THE EFFECT OF TOLUENE SOLUTION ON THE HYDROGEN ABSORPTION OF THE Mg-Ti ALLOY PREPARED BY SYNTHETIC ALLOYING

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ABSTRACT

THE EFFECT OF TOLUENE SOLUTION ON THE HYDROGEN ABSORPTION OF THE Mg-Ti ALLOY PREPARED BY SYNTHETIC ALLOYING. The synthesis and characterization of the Mg–Ti alloy have been carried out through a mechanical alloying technique under toluene solution. The Mg and Ti powders are milled for 10, 20, and 30 h in a high energy ball mill. The milled alloys are then hydrided at a temperature of 300 ^{o}C in order to investigate the possibility used for hydrogen storage materials. The refinement analyses of the x-ray diffraction patterns show that mechanical alloying of the Mg–Ti powders under toluene solution results in the formation of the TiH_2 and Mg_2Ti phases. Quantitative analyses indicate that the mass fractions of the TiH_2 and Mg_2Ti phases are 62.90 % and 30.60 %, while the value for Mg and Ti amount to 2.6 wt% and 1.25 wt%. On hydriding at a temperature of 300 ^{o}C, the milled powders are transformed into Mg_2TiH_4, TiH_2 and γ-MgH_2 phases with the mass fractions of 25.48 wt%, 64.0 wt%, and 10.52 wt%, respectively. Microstructure analyses show that before milling the shape of particle is mostly a ball shape, after 30 h of milling the shape of particles changes into polygonal shape, and upon hydriding the shape of particles changes from a polygonal shape into an irregular one. The final composition of the specimen after hydriding exhibits that Mg-Ti alloy can be promoted as a hydrogen storage material.

Keywords: metal hydride, Mg-Ti system, mechanical alloying, hydriding

INTRODUCTION

In the future fuel technology for transportation will be based on hydrogen as an effort to protect the earth from greenhouse gas (GHG) emissions. An effective and cheap storage system is crucial for the utilization of hydrogen as a pollution-free energy carrier. A number of storage methods are being developed, one of which is storing hydrogen in the form of metal hydrides. Metal hydrides are used as reversible solid-state hydrogen storage at low pressures with high volumetric capacity, i.e. it should contain several kg of metal hydride powder. Magnesium has undergone many years

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of research due to its high hydrogen capacity, absorbing hydrogen up to 7.6 wt% [1-3].

Synthetic alloying by mechanical ball milling is the most common processing technique for producing nano-particle powders, including synthesizing magnesium based alloys [4-7]. Upon milling, repeated collisions between the balls and the powders will induce mechanical deformations, introduce strain into the powder and, as a result, fracture the crystallites into the nanometer size range. Repeated cold welding and fracture events minimize the diffusion distance between each compound, allowing the formation of alloys with unique chemical, physical and mechanical properties. The process has been successfully applied to the synthesis of various materials such as magnetic, tribologic, superlatic, catalytic and hydrogen storage materials [8]. Thus many advantages can be obtained from working with a high energy mechanical ball milling.

Nanosize particles play an important role in metal hydride materials as smaller particles have greater surface area and therefore greater surface contact between the materials and hydrogen [9]. Referring to the Zaluska's experiment, magnesium powders with a grain size of about 1 μm exhibit negligible hydrogen absorption at 300 ^{o}C. At the same time, magnesium with a grain size smaller than 1 μm shows a remarkable enhancement of hydrogen absorption indicating that the smaller the grain size, the faster the absorption. The fastest absorption was observed for powders with an average grain size of about 20–30 nm wherein about 5 wt% hydrogen was absorbed in 40 mins. For a grain size around 50 nm, only 3 wt% was absorbed within the same period [10].

Mg and Ti are well known as light weight hydrogen storage materials. Hydrogen can be stored more safely and compactly in these materials than being compressed or transformed into liquid form. The materials are usually covered with thin layers of oxides or hydroxides and require activation treatment under high temperature (>300 ^{o}C) and at the hydrogen pressure of >3MPa before being used for storage and transport applications [11].

In this research, the wet method mechanical alloying technique, using wet method with toluene as the medium is applied to synthesize the Mg and Ti powders. The milled powders are then hydrided at a temperature of 300 ^{o}C and the results are analyzed. Details of the experiment are presented in this paper.

