

A STUDY ON PREPARATION AND HYDRIDING OF β -Mg₂Al₃ AND γ -Mg₁₇Al₁₂

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(Received June 17, 2009; approved October 5, 2009)

ABSTRACT

A STUDY ON PREPARATION AND HYDRIDING OF β -Mg₂Al₃ AND γ -Mg₁₇Al₁₂.

The mechanism of the synthetic formation of β -Mg₂Al₃ and γ -Mg₁₇Al₁₂ has been studied. Mechanical alloying of Mg and Al powders with the atomic ratio of Mg:Al = 2:3 in toluene solution yields β -Mg₂Al₃ compound after milling for 30 h. The γ -Mg₁₇Al₁₂ can be formed by heating the β -Mg₂Al₃ at 430 °C under high vacuum. The measured hydrogen capacities of β -Mg₂Al₃ and γ -Mg₁₇Al₁₂ 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 γ -Mg₁₇Al₁₂ changes into irregular shapes which are composed of γ -MgH₂ and Al.

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

ABSTRAK

STUDI PENYIAPAN DAN HIDRIDING β -Mg₂Al₃ DAN γ -Mg₁₇Al₁₂. Mekanisme pembuatan β -Mg₂Al₃ dan γ -Mg₁₇Al₁₂ telah dipelajari. Pemaduan mekanik serbuk Mg dan Al dengan perbandingan atomik Mg:Al = 2:3 dalam larutan toluena menghasilkan senyawa β -Mg₂Al₃ setelah penggerusan selama 30 jam. γ -Mg₁₇Al₁₂ dapat terbentuk dengan pemanasan β -Mg₂Al₃ pada suhu 430 °C dalam vakum tinggi. Kapasitas hidrogen terukur dari β -Mg₂Al₃ dan γ -Mg₁₇Al₁₂ 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 γ -Mg₁₇Al₁₂ berubah menjadi tak beraturan yang terdiri dari γ -MgH₂ 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^[1-5].

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^[6,7]. 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.^[8] 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 β - Mg_2Al_3 powder at 430 °C under high vacuum has been conducted to convert the powder into γ - $Mg_{17}Al_{12}$. 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 μm) and aluminum powder (99% purity, metal basis, particle size < 200 mesh or < 74 μm). 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^[9]. Hydrogen absorption is conducted in a Sievert's system that can be operated under high vacuum up to 1×10^{-7} mbar. About 2 – 3 g of β - Mg_2Al_3 powder is put into the hydriding system and hydrided at 300 °C. To make γ - $Mg_{17}Al_{12}$, about 5 g of β - 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 β - 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 β - 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 β - 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.

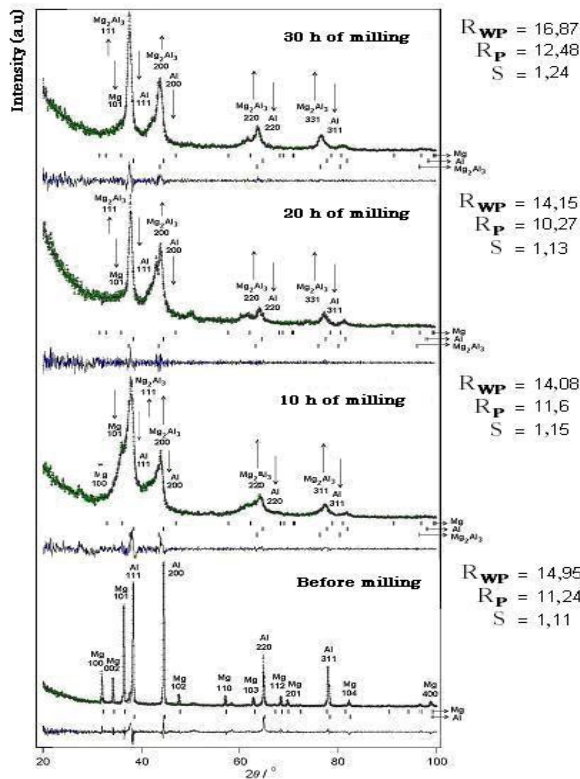


Figure 1. X-ray diffraction patterns of Mg:Al specimens before and after 10, 20 and 30 h of milling.

3.2. Formation of γ - $Mg_{17}Al_{12}$

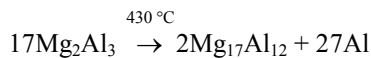
Figure 2 shows the XRD pattern for β - Mg_2Al_3 after heat treatment at 430 °C. It is shown that the specimen has transformed from β - Mg_2Al_3 into γ - $Mg_{17}Al_{12}$. The highest peak for γ -phase can be identified at angle 2θ equal to 36°, corresponding to plane (411), followed by angle 40° at plane (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 γ - $Mg_{17}Al_{12}$ 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 Nissin Giken Super-Misuni NEV 8^[10]. 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 β -phase and 75.3 wt% of the γ -phase.

