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# Synthesis of metal nitrides and carbide powders by a spark discharge method in liquid media

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Metal nitrides and carbides powders were synthesized by the spark discharge method in liquid ammonia at 100 °C and 11 kV of the spark discharge voltage and in n-heptane at 25 °C and 7.5 kV using the pellets of aluminum, titanium, iron and chromium as the starting material. The main products were AlN, $TiN_{0.51}$, $\gamma$-Fe, $\beta$-$Cr_2N$ in liquid ammonia, and $Al_4C_3$, TiC, $\gamma$-Fe, $Fe_2C$ and $Cr_7C_3$ in n-heptane. The agglomerated particle size decreased with increasing melting point of the metal used as the starting material.

## 1. Introduction

Because of the excellent high-temperature strength, thermal shock resistance, hardness and thermal conductivity, metal nitrides and metal carbides have received much attention for a variety of applications. Several methods have been commercially applied for making metal nitrides and carbides, including reacting metal powders with nitrogen and carbon and reacting metal chloride vapour with ammonia at high temperature. However, because these non-oxide ceramics possess low sinterability, many studies have been focused on the fabrication of ultrafine and pure powders of these non-oxide ceramics in order to improve the sinterability. The spark discharge method, in which a spark discharge takes place at the contact points of pellets dipped in the liquid medium, is one of the attractive methods 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. It is expected that a similar technique can be used to fabricate non-oxide ceramic powders. Recently, Kumar and Roy [4, 5] and Ono *et al.* [6] reported the fabrication of various ceramic powders such as aluminium oxide, titanium oxide, zirconium oxide, chromium oxide, silicon carbide, titanium carbide, silicon carbide and aluminium nitride by the reactive-electrode submerged-arc (RESA) technique based on striking an arc between two metallic electrodes submerged in a dielectric liquid such as water, silicon oil, liquid nitrogen and liquid ammonia. Tanaka *et al.* [7] also reported the synthesis of titanium nitride powder by 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. Kumar and Roy [4] speculated that the reaction of the 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 Ishibashi–Iwatani process are hydroxides and other hydrated phases, whereas in the RESA process they are anhydrous phases. However, the details of the reactions have not yet been clarified. In the present study, a series of tests was conducted to fabricate the metal nitrides and carbides by the spark discharge method using various metal pellets.

## 2. Experimental procedure

Schematic illustrations of the apparatus for 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 (Tefron) cell, 20 mm wide, 40 mm long and 30 mm depth, was inserted in the reaction vessel. Pure aluminium and titanium plates, 20 mm × 40 mm × 1 mm, were used for electrode, while pure aluminium, sponge titanium, iron and chromium pellets, 5–6, 2–5, 2–3 and 3 mm diameter, respectively, were used for starting metal pellets and liquid ammonia and *n*-heptane for dielectric liquid media. Aluminium electrodes were used for the preparation of aluminium nitride and aluminium carbide, while titanium electrodes were used for other experiments. Trace amounts of water contaminated in liquid ammonia was removed using sodium metal. About 30 g metal 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 or *n*-heptane. After increasing the temperature of the vessel to a desired temperature using an oil bath, the spark

