

## A STUDY ON PREPARATION AND HYDRIDING OF $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> AND $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub>

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### ABSTRACT

#### A STUDY ON PREPARATION AND HYDRIDING OF $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> AND $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub>.

The mechanism of the synthetic formation of  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> and  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> has been studied. Mechanical alloying of Mg and Al powders with the atomic ratio of Mg:Al = 2:3 in toluene solution yields  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> compound after milling for 30 h. The  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> can be formed by heating the  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> at 430 °C under high vacuum. The measured hydrogen capacities of  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> and  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> as hydrided at 300 °C are 3.2 and 4.9 wt%, respectively. Microstructure of the Mg-Al specimen shows that on hydriding at 300 °C the polygonal shape of the  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> changes into irregular shapes which are composed of  $\gamma$ -MgH<sub>2</sub> and Al.

FREE TERMS: mechanical Alloying, Mg-Al compounds, hydriding

### ABSTRAK

*STUDI PENYIAPAN DAN HIDRIDING  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> DAN  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub>. Mekanisme pembuatan  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> dan  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> telah dipelajari. Pemaduan mekanik serbuk Mg dan Al dengan perbandingan atomik Mg:Al = 2:3 dalam larutan toluena menghasilkan senyawa  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> setelah penggerusan selama 30 jam.  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> dapat terbentuk dengan pemanasan  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> pada suhu 430 °C dalam vakum tinggi. Kapasitas hidrogen terukur dari  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> dan  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> terhidrisasi pada suhu 300 °C adalah berturut-turut 3,2 dan 4,9% berat. Mikrostruktur dari spesimen Mg-Al menunjukkan bahwa sewaktu hidriding pada suhu 300 °C bentuk poligonal dari  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> berubah menjadi tak beraturan yang terdiri dari  $\gamma$ -MgH<sub>2</sub> dan Al.*

*KATA KUNCI: pemaduan mekanik, senyawa Mg-Al, hidriding*

## I. INTRODUCTION

One promising alternative to fossil fuels is hydrogen. Through its reaction with oxygen, hydrogen releases energy explosively in heat engines or quietly in fuel cells.

Hydrogen storage in the form of solid metal hydrides may make it possible to store larger quantities of hydrogen in smaller volumes at low pressure and at temperatures close to room temperature, compared to that in the form of gaseous storage in cylinders. It is also possible to achieve greater volumetric storage densities than liquid hydrogen because the hydrogen molecule is dissociated into atomic hydrogen within the metal hydride lattice structure.

Magnesium and its derived alloys are looked upon as promising candidates of hydrogen storage material due to their high theoretical storage capacity (7.6 wt%), light weight

and low cost. However, they require high temperature over 300 °C to show preferable hydrogen absorption and desorption properties because of the poor absorption/desorption kinetics. For practical application, it is necessary to improve the hydrogen reaction kinetics and lower the working temperature<sup>[1-5]</sup>.

Synthetic alloying of the  $Mg_2Ni$  compound using a high energy ball milling and hydriding the compound into  $Mg_2NiH_4$  were achieved by the present authors<sup>[6,7]</sup>. Examination results indicate that approximately 96 wt% of the  $Mg_2Ni$  compound can be obtained from the individual constituents after 30 hours of milling in toluene solution, which was used to protect the metals from oxidation.

Following the success of the  $Mg_2Ni$  preparation by mechanical alloying, its application to the Mg-Al system has been examined, here in regards to the formation of  $Mg_2Al_3$  and  $Mg_{17}Al_{12}$ . Andreasen et al.<sup>[8]</sup> prepared the Mg-Al alloys using an Edmund Buhler arc melting furnace. Their experimental results showed that  $Mg_{17}Al_{12}$  compound can be produced from approximately 5 g mixture of magnesium and aluminum in stoichiometric atomic ratio. The Mg-Al alloys have attracted considerable attention since the alloys absorb hydrogen up to about 3.02 – 4.44 wt%. In the present study, a high energy mechanical alloying method is used instead of the arc melting to obtain the  $Mg_2Al_3$  compound. Heat treatment of the  $\beta$ - $Mg_2Al_3$  powder at 430 °C under high vacuum has been conducted to convert the powder into  $\gamma$ - $Mg_{17}Al_{12}$ . The mechanism of  $Mg_2Al_3$  and  $Mg_{17}Al_{12}$  formations during the mechanical alloying and heat treatment as well as their hydrogen absorption properties have been studied and are presented in this paper.