EXPERIMENTAL METHODS

The Mg and Ti powders used in the experiment are obtained from Sigma-Aldrich® with a purity of 99.5 % and -325 mesh in size for Mg and a purity of 99.7% and -100 mesh in size for Ti. About 15 grams of Mg and Ti elements with an atomic ratio of Mg:Ti = 2:1 are mixed together with milling balls and then poured into a vial together with the toluene. All the preparation

works are conducted in a glove box under high purity argon atmosphere. The use of toluene solution is to avoid the direct contact of the powders with the oxygen during milling. The ball-to-specimen ratio is 8, and the milling is performed for 10, 20, and 30 h in the toluene solution at room temperature. The vial is made of stainless steel with a diameter of 5.1 cm and 7.6 cm in length. The balls are also made of stainless steel with a diameter of 12 mm. The vial is then put into a high energy milling (HEM) Spex type 8000. One cycle of milling of the Spex 8000 consists of normal blending speed of 4500 rpm, run time of 90 minutes, and off time of 30 minutes. Thus 10 h of milling corresponds to 5 cycles of milling operation.

The hydriding experiment is conducted in a Sievert's system under high vacuum condition with a maximum operating pressure of 1000 mbar. The procedure of the experiment has been published elsewhere [12].

The microstructures of the specimens are observed in a scanning electron microscope, Philip type 550. The quality and quantity of the phases formed are analyzed using an x-ray diffractometer (XRD), Philip, type PW 1710, with Cu as the anode tube and λ = 1.5406 Å. Continuous scanning is conducted at 0.02° step size and 0.5 second/step. The scanning results are analyzed using *Rietveld method* developed by Fuji Izumi [13].

RESULT AND DISCUSSION

Figure 1 shows the XRD refinement result of the Mg-Ti alloy with the atomic ratio of Mg:Ti = 2:1 before milling. The figure reveals no impurities and only Mg and Ti phases are identified.

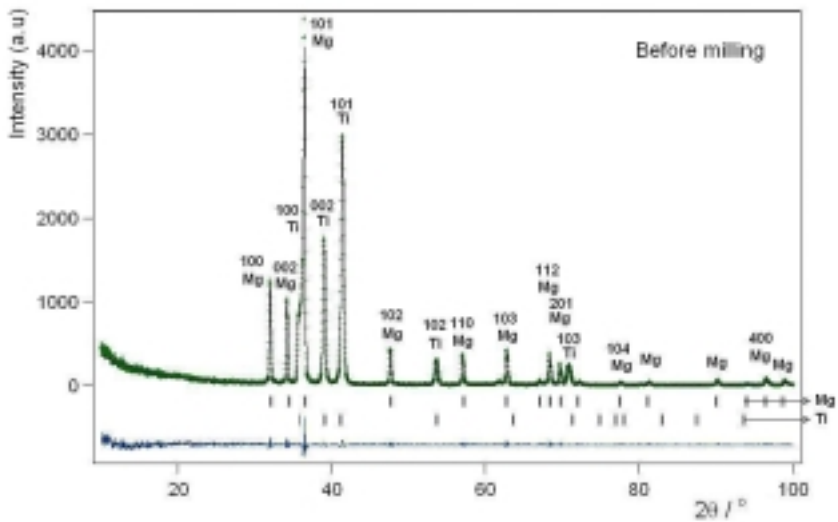


Figure 1. The XRD refinement result of the Mg and Ti before milling.

The structure parameters and Wyckoff positions number of equivalent points per unit cell for the Mg and Ti phases are presented in Table 1.

Table 1. The structure parameters and Wyckoff positions for Mg and Ti phases.

Mg phase (ref. Swanson [14])					Ti phase (ref. Sailer [15])				
Space group : $P6_3/mmc$ (194) Crystal system: hexagonal Lattice parameters : $a = b = 3.223(5)$ Å, dan $c = 5.249(6)$ Å					Space group : $P6_3/mmc$ (194) Crystal system : hexagonal Lattice parameters : $a = b = 2.819(1)$ Å, dan $c = 4.682(2)$ Å				
Atom	Occ	*x*	*y*	*z*	Atom	Occ	*x*	*y*	*z*
Mg	1.0	0.299(1)	0.690(1)	0,25	Ti	1.0	0.5	0.667	0.25

Quantitative analyses of the XRD refinement result yield the mass fractions of 62.76 wt% and 37.24 wt% for Mg and Ti respectively, which are equal to the initial composition of the Mg and Ti metals.

