Atom Indonesia Vol. 35 No. 1 (2009) 11 - 18

THE MECHANISM OF Mg_2Al_3 FORMATION BY MECHANICAL ALLOYING

H. Suwarno[1*], W. A. Adi[2], A. Insani[2]
[1]Center for Nuclear Fuel Technology, BATAN
[2]Center for Nuclear Industry Material Technology, BATAN
Puspiptek, Serpong, Tangerang 15314, Banten, Indonesia

Received 14 August 2008; Received in revised form 12 November 2008; Accepted 11 December 2008

ABSTRACT

THE MECHANISM OF Mg_2Al_3 FORMATION BY MECHANICAL ALLOYING. Synthetic and characterization of the Mg_2Al_3 formation by mechanical alloying have been carried out using a high energy ball milling process. Mechanical alloying is a technique of solid state reactions among two or more metals to form a new alloy through the deformation properties of the metals. The Mg_2Al_3 alloy was formed by milling the individual constituents using a high energy ball milling under the varied milling time of 10, 20 and 30 h. The refinement results on the x-ray diffraction analysis show that the observation and calculation are fit to each other. After milling for 10, 20 and 30 h the mixed Mg and Al metals are converted into Mg_2Al_3 at the composition of 71.82, 90.73 and 96.19 wt%. It is concluded that the Mg_2Al_3 alloy can be performed by high energy mechanical alloying after 30 h of milling. The mechanism of the Mg_2Al_3 formation is discussed.

Keywords: Metal hydrides, Mg_2Al_3, Formation, High energy milling

© 2009 Atom Indonesia. All rights reserved.

INTRODUCTION

The global energy crisis has motivated all researchers to develop hydrogen as the alternative energy. Hydrogen represents an energy carrier that is clean and can be produced without foreign energy imports, being often characterized as the "ultimate fuel of the future". While hydrogen as a commercial energy carrier is still in its development stages, there is growing interest and also growing momentum to address the technical difficulties and barriers that remain, and to move hydrogen forward to reality. One of the hydrogen storage method developed is through metals and its alloyed namely metal hydride [1-3].

Magnesium and magnesium-based alloys are promising hydrogen storage materials due to their high storage capacity and low cost. For example, pure Mg and Mg_2Ni alloy can absorb hydrogen up to 7.6 and 3.6 wt%, respectively. However, they need high temperature over 573K to show preferable hydrogen absorption and desorption properties because of the poor hydriding and dehydriding kinetics. For practical application, it is

* Corresponding author.
E-mail addresses: hadis@batan.go.id (H. Suwarno)

necessary to improve the hydrogen reaction kinetics and lower the working temperature [4-7].

It has been succeeded in preparing the synthetic alloying of the Mg_2Ni compound by using a high energy ball milling and hydriding it into Mg_2NiH_4 [8,9]. From the examination results it is found that about 88% of the Mg_2Ni compound can be obtained from the individual constituents after 25 h of milling process under toluene solution for protecting the metals from oxygen.

Success on preparation of the Mg_2Ni by mechanical alloying, another syntheses in the form of Mg-Al is examined. For instance, Andreasen [10] have success to prepare the Mg-Al alloys using an Edmund Buhler arc melting furnace. His experimental results showed that $Mg_{17}Al_{12}$ compound can be produced from approximately 5 g of a mixture of magnesium and aluminum according to its stoichiometry. The Mg-Al alloys have attracted considerable attention because it can absorb hydrogen up to about 3.02 – 4.44 wt%. Unlike the Andreasen's experiment, the Author uses high energy mechanical alloying method instead of arc melting and the Mg_2Al_3 compound is obtained instead of $Mg_{17}Al_{12}$ compound. Detail mechanism of Mg_2Al_3 formation during mechanical alloying is presented in this paper.

EXPERIMENTAL METHODS

The equipment used in the experiment is a high energy milling (HEM) Spex type 8000 with the specification of machine as 4500 rpm at normal blending speed, run time 90 min, and off time 30 min. This is called one cycle of milling. The HEM consists of a vial, which is filled with balls spinally moving to comminute the powder of initial specimens until new Mg-Al compounds or nanosize particles are obtained. The vials were made from stainless steel with the diameter of 5.1 cm and 7.6 cm in length. The balls are made from stainless steel with the diameter of balls is 12 mm. About 15 grams of Mg and Al elements with atomic ratio of Mg:Al = 2:1 are mixed together with balls and then poured into the vial. The ball to specimen ratio is 8. The varied milling times are 10, 20, and 30 h at room temperature under toluene solution.