## II. EXPERIMENTAL

The milling experiment was performed using a SPEX 8000 type high energy ball mill (HEM) with the specifications as follows: 4500 rpm at normal blending speed, 90 minutes of running time, and 30 minutes of off time. The materials used in this experiment were magnesium powder (99.5% purity, metal basis, particle size < 325 mesh or < 44  $\mu m$ ) and aluminum powder (99% purity, metal basis, particle size < 200 mesh or < 74  $\mu m$ ). About 15 g of a mixture of Mg and Al powders with an atomic ratio of Mg:Al = 3:2 is milled with balls and then poured into a vial (dia. 51 mm and length 76 mm). The ball to specimen ratio by weight is 8:1 (ball dia. 12 mm). The milling was carried out for 10, 20, and 30 h each at room temperature under toluene solution.

Qualitative and quantitative analyses were conducted with an X-ray diffractometer (XRD) of Philip type PW1710, using Cu as the anode tube and  $\lambda = 1.5406 \text{ \AA}$ . Continuous scanning was conducted at 0.02° step size and 0.5 second/step. The scanning results are analyzed by using *Rietveld method* developed by Fuji Izumi<sup>[9]</sup>. Hydrogen absorption is conducted in a Sievert's system that can be operated under high vacuum up to  $1 \times 10^{-7}$  mbar. About 2 – 3 g of  $\beta$ - $Mg_2Al_3$  powder is put into the hydriding system and hydrided at 300 °C. To make  $\gamma$ - $Mg_{17}Al_{12}$ , about 5 g of  $\beta$ - $Mg_2Al_3$  powder was placed inside the hydriding system evacuated at high vacuum, and annealed at a temperature of 430 °C for 1 h. A small part of the annealed powder was then analyzed in the XRD and the rest was hydrided at a temperature of 300 °C. The amount of hydrogen absorbed by the specimen was measured based on the alterations of pressure in the Sievert's system.

### III. RESULTS AND DISCUSSION

#### 3.1. Mechanism of the $\beta$ - $Mg_2Al_3$ Formation

Figure 1 shows the XRD patterns of the Mg-Al specimen before milling and each after 10, 20 and 30 hours of milling. The XRD pattern before milling shows that the specimen consists of Mg and Al without traces of Mg-Al compound phases. After milling, the XRD patterns were changed, an indication that a new phase was formed. The XRD patterns show that the  $\beta$ - $Mg_2Al_3$  phase grew to a considerable degree. Rietveld analyses also showed that the calculation results fit the experimental data, where the value of  $S$  (goodness of fit) is less than 1.3 which is the maximum value permitted according to Izumi. The rates of conversion were approximately 72, 91 and 96 wt% of metal after 10, 20 and 30 hours of milling, respectively. The mechanism of the  $\beta$ - $Mg_2Al_3$  formation has been attributed to mechanical processes as follows. During milling, the Mg and Al powders are periodically trapped among the steel balls that collide with each other resulting in the loss of crystalline state of metal powder, causing the transformation of metal to amorphous state and finally leading to plastic deformation. The Mg and Al powders will break into smaller particles which will stick together due to the cold welding to form a new compound.