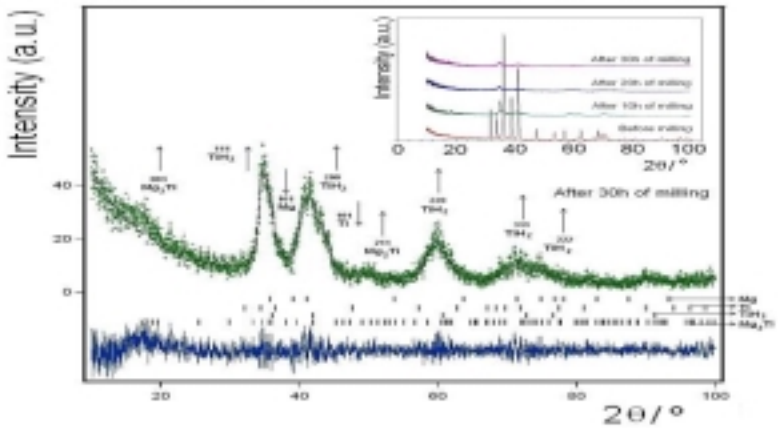


Figure 2. The XRD refinement result of the Mg and Ti after 30 h of milling.

Figure 2 presents the XRD refinement result of the specimen after 30 h of milling. The peak intensities that belong to Mg and Ti almost disappear and only the strongest peaks remain, though at low intensities. The loss of Mg and Ti peaks is suggested to be caused by a change in the crystal structure of the specimens into amorphous states and the formation of a new phase. Several new peaks appear at 2θ close to 19^o, 35^o, 40^o, 45^o, 59^o, and 70^o. The refinement result of these peaks allows the identification of the Mg, Ti, TiH_2 and Mg_2Ti phases. The structure parameters and Wyckoff positions number of equivalent points per unit cell for TiH_2 and Mg_2Ti phases are presented in Table 2.

Table 2. The structure parameters and Wyckoff positions for TiH_2 and Mg_2Ti phases.

TiH_2 phase (ref. Crane [16])					Mg_2Ti phase (ref. Soubeyroux [17])				
Space group : Fm3m (225) Crystal structure : cubic Lattice parameters : $a = b = c = 4.330(3)$ Å					Space group : $P6_222$ (180) Crystal structure : hexagonal Lattice parameters : $a = b = 7.542(1)$ Å, dan $c = 8.516(1)$ Å				
Atom	Occ	*x*	*y*	*z*	Atom	Occ	*x*	*y*	*z*
Ti	1.0	0.0	0.0	0.0	Ti	1.0	0.333	0.667	0.063(1)
H	1.0	0.25	0.25	0.25	Mg(1)	1.0	0.0	0.0	0.0
					Mg(2)	1.0	0.833(1)	0.666(1)	0.25

Quantitative analyses of the XRD refinement result point out that the mass fractions of the Mg, Ti, TiH_2 and Mg_2Ti are 5.26 wt%, 1.25 wt%, 62.90 wt% and 30.60 wt%, respectively. The formation of the TiH_2 phase is suggested to come from the inter-reaction between Ti and hydrogen from the toluene (C_7H_8).

$$6Mg + 3Ti \xrightarrow{\text{Toluene}} Mg_2Ti + TiH_2 + 4Mg + Ti \qquad (1)$$

Eq. (1) indicates that the quantity of Mg is relatively high. Nevertheless, the calculation indicates that the mass fraction of Mg is only about 5.26 wt%. Therefore, it is suggested that some of the Mg particles change into an amorphous state. Figure 2 shows that after 30 h of milling, intensities of the TiH_2 and Mg_2Ti decline and broaden, an indication that the quantity of TiH_2 and Mg_2Ti crystallites have been reduced.

Figure 3 shows that the peaks of the TiH_2 and Mg_2Ti phases normalize after 10, 20 and 30 h of milling and for the TiH_2 phase the peaks in the (111) plane and (200) plane drastically decline. It is exhibited that the decline of the peaks is resulted from the formation of amorphous states, both for the Mg and TiH_2 phases. From the analysis result, it is also suggested that the formation of the TiH_2 disturbs the growth of the Mg_2Ti.

Figure 4 shows the grain sizes of individual crystallites calculated using Scherrer formula. The small size of the particles satisfies the condition for the hydriding process, where the smaller the particle the faster the hydrogen absorption [8].

