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Synthesis of nanometric-size magnesium nitride by the nitriding of pre-activated magnesium powder

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Magnesium nitride (Mg_3N_2) was synthesized by the reaction of magnesium in the highly reactive form (Mg*) with nitrogen at 450 °C under normal pressure. The effect of doping with nickel dichloride on the nitridation of Mg* was investigated. Differential thermal analysis (DTA) of Mg* systems and transmission electron microscopy (TEM) measurement of the product formed were carried out. TEM measurement showed that the particle size of the Mg_3N_2 synthesized was in the nanometric range. The dependence of nitridation of the $NiCl_2$-doped Mg* on temperature was investigated at temperatures ranging from 300 to 500 °C. The nitridation of $NiCl_2$-doped Mg* could occur even at temperature as low as 300 °C.

1. Introduction

Magnesium nitride is a material which has many applications, such as in the preparation of more complex nitrides which exhibit the features of high hardness, high heat conductivity, corrosion and wear resistance, good thermal shock resistance [1–3] and also in the production of special ceramic materials [4–6]. It can also be used as a reagent for the manufacture of foamed alloys [7] and in the recovery of nuclear wastes [8].

In an early patent, the temperature for the synthesis of Mg_3N_2 was above the melting point of Mg (648.8 °C) [9]. In a later report Mg_3N_2 was prepared at temperatures starting from 600 °C (4 h) and ending at 900 °C (8 h) under a nitrogen stream [10]. There are a number of difficulties in synthesizing Mg_3N_2 at such high temperatures because of the relatively low melting point of Mg [11]. Some efforts have been made to reduce the reaction temperature, and, for example, in a field of ionizing radiation (the dose rate, $D_0 = 1.36$ Gy s^{-1}) the nitridation of Mg powder (specific surface area: 0.9 m^2 g^{-1}) could be carried out far below the melting point of Mg. The conversion of Mg was about 14% of the theoretical value at 450 °C under normal pressure for 18 h [11]. It has been reported recently that superfine particles of metal nitrides could be manufactured by gas phase reaction at >800 °C by appling supersonic waves (av. sound pressure level 20–100 Pa, frequency >20 kHz) to the reaction region [12].

In this study, experiments on the nitridation of activated magnesium powder, Mg*, especially samples doped with $NiCl_2$, have been carried out. The effects of doping and temperature on the nitridation of Mg* have been investigated, and some thermal features of the nitriding reaction have been obtained by DTA measurements. TEM and XRD were employed to characterize the nitrided products of Mg*.

2. Experimental

Undoped and doped MgH_2 were prepared by the hydrogenation of magnesium powder with $TiCl_4$ and anthracene as a catalyst in tetrahydrofuran at 60 °C under normal pressure [13, 14]. The prepared MgH_2 was transfered to a Schlenk reactor in an argon atmosphere. The reactor was heated to and kept at 350 °C until the dehydrogenation of MgH_2 was complete, and the highly reactive form of magnesium (Mg*) was formed. The reactor was evacuated and then backfilled and purged with nitrogen (99.99%) twice. It was heated to the desired temperature and the nitridation of Mg* was carried out under normal pressure. The amount of hydrogen release and nitrogen uptake were measured by two constant pressure gas burettes. The yield of Mg_3N_2 was obtained from the percentage of the amount of N_2 uptake relative to the calculated theoretical value.

DTA curves were measured by means of a DTA 1700 thermal analyzer (Perkin-Elmer Co.). Transmission electron microscopy (TEM) was recorded on a SEM-1200 EX electron microscope operated at 100 kV. The samples were treated in an ultrasonic bath of benzene and then dispersed on a holey carbon TEM grid. XRD analysis was carried out using a Ligaku D/max-rB diffractometer, Cu target, tube voltage 50 kV, and tube