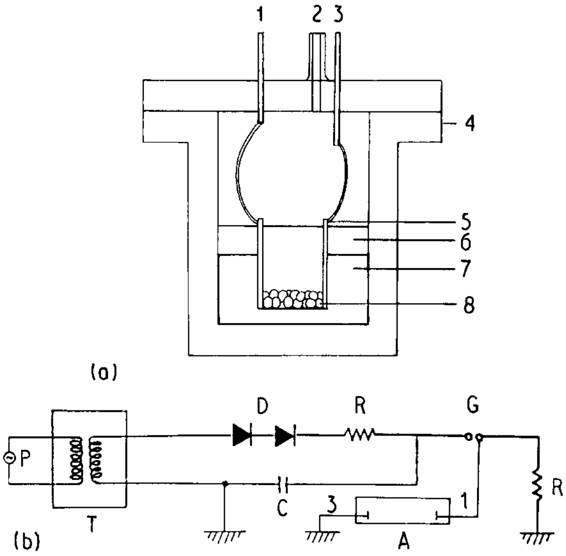

*Figure 1* Schematic illustrations of (a) the apparatus and (b) the spark discharge circuit. 1, spark discharge source; 2, inlet and outlet of ammonia; 3, earth; 4, autoclave (SUS 304); 5, electrode; 6, liquid medium; 7, teflon cell; 8, metal pellet; A, reactor; C, condenser (0.1 μF); D, diode; G, gap; P, primary electric source (50 V, 50 cycles); R, resistance (10 kΩ); T, transformer (170 VA, 100V/15 kV).

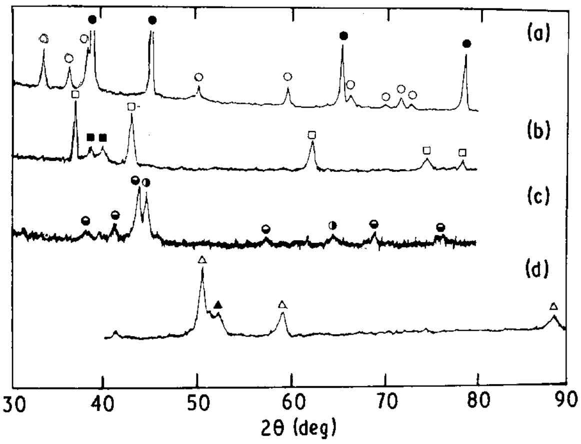

*Figure 2* X-ray powder diffraction patterns of the powders fabricated by the spark discharge reaction in liquid ammonia using (a) aluminium, (b) titanium, (c) chromium and (d) iron pellets, at 100 °C and 11 kV discharge voltage. (a, b, c) Cu$K_\alpha$ radiation, (d) Co$K_\alpha$ radiation. (○) AlN, (●) Al, (□) TiN, (■) Ti, (◒) $Cr_2N$, (◑) Cr, (△) γ-Fe, (▲) α-Fe.

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 7.5 and 11 kV by controlling the gap width. The discharge current frequency was 1–2 $s^{-1}$. After completing the spark discharge reaction, ammonia was evaporated prior to recovering the product powder in a 99.99999% pure nitrogen atmosphere, using a glove box. The powders were characterized by X-ray diffraction analysis (XRD) using nickel-filtered Cu$K_\alpha$ radiation and iron-filtered Co$K_\alpha$ radiation, simultaneous thermogravimetry and differential thermal analysis (TG–DTA), scanning electron microscopy (SEM), centrifugal particle size analysis and the chemical analysis of the components.

## 3. Results and discussion

By the spark discharge reactions in liquid ammonia using aluminium, titanium, iron and chromium pellets at 100 °C and 11 kV discharge voltage, grey, gold, and grey and black powders were obtained, respectively. XRD profiles and scanning electron micrographs of the powders are shown in Fig. 2a–d. The XRD peaks shown in Fig. 2a corresponded to the mixture of AlN of the space group $P6_3mc$ and aluminium. The lattice constants of AlN were determined to be $a = 0.3111$ nm and $c = 0.4997$ nm and agreed well with the values of JCPDS 25-1133 [8]. The amount of powder produced using aluminium pellets was 0.60 g $h^{-1}$. The content of AlN in the powder was 38.2 wt %.