The Mg_2Al_3 compound was prepared by solid state reaction by mixing the elemental constituent of Mg (obtained from Merck with purity of 99,5%, < 3.5 μm) and Al (obtained from Merck with purity of 99,0%, < 10μm) with the atomic ratio of Mg:Al = 2:1.

Qualitative and quantitative analyses were measured by using an X-ray Diffractometer (XRD), Philip, type PW1710, using Cu as the anode tube and λ = 1.5406 Å. Continuous scanning was conducted at 0.02° step size and 0.5 second/step. The scanning results are analyzed by a *Rietveld method* developed by Fuji Izumi [11]. The first data contains parameter of the crystal structure and the second is the data of intensity. The *Rietveld method* then

gives information about the crystal structural parameter in a unit of a cell, intensity of the calculation and observation, number of mass fraction if the sample contains more than one compounds, and the data of Bragg reflection. The HEM and XRD machines are located in the Center for Nuclear Industry Materials Technology, BATAN.

RESULT AND DISCUSSION

The β-phase Mg_2Al_3 and γ-phase $Mg_{17}Al_{12}$ are among the stable Mg-Al compounds that can be formed by solid state reaction using a high energy ball mill. The diffraction analysis of the Mg-Al alloy with the atomic composition of Mg:Al = 2:1 after milling for 0, 10, 20, and 30 h is presented in Figure 1.

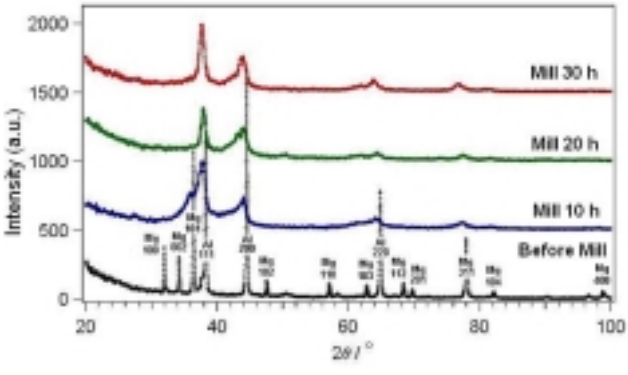


Figure 1. The X-diffraction pattern before and after 10, 20 and 30 h of milling.

From Figure 1 it is showed that before milling the Mg-Al mixture contains no impurities and only Mg and Al phases are identified. During milling for up to 30 h, a mechanical milling process occurs that can be explained as follows. During milling the Mg and Al powders are periodically trapped among the steel balls that collide to each others resulting in the metal powders loss their crystal orientation, transformed into amorphous state and finally plastic deformation. The Mg and Al powders fracture and broken into smaller particles and slurring together by a process called cold welding to form a new compound. After 30 h of milling the mass fraction of the elemental components reducing significantly and the mass fraction of a new Mg_2Al_3 compound increases for > 90 wt%. To identify the peaks of the x-ray analysis before milling we use Hanawalt's Table [12, 13]. To simulate the Mg-Al phases formed after milling we refer also to the Mg-Al phase diagram [10] and the refinement results for the X-ray diffraction after 10, 20 and 30 h of milling are presented in Figures 2, 3, 4 and 5.

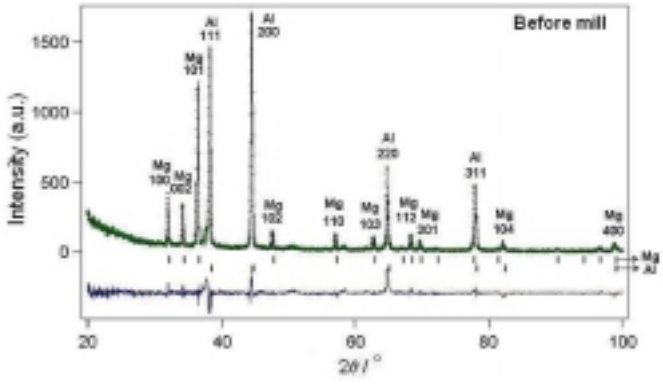


Figure 2. *Refinement* for the X-ray diffraction result before milling.