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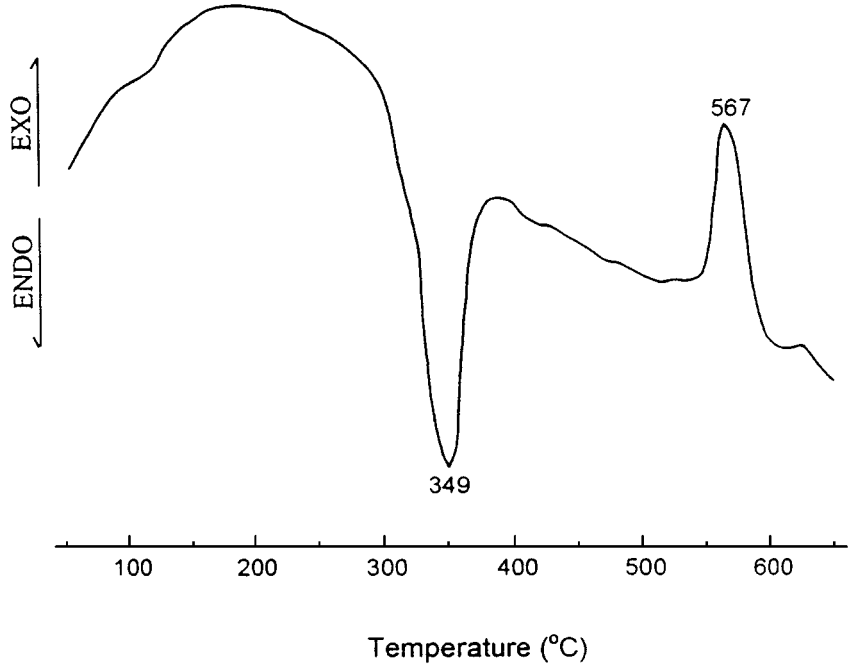


Figure 1 DTA curve of catalytically prepared MgH_2 (undoped). N_2 flow rate 40 ml min^{-1}, heating rate 10 °C min^{-1}.

current 100 mA. All samples were transferred and prepared using a protective nitrogen atmosphere.

3. Results and discussion

3.1. Formation of Mg_3N_2

The idea that the nitridation of Mg* could proceed at low temperature originated from DTA measurements of catalytically prepared MgH_2. In these measurements, it was found that under a nitrogen atmosphere, the DTA curve contained an unknown exothermic peak at ca. 567 °C after the endothermic peak (394 °C) of dehydrogenation (Fig. 1). No endothermic peak related to the melting of Mg* could be observed. However, in the hydrogen atmosphere the exothermic peak mentioned above disappeared. Therefore it was deduced that the unknown exothermic peak was that of Mg* reacting with nitrogen and that the nitriding temperature of Mg* was much lower than that for commercial Mg powder reported in the literature [9, 10].

The nitridation of Mg* was carried out at 450 °C under normal pressure. The conversion of undoped Mg* was 81% after nitridation for 18 h (Fig. 2c). In comparison, no uptake of nitrogen for commercial Mg powder (98% purity, 100–200 mesh) could be observed in 23 h under the same reaction conditions. On the XRD pattern of the nitrided Mg* product, the characteristic peaks of the known structure of Mg_3N_2 [15] and peaks of unreacted Mg* [14] were observed; also several unknown peaks were present, which might belong to intermediate compounds formed in the process of preparing Mg_3N_2 [11].

3.2. Effect of doping on the nitridation of Mg*

In the catalytic preparation of magnesium hydride, transition metal compounds or metal powders have been added in order to improve the rate of hydrogenation of magnesium. These metal components cannot be separated from the final product. Eventually they act as dopants in the pre-activated magnesium powder. Among the dopants which have been investigated, the effects of $NiCl_2$ and La have been studied for the nitridation of Mg*. Mg* doped with 2.5 mol % of $NiCl_2$ or La displayed different reactivities towards N_2. By doping with $NiCl_2$, the yields of Mg_3N_2 were 82 and 90% at 450 °C under normal pressure for 8 h and 18 h, respectively (Fig. 2a). The improvement is obvious compared with the undoped one (Fig. 2c). The nitriding rate of Mg* doped with La powder also improved slightly (Fig. 2b).

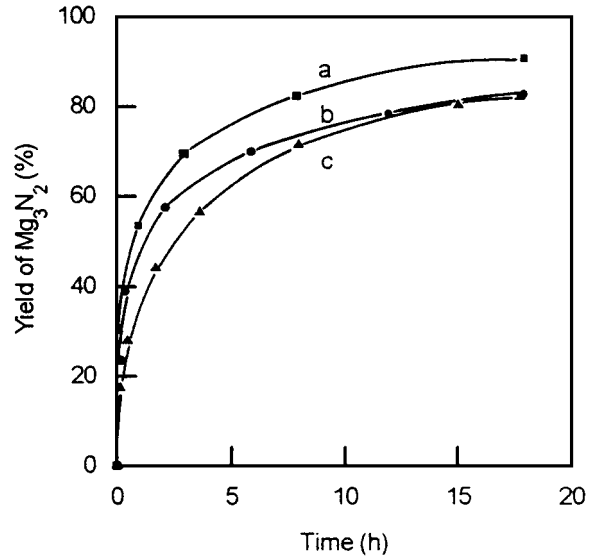


Figure 2 Kinetic curves of nitridation of different Mg* systems at 450 °C under normal pressure. Doping amount 2.5 mol %. Dopants: (a) $NiCl_2$, (b) La powder, (c) none.