The XRD peaks in Fig. 2b could be indexed as the mixture of TiN of the space group Fm3m and small amount of α-Ti of the space group $I4_1/amd$. The lattice constant of TiN was determined as $a = 0.4223$ nm and was significantly smaller than that of the stoichiometric TiN shown by JCPDS 38-1420 [9]. According to the relationship between the lattice constant and composition for $TiN_{1-x}$ [10], the chemical composition of titanium nitride obtained in the present reaction was determined as $TiN_{0.51}$. This value agreed well with those of $TiN_{0.42}$–$TiN_{0.5}$ produced by the spark discharge reaction in liquid nitrogen using titanium electrodes [7]. There were two small peaks around 40°; these were located at slightly lower angles than that corresponding to $d(0\,1\,1)$ of pure α-Ti (ASTM 5-0682) [11]. It is known that in the Ti–N system, both α-Ti and β-Ti are able to coexist above 800 °C [12]. β-Ti can be alloyed at lower nitrogen concentrations than α-Ti and transforms to α-Ti during cooling. Therefore, the two peaks around 40° might be attributed to α-Ti alloyed with different amounts of nitrogen formed by the rapid cooling after the spark discharge reaction. The amount of powder produced using titanium pellets was 0.051 g $h^{-1}$ which was about ten-fold lower than that using aluminium pellets. This might be due to the difference in the melting point of the metals. The content of $TiN_{0.51}$ in the powder was 90.2 wt %.

The XRD peaks shown in Fig. 2c might be attributed to the mixture of chromium and β-$Cr_2N$ of the space group of $P\bar{3}1m$. Because the peaks attributed to β-$Cr_2N$ were located at slightly higher angles than those of the stoichiometric β-$Cr_2N$ (JCPDS 35-803) [13], the chromium nitride obtained in the present experiment seemed to possess a nitrogen defect as $Cr_2N_{1-x}$.

The XRD peaks shown in Fig. 2d could be indexed as the mixture of α-Fe and γ-Fe of the space group Fm3m and $O_h^9$-Im3m, respectively. The lattice constant of α-Fe obtained by the spark discharge reaction was 0.3650 nm. According to the relationship between the lattice constant and nitrogen concentration for nitrogen austenite [14], the nitrogen content in γ-Fe fabricated in the present experiment was determined as 2.9 wt %. It was notable that γ-Fe, being stable