Figure 2 shows the refinement of the X-ray diffraction pattern of the specimen before milling. It shows that the Mg and Al elemental components have found no impurities. The highest peak for Mg metal phase is at plane (101) and for Al metal phase is at plane (200). The quantitative analysis of the specimens obtained that it contains Mg and Al about 43.3 % and 56.7 % in mass fraction, equal to the atomic composition for Mg_2Al_3 compound.

Figure 3 shows the refinement of the X-ray diffraction pattern for the specimen after milling for 10 h. After milling the peaks for Mg, plane (101) at angle 36.39^o, and Al, plane (200) at angle 44.49^o, decline sharply (see symbol ↓) while new peaks grow at angles 38^o, 43^o, 63^o and 76^o symbolized by ↑. These peaks belong to Mg_2Al_3 phase. The refinement result for the X-ray diffraction pattern shows that the growth of Mg_2Al_3 compound increased to 71.82 % and the phases for Mg and Al reduced to 6.37 % and 21.82 %, respectively. The drastic reduction in elemental components come from Mg because Mg amorphous easily than Al.

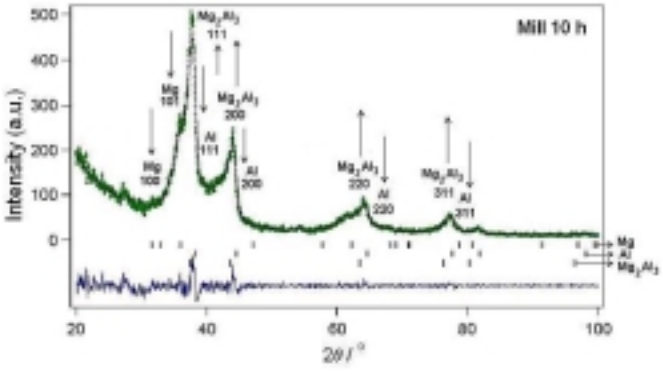


Figure 3. *Refinement* for the X-ray diffraction result after 10 h of milling.

Figure 4 shows the refinement of the X-ray diffraction pattern for the specimen after 20 h of milling. It exhibits that parts of the Mg peaks disappear and only the highest peak of Mg at plane (101) can be seen as a small peak at 36.39°. Similar to Mg peaks, the height of Al peaks reduce sharply at planes (200), (220) and (311) into smaller peaks. After 20 h of milling, the growth of Mg_2Al_3 phase increases to 90.73 % and the mass fraction of Mg and Al decrease to < 1 % and 8.89 %, respectively. Figure 5 shows that the peaks of Mg disappear and that of Al become very weak, an indication that almost all Mg and Al are converted into Mg_2Al_3 compound.

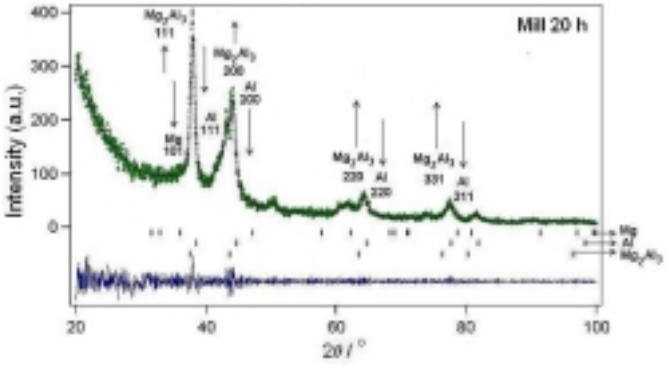


Figure 4. *Refinement* for the X-ray diffraction result after 20 h of milling.

Figure 5 shows the refinement of the X-ray diffraction pattern for the specimen after 30 h of milling, where the Mg peaks totally disappear and only small peak from Al phases identified at plane (200) at angle 44.49°. Qualitative analysis of the specimen showed that the mass fraction of Mg_2Al_3 is about 96.19 %.

