

## Preparation of Magnesium Nitride Using R.F. Inductive Coupled Plasma

Hiroki Fujitsuka, Shigeru Ito, Takashi Fujii and Kazuo Akashi

Department of Industrial Chemistry, Faculty of Science and Technology, Science University of Tokyo,  
Noda, Chiba 278-8510, Japan

Fax: 81-471-23-9890, e-mail: ito@ci.noda.sut.ac.jp

Applying a nitrogen glow plasma, the magnesium bulk (size: 10mm × 10mm × 5mm, purity: 99.9%) was directly nitrated under the following conditions; plate power: 2.0-6.0kW, heating temperature: 250-650°C, pressure: 70-160 Pa, time: 30 min. The magnesium bulk was completely nitrated to produce Mg<sub>3</sub>N<sub>2</sub> in the temperature range of 500-600°C under 70 Pa. Single phase of Mg<sub>3</sub>N<sub>2</sub> was detected by XRD. However inner part of the product was disappeared by the evaporation of Mg. The yield of Mg<sub>3</sub>N<sub>2</sub>, which was 14.6 % under 70 Pa, was increased to 28.5 % under 125 Pa and 36.2 % under 160 Pa.

Key words: magnesium bulk, Mg<sub>3</sub>N<sub>2</sub>, nitrogen glow plasma

### 1. INTRODUCTION

Little has been known for a nitride Mg<sub>3</sub>N<sub>2</sub>. However, Mg<sub>3</sub>N<sub>2</sub> has been recently used as a promoter for transformation of h-BN to c-BN<sup>1)</sup>, or for sintering of Si<sub>3</sub>N<sub>4</sub><sup>2)</sup>. In addition, new complex compounds such as Mg<sub>3</sub>N<sub>2</sub>-P<sub>3</sub>N<sub>5</sub> have been synthesized using Mg<sub>3</sub>N<sub>2</sub>. Mg<sub>3</sub>N<sub>2</sub> has been prepared by the direct nitriding of magnesium<sup>3)</sup>, nitrogen plasma jet method<sup>4)</sup> and low-pressure chemical vapor deposition method<sup>5)</sup> etc.. Magnesium powders were required as a starting material in the direct nitriding. However, fine powder of magnesium contains relatively large amount of oxygen, because of thin oxide layer on the surface of the magnesium particles. Therefore, it seems that the product obtained from the magnesium powder contains a large amount of oxygen impurity. Furthermore, the high power was required in the nitrogen plasma jet method and in the low-pressure chemical vapor deposition method. If magnesium bulk such as 1mm × 1mm × 1mm in size can be directly nitrated by applying a low power, these problem will be solved. Similar problems arise in nitriding of aluminum, in which fine powders of aluminum has been conventionally used. We have solved this problem using a glow plasma with a relatively low plate power<sup>6)</sup>. In this process, the aluminum bulk with 10mm × 10mm × 5mm in

size was completely nitrated in a short period of time, using activated nitrogen. Aluminum and magnesium have similar properties; light metal with low melting point (melting point of aluminum: 660°C, melting point of magnesium: 650°C), a strong affinity for oxygen and negative free energy of formation for the nitride. In this study, the direct nitriding of magnesium bulk have been studied, applying a nitrogen glow plasma.

### 2. EXPERIMENTAL

Magnesium bulk (10mm × 10mm × 5mm, purity 99.9%) was used as a starting material. The magnesium plate was polished and ultrasonically cleaned in acetone for 10 min.

Fig.1 shows the schematic arrangement for the generation of the r.f. plasma (Nihon Koshuha Co. Ltd., frequency: 4 MHz, max power: 10 kW). The sample was put on the sample holder in a double walled and water cooled cylindrical quartz tube. The reaction chamber was evacuated to 10 Pa. Nitrogen gas was then flowed into the reaction chamber with 50-500scm. The pressure in the reaction chamber was maintained at 70-160 Pa. After the atmosphere in the chamber was sufficiently substituted, the nitrogen glow plasma was generated by a power supply with a plate power of 2.0-6.0 kW in a double walled and water

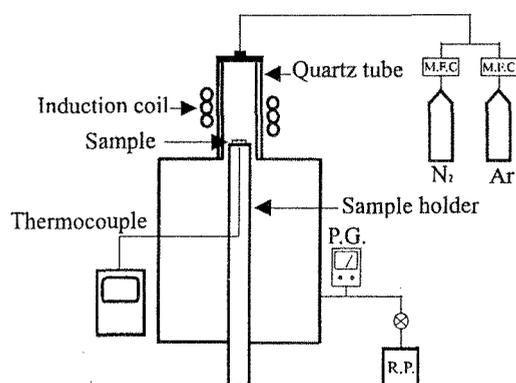


Fig.1 Schematic arrangement for the generation of the r.f. plasma.

cooled cylindrical quartz tube coated with BN powder. The sample was nitrated in the plasma at 250-650°C for 30 min. Temperature of the sample was measured at the backside of the sample and was controlled by adjusting the sample position in the plasma. In this study, the saturated temperature during nitriding was defined as the nitriding temperature.