In literature, Bouaricha et al. have also prepared the Mg-Al alloy using the SPEX 8000, shaker type mill^[11], 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 γ - $Mg_{17}Al_{12}$, except for the specimen with the atomic ratio of Mg:Al = 37:63, where mostly β - 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 β - Mg_2Al_3 is formed.

The β - γ transformation can be expressed by the following reaction:



Theoretically, the mass fraction of the γ -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 γ -phase by as much as 61%, an indication that almost all the β -phase has transformed into γ -phase.

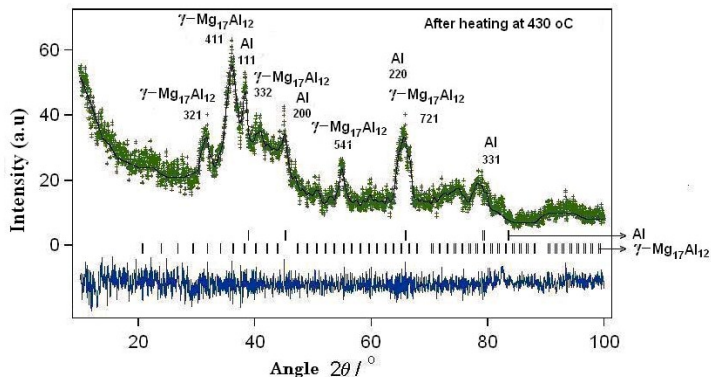


Figure 2. X-ray diffraction pattern of Mg:Al after 30 h of milling and heat treatment at 430 °C.

3.3. Hydriding of β -Mg₂Al₃ and γ -Mg₁₇Al₁₂

Figure 3 shows the results of hydriding β -Mg₂Al₃ and γ -Mg₁₇Al₁₂ specimens. It is shown that the β -phase absorbed hydrogen up to 3.2 wt% and that the γ -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 β -Mg₂Al₃ contains less magnesium than γ -Mg₁₇Al₁₂. These compounds have different plateau pressures, where the β -Mg₂Al₃ phase has a higher pressure than the γ -Mg₁₇Al₁₂ 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^[10]. 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^[11].

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.

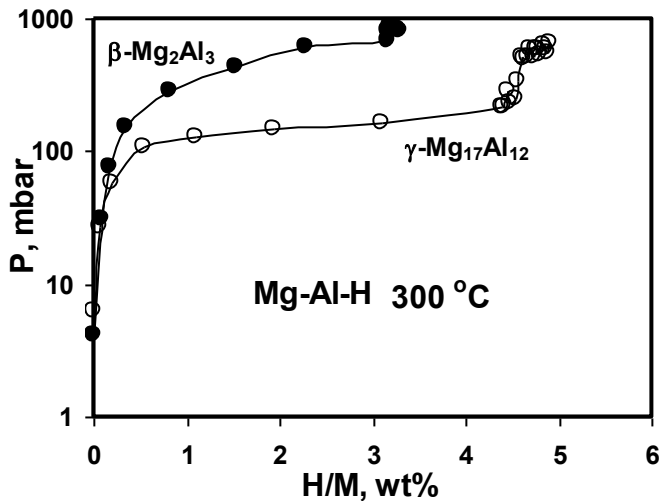


Figure 3. P - c - T isotherms at 300 °C for hydriding β -Mg₂Al₃ and γ -Mg₁₇Al₁₂.

Figure 4 shows the hydriding rates of both the β -Mg₂Al₃ and γ -Mg₁₇Al₁₂ phases at 300 °C. The two curves show almost similar absorption lines before inflected at 3.15 wt% and 4.38 wt% for the β -Mg₂Al₃ and γ -Mg₁₇Al₁₂ 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%^[8]. Meanwhile, no information was reported about the hydriding rates by Crivello et al. and Bouaricha et al.

