The XRD profiles of the powders are shown in Fig. 7. α-Ti was converted to Ti_2N and TiN_{1-x} at 900 and 1100 °C respectively. Therefore, titanium nitride was obtained as a single phase above 1100 °C.

The temperature dependence of the lattice constant of titanium nitride obtained by calcination in nitrogen is shown in Fig. 8. The lattice constant of titanium nitride increased with increasing nitridation temperature and agreed with that of stoichiometric TiN at 1200 °C.

The scanning electron micrographs of the powders as-prepared and nitrided at 900 and 1100 °C are shown in Fig. 9. The powders retained their spherical shape even after calcination at 1100 °C, but the particle size and roughness on the surface of the spherical particles decreased.

The crystallite size and specific surface area of as-prepared and nitrided powders are shown in Fig. 10.

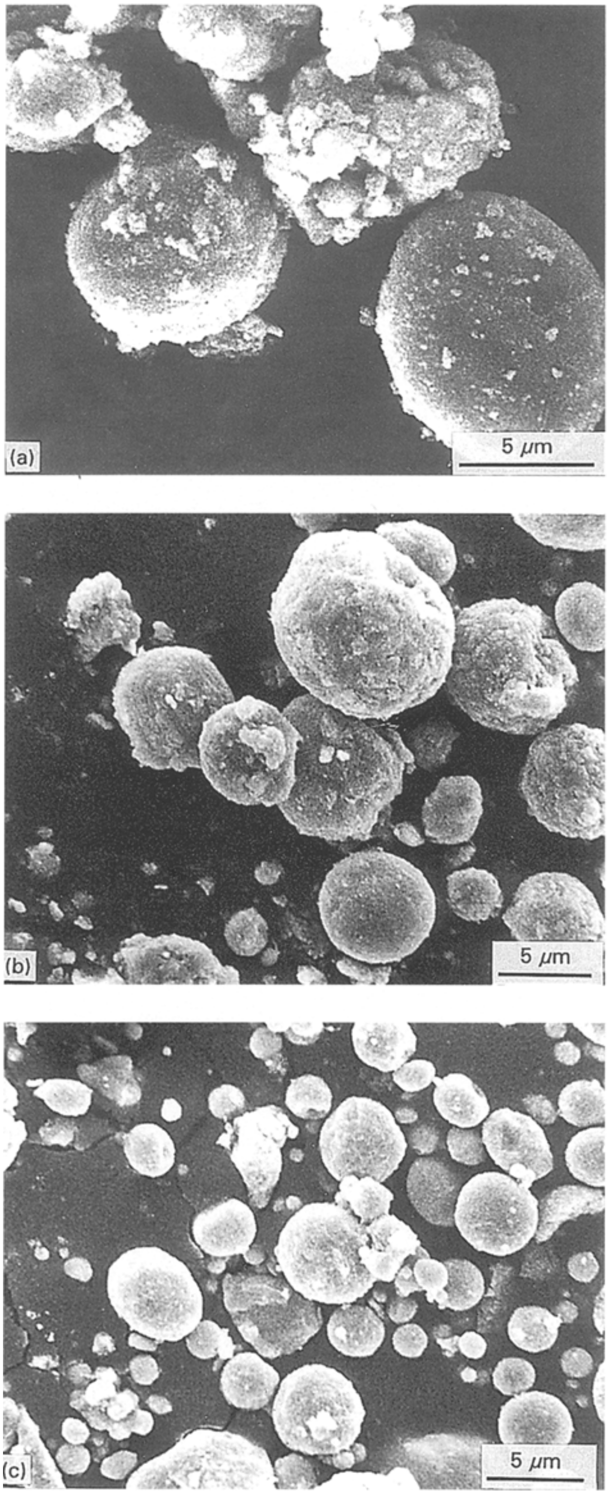

Figure 9 Scanning electron micrographs of the powders (a) as-prepared by the spark-discharge reaction in liquid ammonia using titanium pellets at − 78 °C and 5 kV discharge voltage for 1 h, and calcined in a nitrogen atmosphere at (b) 900 and (c) 1100 °C for 2 h.

The nitridation above 800 °C resulted in a significant increase of the crystallite size and a decrease in the specific surface area. These results suggest that the sintering of primary particles proceeded at a low temperature, such as 800 °C.

4. Conclusions

1. Titanium nitride powders, TiN_{1-x} ($x \cong 0.5$), mixed with small amounts of α-Ti were synthesized by the spark-discharge method in liquid ammonia at − 78 to 130 °C and 1.2–10.5 kV discharge voltage using titanium pellets as the starting material.

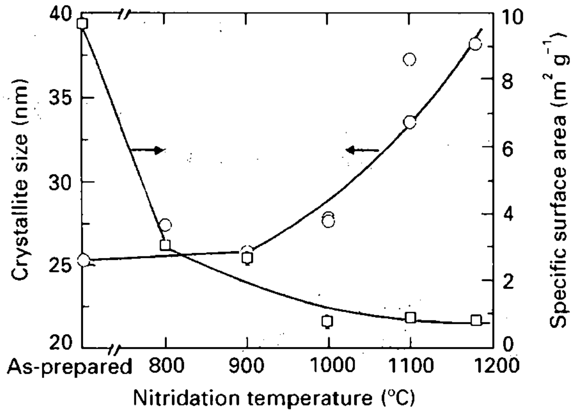

Figure 10 Crystallite sizes and specific surface areas of the powders as-prepared by the spark-discharge reaction in liquid ammonia using titanium pellets at − 78 °C and 5 kV discharge voltage for 1 h and calcined in a nitrogen atmosphere at various temperatures for 2 h.

2. The titanium nitride content in the powder fabricated by a spark-discharge reaction increased with increasing temperature of the liquid ammonia, but the powder production rate significantly decreased.

3. The mixed powders of TiN_{1-x} and α-Ti could be converted to stoichiometric TiN by calcination in nitrogen around 1200 °C.

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