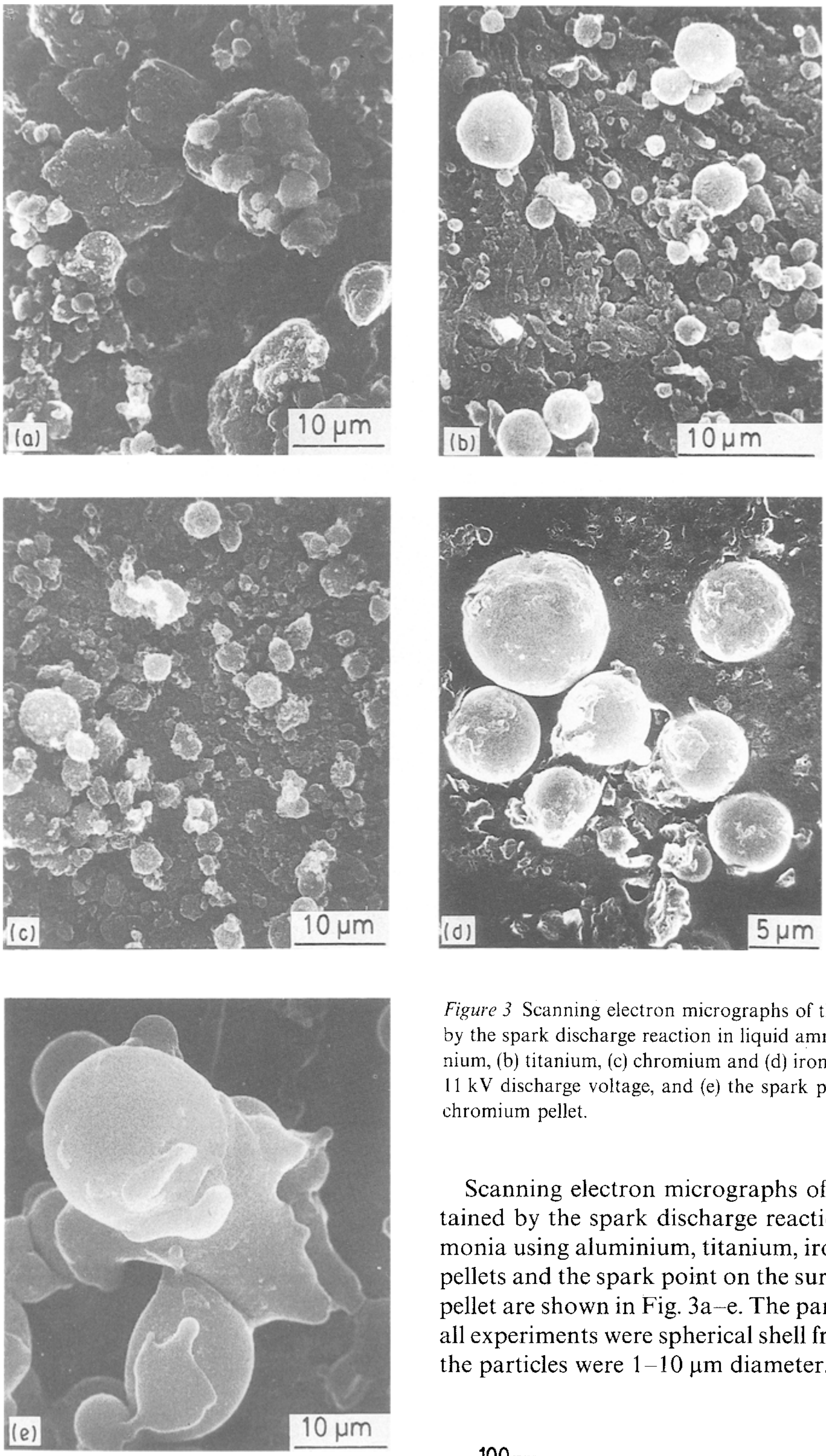

*Figure 3* Scanning electron micrographs of the powders fabricated by the spark discharge reaction in liquid ammonia using (a) aluminium, (b) titanium, (c) chromium and (d) iron pellets, at 100 °C and 11 kV discharge voltage, and (e) the spark point on the surface of chromium pellet.

above 600 °C was produced as the main product in the present experiment. It is known that γ-Fe is very difficult to obtain around room temperature by conventional methods, because γ-Fe easily transforms to α-Fe during cooling step. Therefore, it was suspected that the spark provided a high temperature for a short duration to form the high-temperature phase, γ-Fe, and then γ-Fe was quenched by rapid cooling with the surrounding liquid ammonia. These results indicate that the spark discharge process is applicable to fabricate a compound which is stable at high temperature.

Scanning electron micrographs of the powders obtained by the spark discharge reactions in liquid ammonia using aluminium, titanium, iron and chromium pellets and the spark point on the surface of chromium pellet are shown in Fig. 3a–e. The particles obtained in all experiments were spherical shell fragments. Most of the particles were 1–10 μm diameter. Fig. 3d indicates

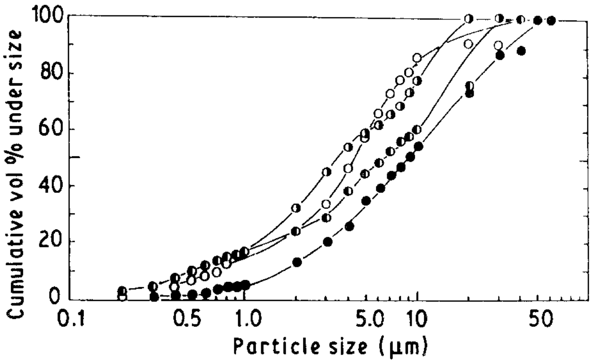

*Figure 4* Particle size distributions of powders fabricated by the spark discharge reaction in liquid ammonia using (●) aluminium, (◑) titanium, (○) chromium and (◐) iron pellets, at 100 °C and 11 kV discharge voltage.