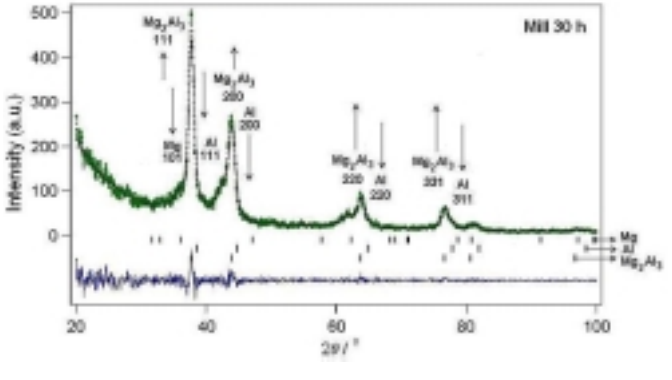
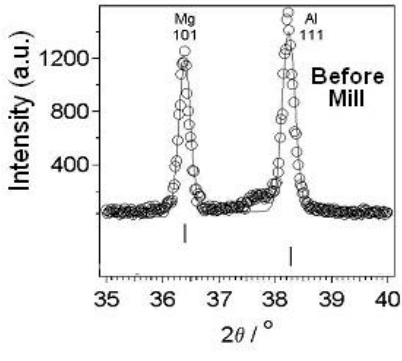
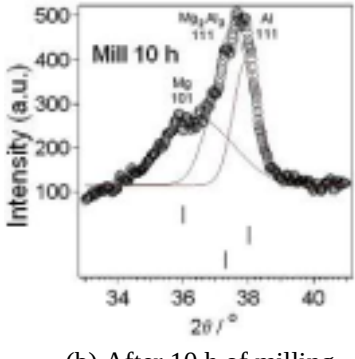


Figure 5. *Refinement* for the X-ray diffraction result after 30 h of milling.

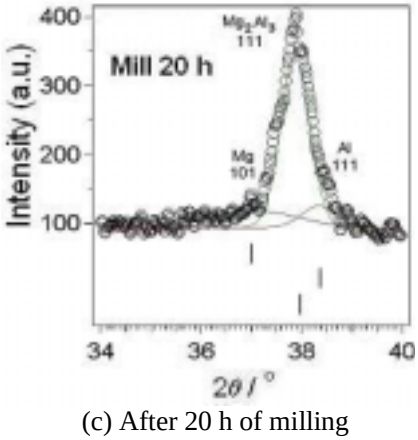
Figure 6 illustrates the growth of Mg_2Al_3 phase during 30 h of milling. Before milling (Figure 6a), peaks of Mg at plane (101) and Al at plane (111) are the highest. After 10 h of milling (Figure 6b), peaks of Mg (101) and Al (111) decrease sharply. The disorder of Mg and Al peaks is resulted from the amorphous states of metals due to milling. After 20 and 30 h of milling (Figure 6c and 6d) the peaks of Mg and Al disappear, an indication of the decrease of mass fraction of both Mg and Al powder due to amorphous state and conversion of the Mg and Al into Mg_2Al_3 phase, while no $Mg_{17}Al_{12}$ phase can be identified.



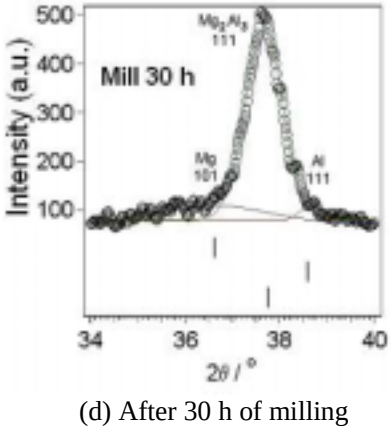
(a) before milling



(b) After 10 h of milling



(c) After 20 h of milling



(d) After 30 h of milling

Figure 6. Illustration of the Mg_2Al_3 growth due to mechanical milling.

Bouaricha et al [14]. also examined the Mg-Al alloys at various composition of constitutional components Mg:Al = 90:10, 75:25, 58:42, 37:63, and 20:80. Most of his experimental results convert the Mg-Al powder into $Mg_{17}Al_{12}$ compound. According to the Mg-Al phase diagram [15], the solubility of Al in the hcp structure of Mg is 11 at.% at 437^{o}C. It means that

the more Al in the Mg-Al alloy, the $Mg_{17}Al_{12}$ will be formed. Busk's data [16] on the variation lattice constant *a* and *c* of Mg with Al content of the hexagonal phase also support the Bouaricha's results.

