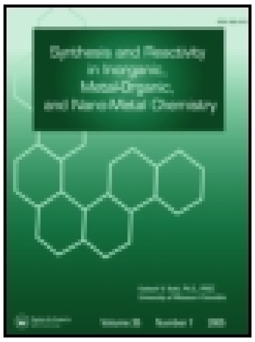

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NITRIDATION OF MAGNESIUM POWDER OF NANOMETRIC SIZE FROM THE THERMAL DECOMPOSITION OF MAGNESIUM ANTHRACENE

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ABSTRACT

Highly reactive magnesium powder of nanometric size, which was generated by the thermal decomposition of magnesium anthracene·3THF under vacuum, can react with N_2 under atmospheric pressure, even at 300℃, to form magnesium nitride. The rate and extent of the reaction can be improved effectively by doping the magnesium powder with a small amount of nickel or titanium compounds.

INTRODUCTION

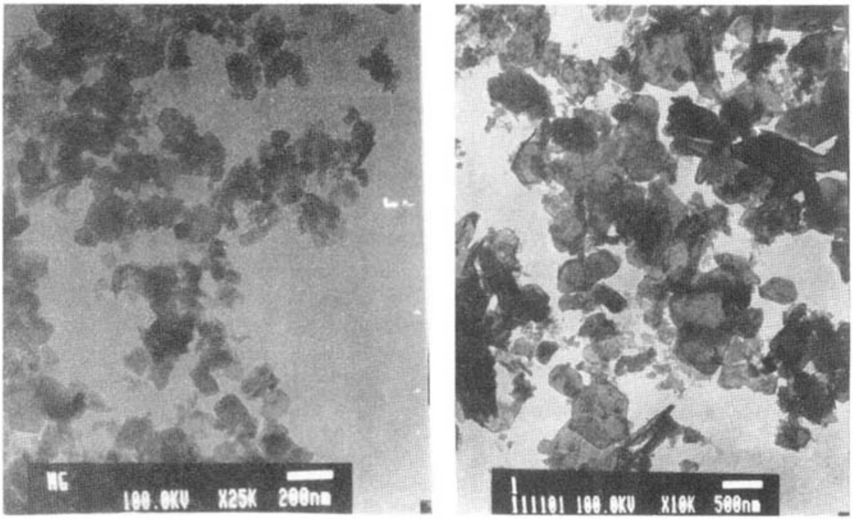
Magnesium nitride can be used as a sintering aid for silicon nitride and boron nitride powders[1,2]. It can also be used as a reagent for the manufacture of foamed alloys[3] and for the recovery of nuclear wastes[4]. Various techniques for the preparation of magnesium nitride have been reported in the literature[5-9].

Among these techniques the direct nitridation of magnesium powder has often been used[2,5]. In this technique, the temperature of nitridation usually starts from 600℃ and ends at 900℃. Some effort has been made to reduce the reaction temperature. For example, in a field of ionizing radiation (dose rate Do = 1.36 GY/sec.), the nitridation of magnesium powder was carried out at 450℃ under normal pressure of N_2 atmosphere. The yield of Mg_3N_2 was 14% in 18 h[6]. The highly reactive magnesium powder generated by the dehydrogenation of reactive MgH_2 could react with N_2 under mild conditions[10].

It has been found that the decomposition of magnesium anthracene·3THF under vacuum results in the generation of a highly reactive pyrophoric form of magnesium[11,12]. This form of magnesium has been studied in the hydrogenation and used for Grignard reactions. In this paper, we report the reaction between the reactive magnesium powder with N_2 under mild conditions. The aim of this paper was not to provide a method for the preparation of pure magnesium nitride but to show that the magnesium powder of nanometric size can react with N_2 under mild conditions, its reaction temperature is far below those reported in the literature, and the magnesium nitride obtained is also of nanometric size.