The x-ray diffraction analysis (XRD) was used to identify crystalline phase in the product. Microstructure of the surface of the sample was observed by scanning electron microscope (SEM). The emission spectroscopic analysis of the plasma was performed by the use of Plasma Analyzer KA501A.

### 3. RESULTS AND DISCUSSION

#### 3.1 Nitriding of magnesium bulk by nitrogen glow plasma.

Nitriding of magnesium plate (10mm × 10mm × 5mm) was performed at the heating temperature of 250-650°C under 70 Pa and plate power of 2.0 kW. The magnesium plate was not nitrated at the temperature of 250-400°C, and was hardly nitrated at 400-500°C. On the other hand, magnesium plate was completely nitrated at the heating temperature of 500-600°C. Fig.2 shows the XRD pattern of the product obtained at 500°C. Because the product was crushed to powder using a mortar, this XRD pattern shows not only the surface of the product but also the inner part and the backside of the product. Single phase of magnesium nitride was detected in this XRD pattern. It was confirmed that the

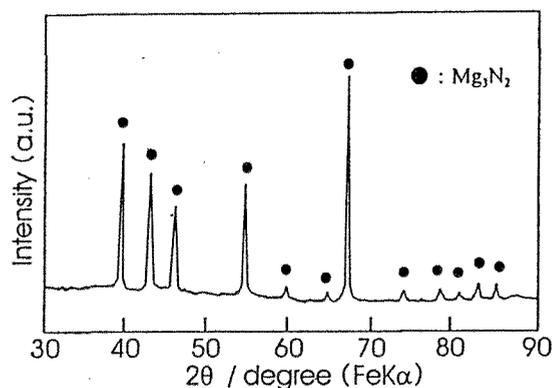


Fig.2 XRD pattern of the product obtained at 500°C.  
(pressure 70Pa, power 2.0kW)

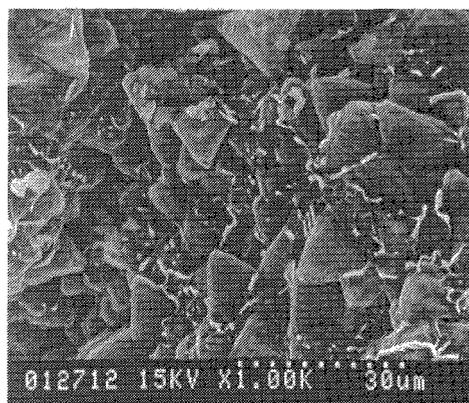


Fig.3 SEM photograph of the surface of the product.  
(temperature 500°C, pressure 70Pa, power 2.0kW)

magnesium plate was able to completely nitrated by nitrogen glow plasma to produce  $Mg_3N_2$ . Fig.3 shows the SEM photograph of the surface of the product. Trigonal pyramid particles with 10-50  $\mu m$  in size were observed at the surface of the product. The cross section of the product has columnar structure of  $Mg_3N_2$ .

Fig.4 shows the temperature of the sample as a function of reaction time. The temperature was rapidly raised because of heating by nitrogen glow plasma. After the temperature reached to maximum, it decreased and then saturated at a constant value. In this paper, the heating temperature means this constant value. Broad peak in Fig.4 is due to the exothermic reaction of nitriding ( $\Delta H^\circ = -110.3 \text{ kcal/mol}$  at 298K). The

nitriding appears to be completed in 20 min. When the sample was taken out of the furnace at the maximum sample temperature, the magnesium still remained in the center of the sample. Fig. 5 illustrates the sample before and after nitriding. Magnesium seemed to be evaporated during the reaction. At the beginning of reaction, color of plasma was orange caused by nitrogen. When the exothermic reaction occurred, color of plasma changed to green. The color of plasma changed to orange again with the decrease of temperature. According to emission spectroscopic analysis, large peak appeared 5150 Å, while color of plasma was changing to green. When magnesium plate was heated in an oxygen plasma or hydrogen plasma, color of plasma also changed to green and large peak appeared 5150 Å. Therefore, it is deduced that this peak was not caused by nitrogen but by magnesium. After nitriding, deposit was observed on a double walled and water cooled cylindrical quartz tube. According to the XRD analysis, the deposit was  $Mg_3N_2$ .

From the results mentioned above, it seems that the nitriding of magnesium bulk proceeds as follows; ①  $Mg_3N_2$  is prepared at the surface of magnesium. ② The temperature of the sample was efficiently raised enough to evaporate magnesium by means of exothermic reaction of nitriding and heat of plasma. ③ The vaporized magnesium rapidly reacted with nitrogen in gas-phase to form  $Mg_3N_2$  powder.