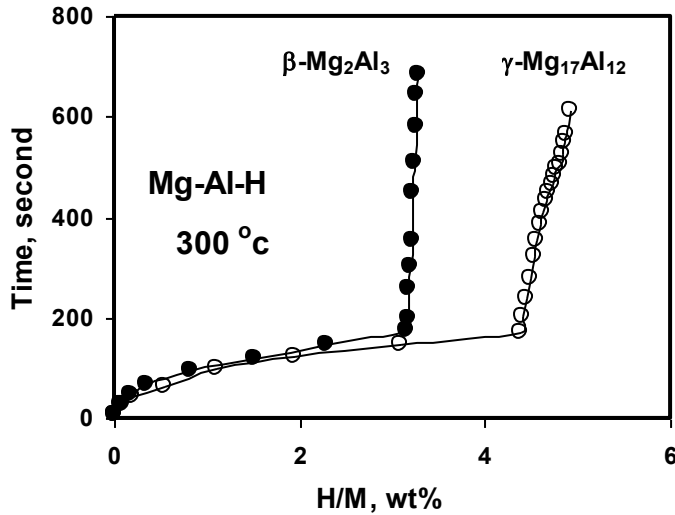
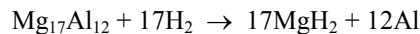


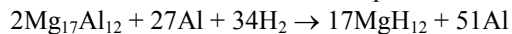
Figure 4. Hydriding rates of the β -Mg₂Al₃ and γ -Mg₁₇Al₁₂ phases at 300 °C

3.4. XRD of the Hydriding Results

Figure 5 indicates the XRD pattern of γ -Mg₁₇Al₁₂ specimen hydrided at 300 °C. Referring to Figure 2 and 5, the mass fractions of γ -Mg₁₇Al₁₂ and γ -MgH₂ are evaluated to be 61 wt% and 39 wt%, respectively. The chemical reaction for the hydriding process of γ -Mg₁₇Al₁₂ 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 γ -MgH₂ 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 β -Mg₂Al₃ phase and 4.9 wt% for γ -Mg₁₇Al₁₂, the calculation result is too low. It is probably due to the fact that not all the β -Mg₂Al₃ specimen was converted to γ -Mg₁₇Al₁₂.

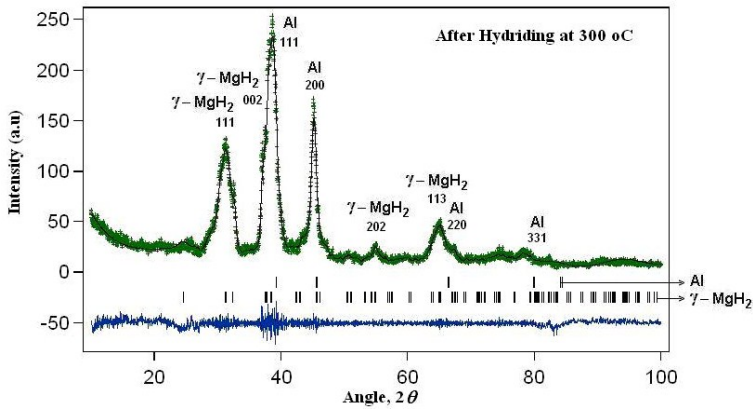
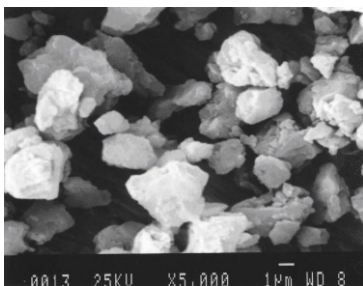


Figure 5. X-ray diffraction patterns of γ -Mg₁₇Al₁₂ hydrided at 300 °C. The γ -Mg₁₇Al₁₂ is transformed to γ -MgH₂ and Al phases.

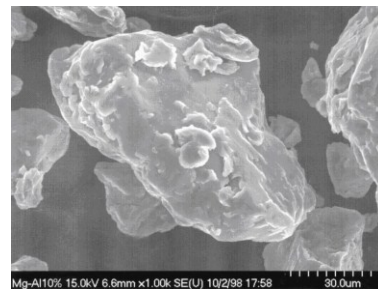
3.5. Microstructures of the Mg-Al Specimens

Microstructures of the specimens have been analyzed using a scanning electron microscope (SEM). Figure 6 shows the microstructure of (a) the β -Mg₂Al₃ after 30 h of milling, together with those of (b) Bouaricha et al.^[11] and (c) Crivello et al.^[10]. The microstructure analyses show that the particle shapes are polygonal^[12] with the varied particle sizes of 2 – 7 μ 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 γ -MgH₂ has been formed.