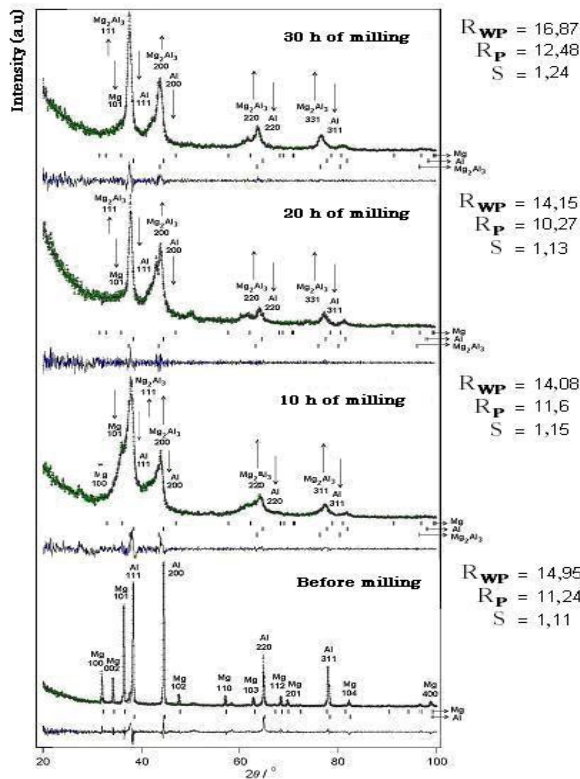


Figure 1. X-ray diffraction patterns of Mg:Al specimens before and after 10, 20 and 30 h of milling.

### 3.2. Formation of $\gamma$ - $Mg_{17}Al_{12}$

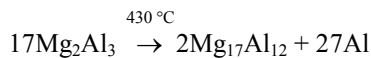
Figure 2 shows the XRD pattern for  $\beta$ - $Mg_2Al_3$  after heat treatment at 430 °C. It is shown that the specimen has transformed from  $\beta$ - $Mg_2Al_3$  into  $\gamma$ - $Mg_{17}Al_{12}$ . The highest peak for  $\gamma$ -phase can be identified at angle  $2\theta$  equal to 36°, corresponding to plane (411), followed by angle 40° at plane (332) and angle 65° at plane (721). The other crystal orientations identified at plane directions [h21], i.e. angle 31, 47 and 65° with the Miller indexes (321), (521) and (721), respectively, are suggested to be brought about due to milling and heating, though it should be proved later. The quantities of  $\gamma$ - $Mg_{17}Al_{12}$  and Al phases were estimated to be 61 wt% and 39 wt%, respectively.

Crivello et al. have also prepared the Mg-Al alloy with the atomic ratio of Mg:Al = 1:1 by mechanical alloying under vacuum using High Energy Nisshin Giken Super-Misuni NEV 8<sup>[10]</sup>. His experimental results showed that after 5 h of ball milling and 3 h of heating at 100 °C, the Mg-Al powders were converted to 24.7 wt% of the  $\beta$ -phase and 75.3 wt% of the  $\gamma$ -phase.

In literature, Bouaricha et al. have also prepared the Mg-Al alloy using the SPEX 8000, shaker type mill<sup>[11]</sup>, which differs from the present experiment. According to them, before milling the Al powder was leached to avoid contamination with oxygen. In addition, Bouaricha selected ball to powder ratio at 10:1. His experimental results at various Mg-Al compositions showed that most of the specimens were converted to  $\gamma$ - $Mg_{17}Al_{12}$ , except for the specimen with the atomic ratio of Mg:Al = 37:63, where mostly  $\beta$ - $Mg_2Al_3$  was formed.

Unlike experiments by Andreasen et al., Crivello et al. and Bouaricha et al., the current experiment uses toluene, instead of argon, as the medium of milling. It is suggested that the presence of toluene avoids the overheat generation during milling process. Therefore, only  $\beta$ - $Mg_2Al_3$  is formed.

The  $\beta$ - $\gamma$  transformation can be expressed by the following reaction:



Theoretically, the mass fraction of the  $\gamma$ -phase is 67 wt%, assuming the atomic masses of Mg and Al are 24.21 g/mol and 26.98 g/mol, respectively. The current experiment yields  $\gamma$ -phase by as much as 61%, an indication that almost all the  $\beta$ -phase has transformed into  $\gamma$ -phase.