### 3.2 Improvement of yield

Magnesium bulk was completely nitrided by nitrogen glow plasma. However, yield of the product was 14.6 % at 500 °C under 70 Pa, because most of inner part of the sample has been evaporated. The yield;  $y$  was defined as

$$y = (a / b) \times 100 \quad (1),$$

where  $a$  is the weight of the magnesium converted to  $Mg_3N_2$ , and  $b$  is the weight of magnesium used. Vapor pressure of magnesium exceeded the pressure in the reaction chamber by exothermic reaction of nitriding. Hence inner part of the magnesium was evaporated. Therefore, nitriding was performed at higher pressures; 125 Pa or 160 Pa. Fig. 6 shows the yield of  $Mg_3N_2$  as a function of pressure in the

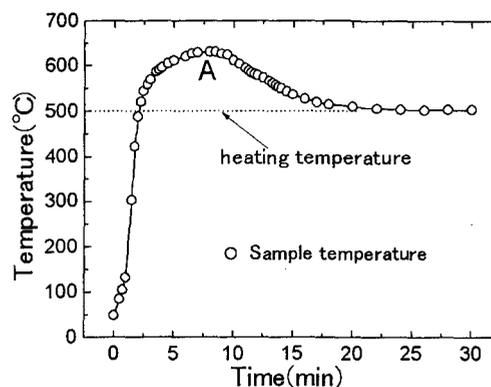


Fig. 4 Temperature of the sample vs. nitriding time. (temperature 500 °C, pressure 70 Pa, power 2.0 kW)

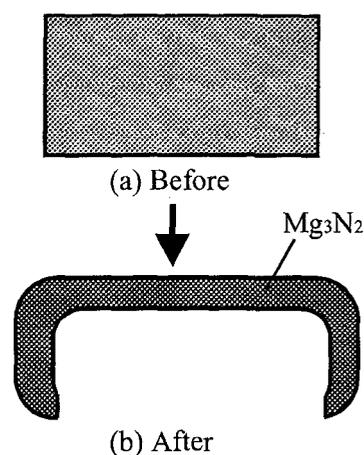


Fig. 5 Schematic illustration of cross section of the samples. (a) Before nitriding (b) After nitriding

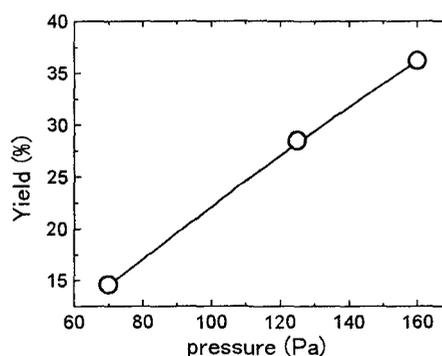


Fig. 6 Yield of the product vs. pressure in the reaction chamber. (temperature 500 °C, power 2 kW)

reaction chamber. The yields of  $Mg_3N_2$  increased with rising the pressure in the reaction chamber. The yield of  $Mg_3N_2$  was obtained as 36.2 % under the pressure of 160 Pa.

#### 4. CONCLUSION

In this study, the magnesium bulk was completely nitrated to form  $Mg_3N_2$  by nitrogen glow plasma. Furthermore, nitrating temperature was relatively low compared to that of the conventional nitrating of magnesium powder; 800°C. The nitrating appeared to be completed in 20 min. The yield was improved by increasing the pressure in the reaction chamber. The maximum yield 36.2% was obtained under 160Pa.

#### REFERENCES

- 1) H. Lorenz, B. Lorenz, U. Kuhne and C. Hohlfeld, *J. Mater. Sci.*, **23**, 3254 (1988)
- 2) K. Negita, *J. Mater. Sci. Letters*, **4**, 755 (1985)
- 3) K. Itatani, H. Saito, A. Kishioka and M. Kinoshita, *Proceedings of Annual Meeting of Ceramic Society of Japan*, 504 (199)
- 4) C. S. Stokes and W. W. Knipe, *INDUSTRIAL AND ENGINEERING CHEMISTRY*, **3** (4), 287-288 (1960)
- 5) T. Murata, K. Itatani, F. S. Howell, A. Koshioka and M. Kinoshita, *J. Am. Ceram. Soc.*, **76** (11), 2909-2911 (1993)
- 6) S. Ito, K. Akashi, H. Takahashi and K. Yoshida, *12<sup>TH</sup> INTERNATIONAL SYMPOSIUM ON PLASMA CHEMISTRY Proceedings*, **3**, 1261-1266 (1995)

(Received December 17, 1999; accepted February 17, 2000)