Crivello et al. also examined the Mg_xAl_{100-x} at x = 47.5 ~ 70 alloy by incremental step of 2.5 [17]. Most of his experimental results obtained $Mg_{17}Al_{12}$ as the major yields. For atomic ratio of Mg:Al = 50:50, his experiment found about 25 % of the alloy was β-phase Mg_2Al_3 coexist with the γ-phase $Mg_{17}Al_{12}$ according to the rietveld refinement.

From our experimental results, where mostly β-phase Mg_2Al_3 and no γ-phase $Mg_{17}Al_{12}$ can be identified, it is suggested that there are different method of preparation. Andreasen used arc melting furnace on his alloying work while Bouaricha and Crivello used HEM. Although we used also HEM, after milling we do not treat further the specimens, e.g. by annealing. Therefore it is suggested that after finishing the 30 h of milling is followed by annealing the specimen at temperature of > 350 ^oC the complete ordered structure of the specimen will be obtained in the form of β-phase Mg_2Al_3 and γ-phase $Mg_{17}Al_{12}$. Continuous examination by varying the Mg-Al compositions should be conducted.

CONCLUSION

The Mg-Al alloy has been synthetized by high energy ball milling method. The refinement results of the X-ray diffraction pattern showed that the calculation fit properly with the observation. The rate of β-phase Mg_3Al_2 formation after 10, 20, and 30 h of milling is 71.82 %, 90.73 % and 96.19 %. Further experiment is being conducted in order to investigate the formation of γ-phase $Mg_{17}Al_{12}$.

ACKNOWLEDGEMENT

The Author would like to express our great thank to the State Minister of Research and Technology for the financial support under the Program Insentif, KNRT, budget's year 2008. Thank also addressed to PT. BATAN Teknologi on providing facilities and supports to this research program. Finally, thank also addressed to the director of the Center for Nuclear Fuel Technology, BATAN and the director of the Center for Nuclear Industry Material Technology, BATAN.

REFERENCES

1. K. HUANG, Y.P. FISHER, *J. Alloys Comp.*, **227,** 121 (1995).
2. A. ZALUSKA, L. ZALUSKI, J.O. STROM-OLSEN, *J. Alloys Comp*., **228,** 217 (1999).
3. G. Liang, J. Huot, S. Boily, A.V. Neste, R. Schultz, *J. Alloys Comp*., **348,** 319 (2003).
4. B. ARNASON, T.I. SIGFUSSON, *Int. J. Hydrogen Energy*, **25,** 389 (2000).
5. A. ZUTEL, Materials for Hydrogen Storage, http://www.elsevier.com, (2006).
6. H. BUCHENER, R. POVEL, *Int. J. Hydrogen Energy*, **7,** 259 (1982).
7. M. DORNHEIM, T. KLASSEN, R. BORMANN, Hydrogen Storage Materials, Institute for Materials Research, GKSS Research Center, Geesthacht, Germany.
8. H. SUWARNO, A.A. WISNU, I. ANDON, International Conference Solid State Ionic, Proceeding, PTBIN, Serpong (2007).
9. H. SUWARNO, *Indonesian Journal of Material Science*, Spec. Ed., 153-157, Dec. (2008).
10. A. ANDREASEN, M.B. SORENSEN, R. BURKARL, B. MOLLER, A.M. MOLENBROEK, A.S. PEDERSEN, J.W. ANDREASEN, M.M. NIELSEN, T.R. JENSEN, *J. Alloys Comps.*, (2006), Accepted, or www.risoe.dk/rispubl/art/2006_15.pdf
11. F. IZUMI, Rietan Manual, (1994) (private communication).
12. D.W. LEVINSON, D.J. MC. PHERSON, *Trans. of The Am. Soc. For Metal*, **48**, 689 (1956).
13. H.L. LUO, C.C. CHAO, P. DUWES, *Trans. of The Metal. Soc. of Aime*, **230**, 1488 (1964).
14. S. BOUARICHA et al., *J. Alloys Comps.*, **297**, 282 (2000).
15. A.A. NAYEB-HASHEMI, J.B. CLARK (Eds.), : "Phase Diagrams of Binary Magnesium Alloys", Monograph Series on Alloy Phase Diagrams, ASM International, (1988).
16. R.S. BUSK, *Trans. AIME.*, **188**, 1460 (1950).
17. J.C. CRIVELLO, T. NOBUKI, S. KATO, M. ABE, T. KUJI, *J. Advanced Science*, **19**, 3 (2007).