3.3. Dependence of nitridation of $NiCl_2$-doped Mg* on temperature

The temperature dependence of nitridation of $NiCl_2$-doped Mg* was investigated, and results showed that it

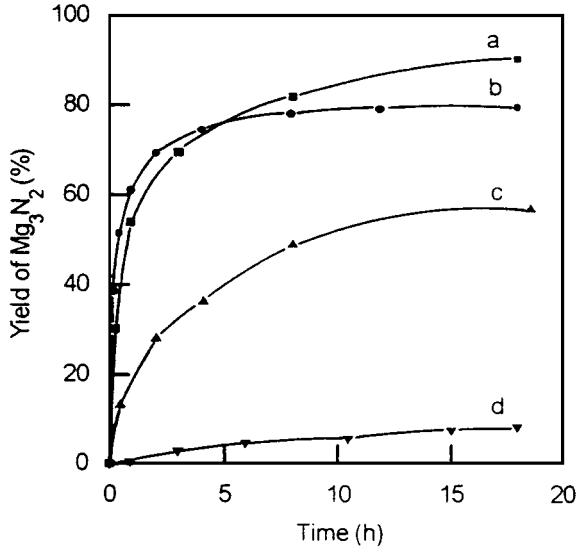


Figure 3 Temperature dependence of nitridation of $NiCl_2$-doped Mg* under normal pressure. Doping amount 2.5 mol %. (a) 450 °C, (b) 500 °C, (c) 400 °C, (d) 300 °C.

could react with N_2 at temperatures as low as 300 °C (the nitridation of undoped Mg* occurs at ca. 350 °C). The rate of nitridation increased noticeably with increasing temperature, but the ultimate yield of Mg_3N_2 at 500 °C was lower than that at 450 °C, which may be due to the sintering of some of the Mg* during the course of reaction at 500 °C (Fig. 3).

3.4. Dependence of Mg* nitridation on doping level

Doping with 2.5 mol % $NiCl_2$ obviously improved the nitridation behavior, whereas doping with 0.4 mol % $NiCl_2$ exhibited little positive effect on the reaction rate; in contrast, doping with 20 mol % $NiCl_2$ stopped the nitridation process entirely (Fig. 4). From XRD measurements, Mg_2Ni and $MgNi_2$ species were found in the samples containing 2.5 mol % and 20 mol % $NiCl_2$-doped Mg*, and a considerable amount of $MgCl_2$ was present in the latter case [14]. It is believed that Mg_2Ni and $MgNi_2$ may catalyze the nitridation of Mg* as they did in the case of the hydrogenation of Mg*, while the presence of a large amount of $MgCl_2$ could inhibit the reaction.

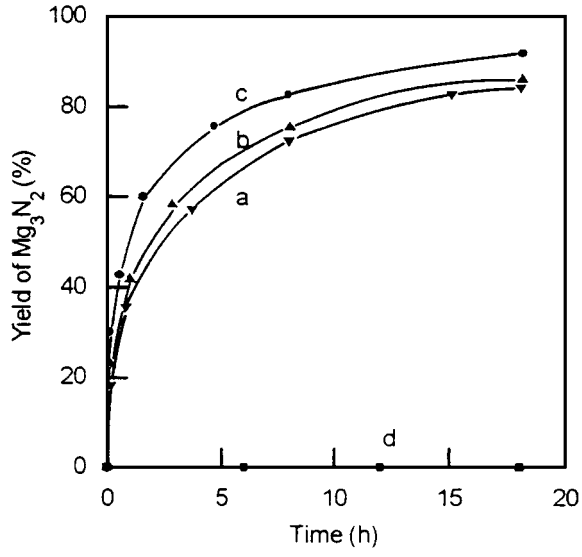


Figure 4 Dependence of nitridation of Mg* on the doping amount of $NiCl_2$ at 450 °C under normal pressure. Doping amount (mol %): (a) 0, (b) 0.4, (c) 2.5, (d) 20.