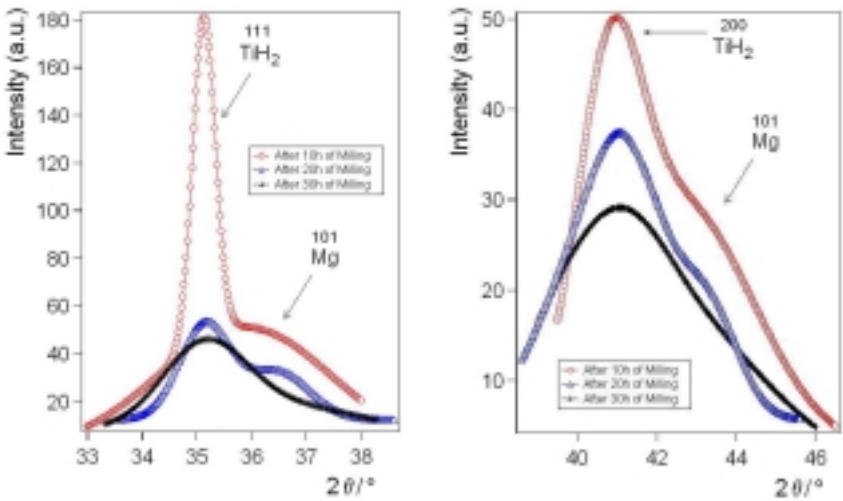


Figure 3. Normalization of Gaussian for TiH_2 and Mg_2Ti peaks.

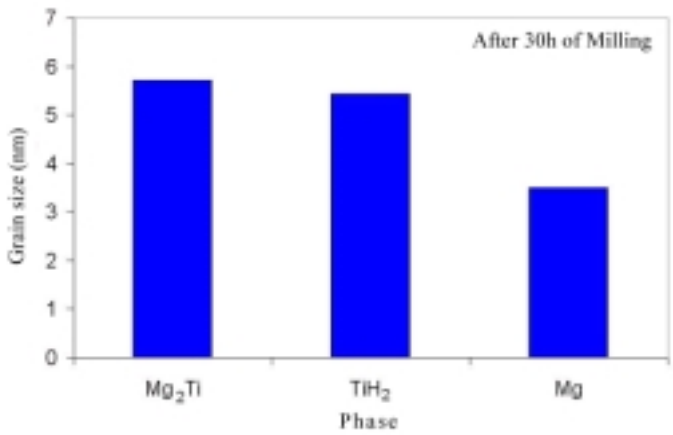


Figure 4. Crystallite sizes of Mg_2Ti, TiH_2, and Mg phases calculated using Scherrer formula after 30 h of milling.

Figure 5 shows the XRD refinement result of the specimen after hydriding at 300 ^oC. Three phases are observed, indicated as the Mg_2TiH_4, TiH_2 and γ-MgH_2 phases with the mass fractions of 25.48 wt%; 64.0 wt%; and 10.53 wt% respectively. The suggested reaction during the hydriding process is presented as follow:

$$Mg_2Ti + TiH_2 + 4Mg + Ti + 7H_2 \rightarrow Mg_2TiH_4 + 2TiH_2 + 4MgH_2 \quad (2)$$

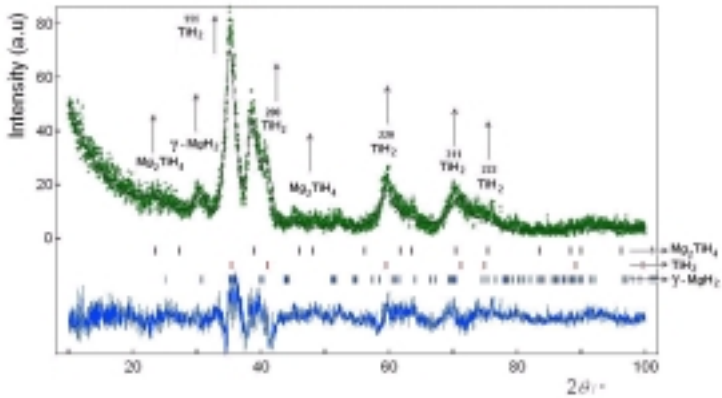


Figure 5. The XRD refinement result of the specimen after 30 h of milling.

The structure parameters and Wyckoff positions for the Mg_2TiH_4 and γ-MgH_2 phases are presented in Table 3 below.

Table 3. The structure parameters and Wyckoff positions for Mg_2TiH_4 and γ- MgH_2 phases.