(a)



(b)

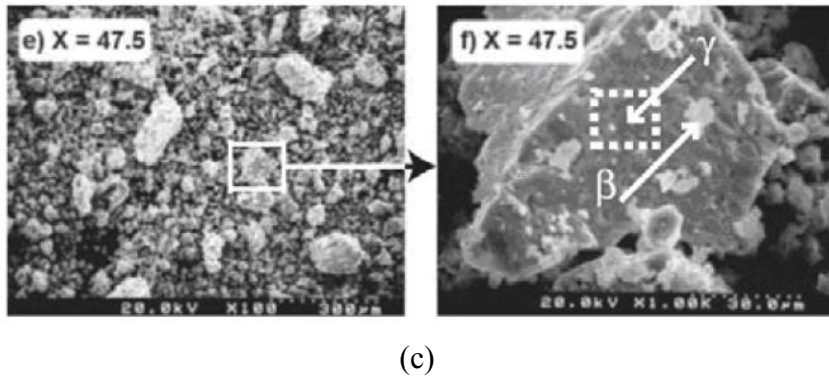


Figure 6. SEM photographs: (a) the Mg-Al specimen after 30 h milling of this study, (b) Bouaricha et al.[11], and (c) Crivello et al

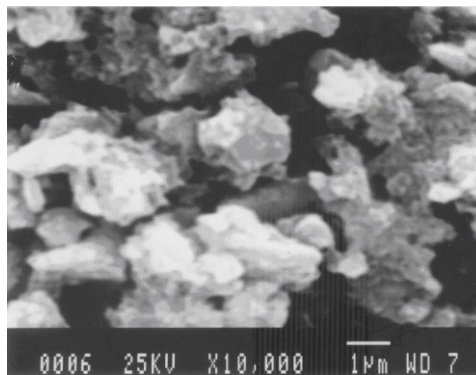


Figure 7. SEM photograph of the Mg-Al specimen after hydriding

IV. CONCLUSION

Syntheses of β -Mg₂Al₃ and γ -Mg₁₇Al₁₂ 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 β -Mg₂Al₃ phase after milling for 30 h. The γ -Mg₁₇Al₁₂ phase can be obtained by heating the β -Mg₂Al₃ 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 β -Mg₂Al₃ and γ -Mg₁₇Al₁₂ phases at 300 °C are 3.2 wt% and 4.9 wt%, respectively.

V. ACKNOWLEDGEMENT

The authors would like to express their great thanks to the State Minister of Research and Technology, KNRT, for the financial support under the Incentive Program, fiscal year 2008 and to PT. BATAN Teknologi for providing facilities and supports for this research

program. Thanks are also addressed to the Director of the Center for Nuclear Fuel Technology as well as the Director of the Center for Nuclear Industry Materials Technology, BATAN.

VI. REFERENCES

1. ZALUSKA, A., ZALUSKI, L., and STROM-OLSEN, J.O., *Journal of Alloys and Compounds*, Vol.228, 1999, p.217.
2. ARNASON, B., and SIGFUSSON, T.I., *Int. J. Hydrogen Energy*, Vol.25, 2000, p.389.
3. LIANG, G., HUOT, J., BOILY, S., NESTE, A.V., and SCHULTZ, R., *Journal of Alloys and Compounds*, Vol.348, 2003, p.319.
4. UEDA, T.T., TSUKAHARA, M., KAMIYA, Y., and KIKUCHI, S., *Journal of Alloys and Compounds*, Vol.386, 2005, p.253.
5. BUCHENER, H., and POVEL, R., *Int. J. Hydrogen Energy*, Vol.7, 1982, p.259.
6. SUWARNO, H., WISNU, A.A., and ANDON, I., “The X-Ray Diffraction Analyses on the Mechanical Alloying of the Mg₂Ni Formation”, *International Conference on Solid State Ionic Proceeding*, Jakarta, Indonesia, August 3 – 4, 2007.
7. SUWARNO, H., “Preparation and Characterization of Mg₂NiH₄ for Hydrogen Storage Material”, *Journal of Material Science of Indonesia*, Special edition, December, 2008, p.177.
8. ANDREASEN, A., SORENSEN, M.B., MOLLER, B., MOLENBROEK, A.M., PEDERSEN, A.S., ANDREASEN, J.W., NIELSEN, M.M., and JENSEN, T.R., *Journal of Alloys and Compounds*, Vol.404-405, 2005, p.323.
9. IZUMI, F., *Rietan Manual*, 1994. (Private communication)
10. CRIVELLO, J.C., NOBUKI, T., KATO, S., ABE, M., and KUJI, T., *Journal of Advanced Science*, Vol.19, 2007, p.88.
11. BOUARICHA, S., DODELET, J.P., GUAY, D., HOUT, J., BOILY, S., and SCHULZ, R., *J. Alloys Comps.*, Vol.297, 2000, p.282.
12. GERMAN, M.R., “*Powder Metallurgy Science*”, 2nd ed., Metal Powder Industries, New Jersey, 1994.