RESULTS AND DISCUSSION

The thermal decomposition of magnesium anthracene·3THF was carried out under normal pressure of Ar or vacuum, respectively. The evaluation of the resulting magnesium powders by a transmission electron micrograph shows that they differ greatly in particle size (Fig. 1). The particle size of the magnesium powder (Mg^*) obtained under vacuum (0.1-0.3 mm Hg) at 150-200℃ is around 76 nm. The particle size of the magnesium powder ($Mg^\#$) obtained under atmospheric pressure of Ar at 150-200℃ is around 266 nm. Under atmospheric pressure of N_2, Mg^* can react with N_2 even at 300℃ (Fig. 2). At 450℃, the conversion of Mg^* to Mg_3N_2 reaches 70% in 22 h. In comparison, $Mg^\#$ is not as



a

b

Fig. 1. Transmission Electron Micrograph of Mg* (a) and Mg$^{\#}$ (b)

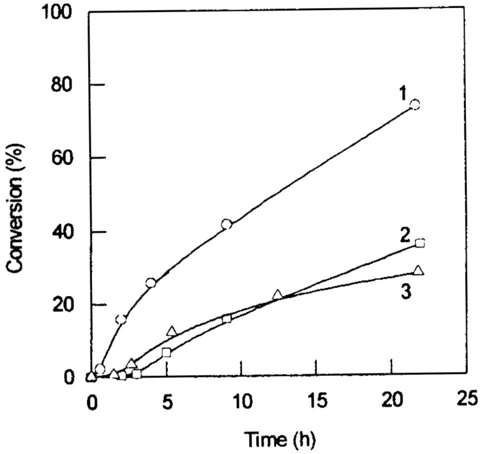


Fig. 2. Kinetic Curves of Nitridation of Mg* and Mg$^{\#}$ under Atmospheric Pressure of N_2

1: Mg* at 450℃ 2: Mg* at 300℃ 3: Mg$^{\#}$ at 450℃

reactive as Mg*. The conversion of $Mg^{\#}$ to Mg_3N_2 is only 26% in 22 h. Under the same reaction conditions, the amount of N_2 uptake in the reaction of commercial magnesium powder (average particle size 155 μm) with N_2 is negligibly small. This difference in reactivity is due to the different particle sizes of these magnesium powders. For a reaction involving a solid surface, the reaction rate is proportional to its specific surface area. For the reaction of magnesium powder with N_2, an increase in the reaction rate by orders of magnitude is expected for the Mg powder of nanometric size in comparison with the commercial one, because the difference of the specific surface areas between Mg* (54 m^2/g, BET method) and the commercial magnesium powder is around 3 orders of magnitude as a consequence of the difference of the particle diameters between the Mg* and the commercial one (the specific surface area of a solid is inversely proportional to its particle size).

In order to raise the rate of nitridation of Mg* still further, attempts were made to dope Mg* with $NiCl_2$, Cp_2TiCl_2 and $TiCl_4$, respectively, (the amount of doping was 2.5 mol% of Mg*). As a result, it was found that $NiCl_2$, Cp_2TiCl_2 and $TiCl_4$ promoted the nitridation of Mg* effectively. From Figs. 3 and 4 it can be seen that $TiCl_4$ is the most efficient dopant at 300℃. At 450℃, $NiCl_2$ is more efficient.

The Mg_3N_2 generated by the reaction of Mg* with N_2 under atmospheric pressure at 450℃ is also of nanometric size (Fig. 5). The primary particle size of Mg_3N_2 is around 52 nm. We tried to run X-ray powder diffraction and elementary analysis of the sample in other laboratories and in other institute. Unfortunately, the results were not satisfactory, because the magnesium nitride of nanometric size is very sensitive to air and moisture forming magnesium oxide and magnesium hydroxide immediately. The laboratories in which the measurements were taken could not provide the conditions to avoid the contact of the samples from air and moisture. As a result, there were peaks of $Mg(OH)_2$, MgO in addition to the peaks of Mg_3N_2 in the XRD pattern.

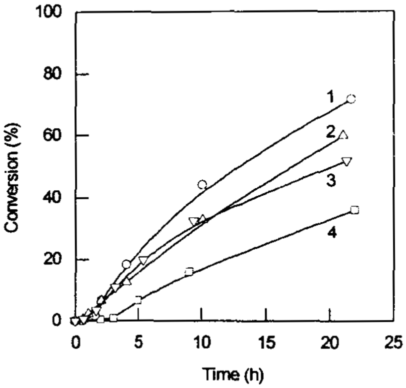


Fig. 3. Kinetic Curves of Nitridation of Doped Mg* under Normal Pressure of N_2 at 300℃
1: doped with 2.5 % of $TiCl_4$;
2: doped with 2.5 % of $NiCl_2$;
3: doped with 2.5 % of Cp_2TiCl_2;
4: without doping