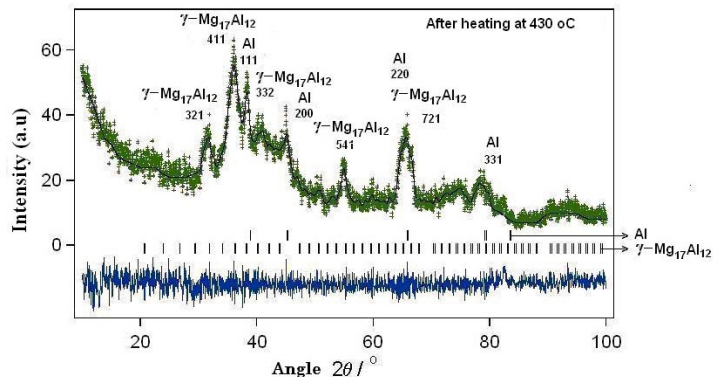


Figure 2. X-ray diffraction pattern of Mg:Al after 30 h of milling and heat treatment at 430 °C.

### 3.3. Hydriding of $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> and $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub>

Figure 3 shows the results of hydriding  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> and  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> specimens. It is shown that the  $\beta$ -phase absorbed hydrogen up to 3.2 wt% and that the  $\gamma$ -phase up to 4.9 wt%. The difference in the hydrogen capacity between these compounds can be understood to be due to the fact that  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> contains less magnesium than  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub>. These compounds have different plateau pressures, where the  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> phase has a higher pressure than the  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> phase.

Crivello et al. reported their experimental results that at the atomic ratios of Mg:Al = 50:50 and 58.6:41.4, the maximum hydrogen absorption capacities were 3.5 and 3.7 wt% (equal to 0.92 and 0.97 H/M normalized) respectively at a hydriding temperature of 350 °C<sup>[10]</sup>. In addition, they observed two sloping plateaux, an indication that the hydride formation was realized in a two-step process with the inflexion points at a relatively low pressure corresponding to 1.1 and 2.1 wt%.

Bouaricha et al. obtained the values of  $[H/M]_{\text{norm}}$  at a hydriding temperature of 400 °C which were equal to 1.69 and 1.81 for the atomic ratios of Mg:Al = 75:25 and 58:42, respectively<sup>[11]</sup>.

Compared to the Crivello et al. and Bouaricha et al.'s  $P$ - $c$ - $T$  diagrams, the present experiment presents higher plateau pressures, attributable to the fact that the experimental methods are different. Actually, Crivello et al. and Bouaricha et al. used higher pressures, while the current experiment was done at lower pressures.

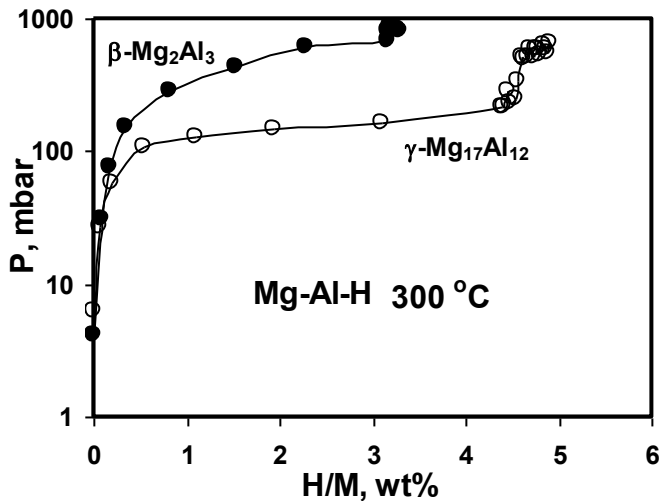


Figure 3.  $P$ - $c$ - $T$  isotherms at 300 °C for hydriding  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> and  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub>.

Figure 4 shows the hydriding rates of both the  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> and  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> phases at 300 °C. The two curves show almost similar absorption lines before inflected at 3.15 wt% and 4.38 wt% for the  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> and  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> phases, respectively. The figure indicates that the specimens absorbed hydrogen very fast at the beginning before suddenly inflected into slow rates. The sharp inflexion occurred after approximately 170 seconds. Andreasen et al. reported that complete hydriding spent time for approximately 17 h with the total hydrogen uptake of

approximately 3.1 wt%<sup>[8]</sup>. Meanwhile, no information was reported about the hydriding rates by Crivello et al. and Bouaricha et al.