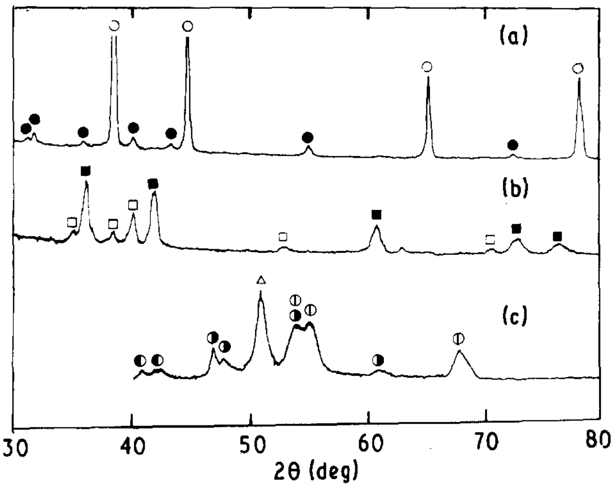

*Figure 5* X-ray powder diffraction patterns of the powders fabricated by the spark discharge reaction in *n*-heptane using (a) aluminium, (b) titanium, and (c) iron pellets at 25 °C and 7.5 kV discharge voltage. (a,b) Cu$K_\alpha$ radiation, (c) Co$K_\alpha$ radiation, (●) $Al_4C_3$, (○) Al, (■) TiC, (□) α-Ti, (⦶) γ-Fe, (◑) $Fe_2C$, (◐) unknown, (△) α-Fe.

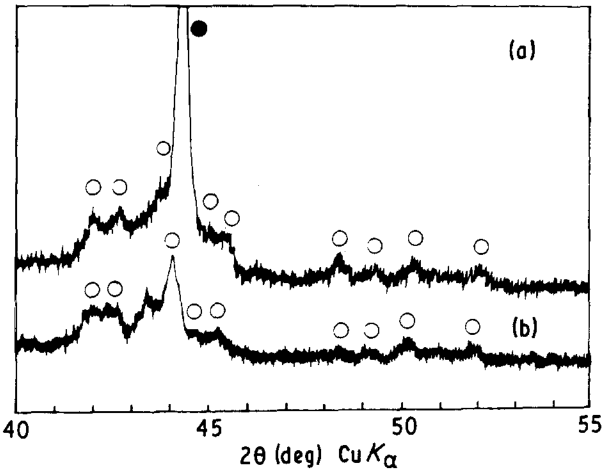

*Figure 6* X-ray powder diffraction patterns of the powders fabricated by the spark discharge reaction in *n*-heptane using chromium pellets at 25 °C and 7.5 kV discharge voltage. (a) As-prepared, (b) treated with 6 M HCl at 25 °C for 24 h. (○) $Cr_7C_3$, (●) Cr.

that chromium was melted at the spark point. Therefore, the spark seemed to provide a high temperature above the melting point of chromium, 1860 °C, resulting in vaporization of small parts on the pellets and surrounding ammonia to cause their reaction.

The particle size distributions of powders fabricated from aluminium, titanium, iron and chromium pellets are shown in Fig. 4. The mean particle sizes of the powders fabricated from aluminium, iron, titanium and chromium pellets were 8.7, 6.3, 3.6 and 4.3 μm, respectively. Because the melting points of aluminium, iron, titanium and chromium are 660.2, 1535, 1725 and 1905 °C, respectively, the particle size of the powder seemed to decrease with increasing melting point of the metal used as the starting material.

The spark discharge reactions in *n*-heptane at 25 °C were also conducted using aluminium, titanium, iron and chromium pellets as the starting materials. The XRD profiles of the powders obtained are shown in Figs 5a–c and 6a. The XRD peaks corresponded to the mixtures of $Al_4C_3$ and aluminium, TiC and titanium, γ-Fe, $Fe_2C$, α-Fe and an unknown phase, and $Cr_7C_3$ and chromium, respectively. The powders also contained significant amount of carbon. The peak ratios of metal carbides/metal were much smaller than those of metal nitride/metal shown in Fig. 2. In the case of the $Cr_7C_3$–Cr mixture, chromium could be selectively leached by HCl solution to obtain $Cr_7C_3$ as single phase to X-rays as shown in Fig. 6b.

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