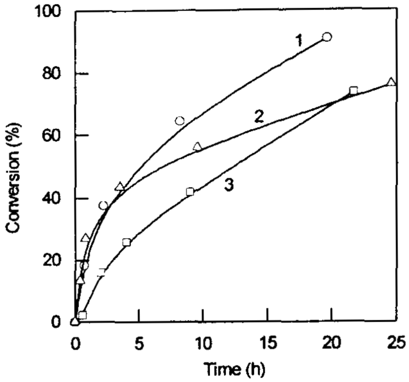


Fig. 4. Kinetic Curves of Nitridation of Doped Mg* under Normal Pressure of N_2 at 450℃
1: doped with 2.5 % of $NiCl_2$;
2: doped with 2.5 % of Cp_2TiCl_2;
3: without doping

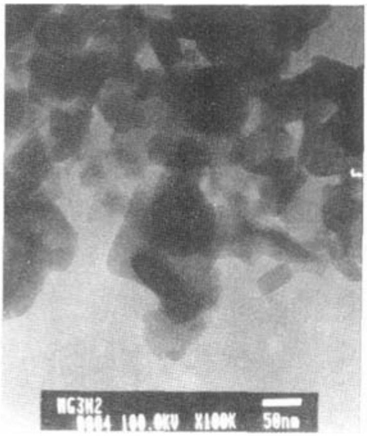


Fig. 5. Transmission Electron Micrograph of Mg_3N_2

EXPERIMENTAL

All reactions and operations were carried out under argon or nitrogen.

Starting Materials

Mg powder, anthracene and Cp_2TiCl_2 were commercially available and were used without further purification. THF was refluxed and distilled from sodium benzophenone under argon. $NiCl_2{\cdot}6H_2O$ was dehydrated with $SOCl_2$. $TiCl_4$ was distilled prior to use. High purity N_2 gas (99.995%) was used and dried by passage through a 4 Å molecular sieve column prior to use. Magnesium anthracene·3THF was prepared as described in the literature[13].

Preparation of Mg*

In a typical experiment 2 g of magnesium anthracene·3THF were placed into a 150 mL two-necked tube connected to a vacuum line by a glass elbow fitted with glass wool (to prevent suction of Mg* dust from the tube). Under vacuum (0.1-0.3 mm Hg) the tube was heated gradually from room temperature to 200℃ and maintained at 200 ℃ for 2 h, in the course of which magnesium anthracene·3THF was decomposed, THF was released and condensed in a receiver cooled with liquid nitrogen. Anthracene was recovered as sublimate. After the thermolysis was complete, heating was stopped and the tube was cooled to room temperature under vacuum and Mg* powder was obtained. The blackish Mg* powder was transferred under argon to a dry glass container, which had been evacuated and flushed with Ar three times beforehand. The method for the generation of $Mg^{\#}$ was the same as that for the Mg*, except that the thermal decomposition of magnesium anthracene·3THF was undertaken under atmospheric pressure of Ar.

Preparation of Magnesium Nitride of Nanometric Size

A dry 150-mL two-necked reaction tube was inserted into an electrically heated oven and connected to a vacuum and argon systems. After the reaction tube had been evacuated and flushed with argon three times, Mg* was transferred into it under argon. After further alternately evacuating and flushing with N_2 three times, Mg* was heated at 300℃ or 450℃ under atmospheric pressure of N_2. As the reaction of Mg* with N_2 took place, the volume of N_2 uptake was recorded by a constant-pressure gas burette filled with nitrogen. After 20 h or more, the oven was allowed to cool to room temperature and fine grey Mg_3N_2 powder was obtained. Since Mg_3N_2 is the only stable product between the reaction of magnesium and nitrogen, the percentage of conversion obtained in Figs. 2, 3 and 4 were calculated based on the volume of N_2 uptake. This magnesium nitride was contaminated with carbon, which was originated from the thermal decomposition of magnesium anthracene·3THF. The content of carbon was around 10 %.

Measurements

The carbon content was determined by elemental analyzer (Carlo Erba Model: 1106). The primary particle size of Mg_3N_2 powder was examined by a transmission electron microscopy (TEM) (Model: JEM-1200EX). Selective area electron diffraction (SAED) of the magnesium nitride powder indicates that the sample is polycrystalline. However, it is hard to say whether the magnesium nitride powder itself is polycrystalline or it is a mixture of magnesium nitride and its contaminated product (MgO, $Mg(OH)_2$) formed during SAED measurement, although we had done our best to avoid the sample from contamination with air and moisture during measurement.

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