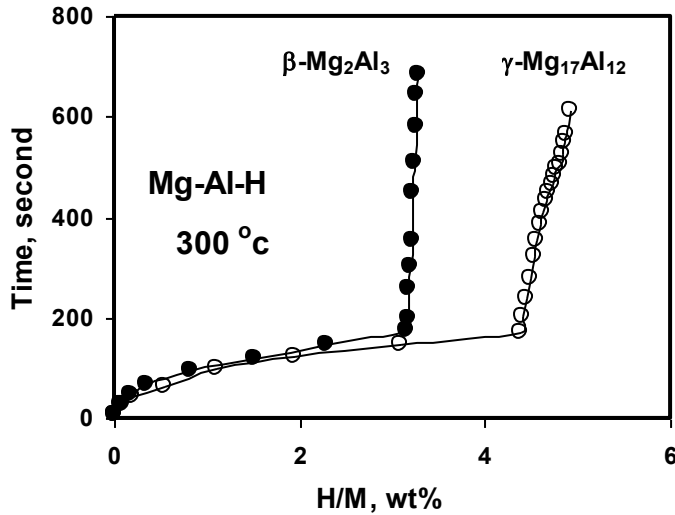
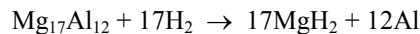


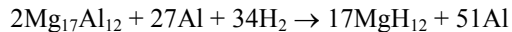
Figure 4. Hydriding rates of the  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> and  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> phases at 300 °C

### 3.4. XRD of the Hydriding Results

Figure 5 indicates the XRD pattern of  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> specimen hydrided at 300 °C. Referring to Figure 2 and 5, the mass fractions of  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> and  $\gamma$ -MgH<sub>2</sub> are evaluated to be 61 wt% and 39 wt%, respectively. The chemical reaction for the hydriding process of  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> can be described as follows:



Meanwhile, by taking into account the XRD pattern in Figure 2, the equation to describe the actual chemical reaction that occurred in the specimen is as follows:



The theoretical mass yield of  $\gamma$ -MgH<sub>2</sub> is 40 wt%, taking the atomic mass of H to be 1.0 g/mol, while the present result is 39 wt% or the hydrogen absorbed is about 3 wt%. Compared to the hydrogen capacities presented in the *P-c-T* diagram in Figure 3, i.e. 3.2 wt% for the  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> phase and 4.9 wt% for  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub>, the calculation result is too low. It is probably due to the fact that not all the  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> specimen was converted to  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub>.

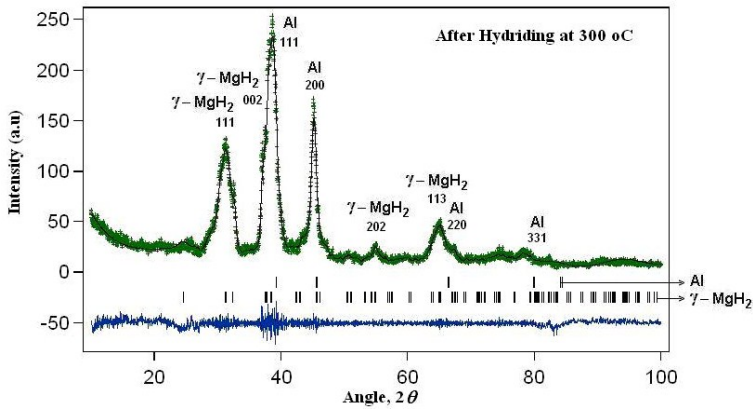
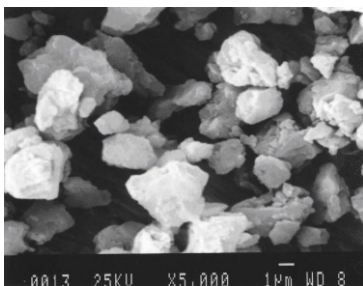


Figure 5. X-ray diffraction patterns of  $\gamma\text{-Mg}_{17}\text{Al}_{12}$  hydrided at 300 °C. The  $\gamma\text{-Mg}_{17}\text{Al}_{12}$  is transformed to  $\gamma\text{-MgH}_2$  and Al phases.