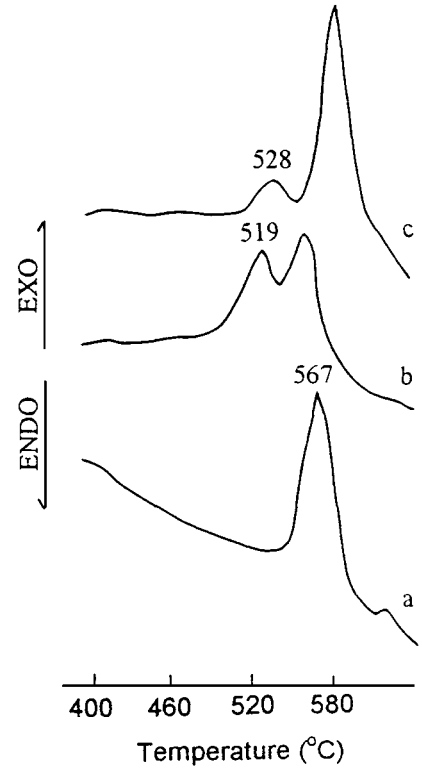


Figure 5 DTA curves of doped and undoped Mg*. N_2 flow rate 40 ml min^{-1}, heating rate 10 °C min^{-1}. Doping amount 2.5 mol %. Dopants: (a) none, (b) $NiCl_2$, (c) La powder.

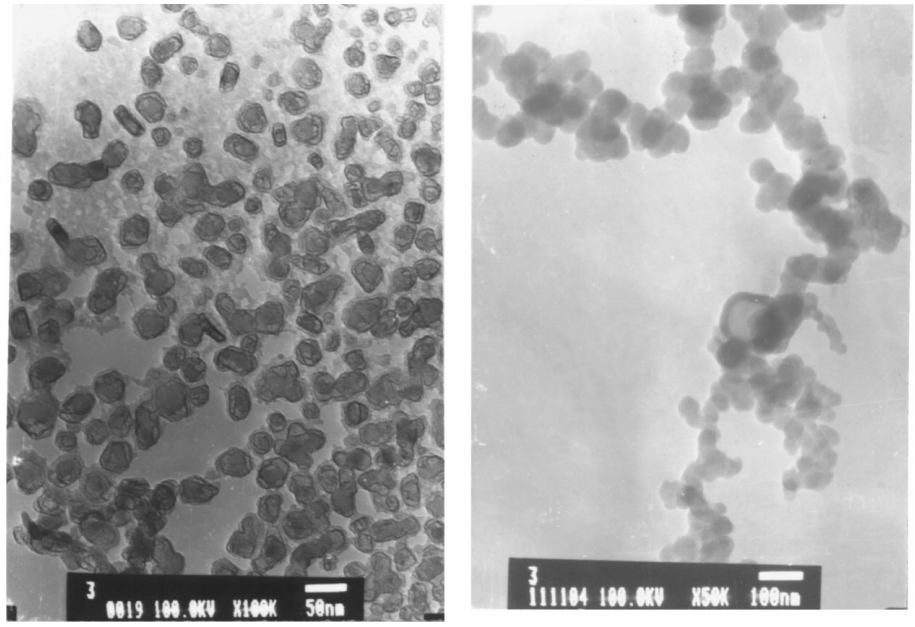
3.5. Characterization of the nitridation process and the products formed

3.5.1. DTA measurements

DTA curves for the nitridation of undoped Mg* in a nitrogen atmosphere exhibited a single exothermic peak at 567 °C (Fig. 5a) (the exothermic peak for the nitridation of commercial Mg powder begins at temperatures higher than 600 °C). However, the nitridation peaks of $NiCl_2$- and La-doped Mg* are both doublets, with the first peak occurring at 519 °C (Fig. 5b), and 528 °C (Fig. 5c) respectively; both of these are lower than 567 °C. The appearence of the double exothermic peaks might indicate the existence of two active species of doped Mg*. The results of these DTA measurements are consistent with those for the nitriding of Mg* at constant temperatures.

3.5.2. TEM measurements

It is known that the particle size of MgH_2 powder prepared catalytically is in the nanometric range [14, 15]. After dehydrogenation and nitridation the particle size of the product still remains in the nanometric region. TEM measurements show that the average particle size of the Mg* is around 30 nm (Fig. 6a) and that of the nitrided product, Mg_3N_2, is around 50 nm (Fig. 6b).



(a) (b)

Figure 6 TEM micrographs of (a) Mg* and (b) its nitrided product.

4. Conclusions

Highly reactive magnesium powder, Mg*, doped with transition metal compounds, obtained from the dehydrogenation of catalytically prepared MgH_2, can react with nitrogen at normal pressure at temperatures as low as 300 °C. At 450 °C the doped and undoped Mg* powders can react fairly rapidly with nitrogen to form magnesium nitride. Doping with $NiCl_2$ remarkably improves the nitriding behavior of Mg*. The average particle size of the prepared nitride is around 50 nm.

Acknowledgements

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