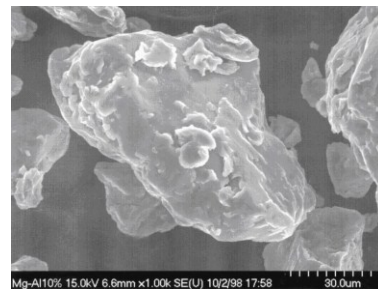
### 3.5. Microstructures of the Mg-Al Specimens

Microstructures of the specimens have been analyzed using a scanning electron microscope (SEM). Figure 6 shows the microstructure of (a) the  $\beta\text{-Mg}_2\text{Al}_3$  after 30 h of milling, together with those of (b) Bouaricha et al.<sup>[11]</sup> and (c) Crivello et al.<sup>[10]</sup>. The microstructure analyses show that the particle shapes are polygonal<sup>[12]</sup> with the varied particle sizes of 2 – 7  $\mu\text{m}$  distributed homogeneously on the surface of the specimens. Compared to the particles of Bouaricha et al. and Crivello et al., the present microstructure shows more uniform but larger particle sizes with polygonal structures.

Figure 7 shows the SEM photograph for the hydrided Mg-Al specimen. The change in the shape from polygonal to irregular indicates that the new phase  $\gamma\text{-MgH}_2$  has been formed.



(a)



(b)

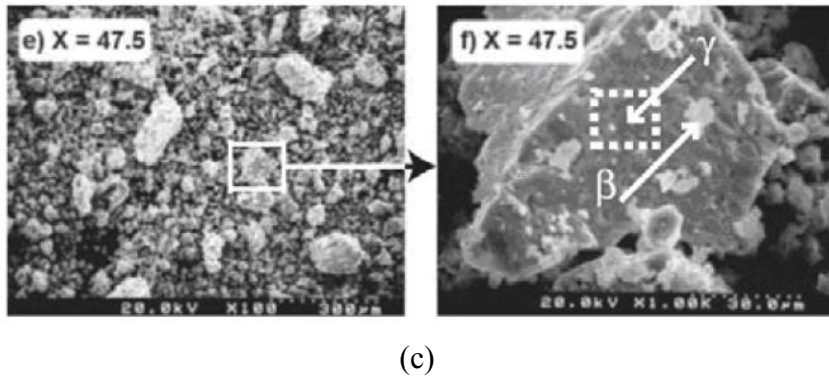


Figure 6. SEM photographs: (a) the Mg-Al specimen after 30 h milling of this study, (b) Bouaricha et al.[11], and (c) Crivello et al

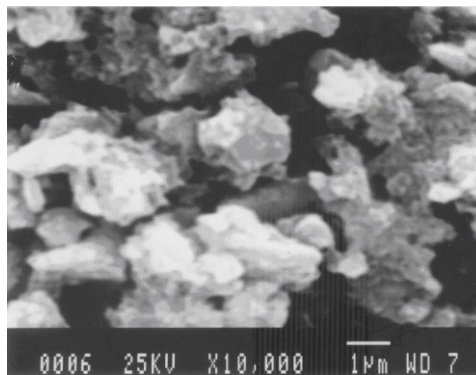


Figure 7. SEM photograph of the Mg-Al specimen after hydriding

#### IV. CONCLUSION

Syntheses of  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> and  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> have been carried out by means of mechanical alloying under toluene and then heat treatment, respectively. Their hydriding properties have been investigated. Almost all the Mg-Al powders can be synthesized into  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> phase after milling for 30 h. The  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> phase can be obtained by heating the  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> phase at 430 °C for 1 h under high vacuum. Surface morphology of the specimen was examined with SEM to reveal that the synthesized particles have a polygonal shape similar to the observation made by other researchers who used slightly different methods. Hydrogen capacities of the  $\beta$ -Mg<sub>2</sub>Al<sub>3</sub> and  $\gamma$ -Mg<sub>17</sub>Al<sub>12</sub> phases at 300 °C are 3.2 wt% and 4.9 wt%, respectively.

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