Mg_2TiH_4 phase (ref. Genossar [18])					γ-MgH_2 phase (ref. Bastide [19])				
Space group : F43m Crystal structure : cubic Lattice parameters : $a = b = c = 6.525$ Å					Space group : Pbcn (60) Crystal structure : Orthorhombic Lattice parameters : a = 5.09(4) Å, b = 4.98(6) Å and c = 5.046(1) Å				
Atom	Occ	*x*	*y*	*z*	Atom	Occ	*x*	*y*	*z*
Ti	1.0	0.0	0.0	0.0	Mg	1.0	0.0	0.259(1)	0.25
Mg	1.0	0.25	0.25	0.25	H	1.0	0.334(2)	0.455(1)	0.512(2)
H	0.5	0.516	0.516	0.516					

Figure 6 shows the growth of new phases during the hydriding process. Before hydriding, the peaks identified as TiH_2 phase in the plane (111) are quite low (after 30 h of milling). After hydriding the peaks of the TiH_2 phase intensify. In addition, new phases are found at 2θ of about 31° and 39°. These phases are identified as γ-MgH_2 phase in the (111) plane and Mg_2TiH_4 phase in the (220) plane. The growth of the TiH_2 peaks and new peaks identified as the γ-MgH_2 and Mg_2TiH_4 support the view that the longer milling time will result in the higher the hydrogen capacity of the specimen.

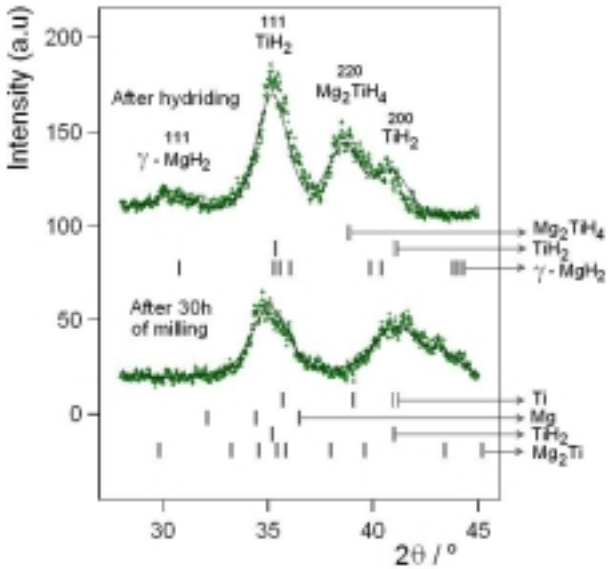
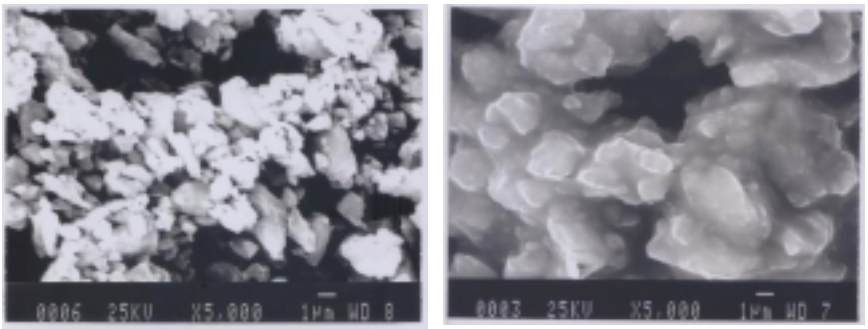


Figure 6. Phase identification of the specimen before and after hydriding process.

Figure 7 depicts the morphology of the specimens before and after the hydriding process. Before hydriding, the crystallites are in a polygonal form. After hydriding, the particle shape change into an irregular one [20], an indication that diffusion of particle occurs and new phases are formed. As previously indicated by the XRD analyses, new phases of Mg_2TiH_4, TiH_2 and γ-MgH_2 are grown.



(a) After 30 h of milling. (b) After hydriding at 300 ^oC.

Figure 7. Morphology of the specimens for (a) Mg-Ti-H after milling and (b) Mg-Ti-H after hydriding.

CONCLUSION

The synthesis and characterization of the Mg-Ti and Mg-Ti-H alloys have been carried out in order to investigate the possibility to be used as a hydrogen storage materials. The XRD refinement results of the Mg-Ti specimens show that mechanical alloying of the Mg-Ti powders under toluene solution results in the formation of the Mg, Ti, TiH_2 and Mg_2Ti phases. The formation of TiH_2 in the specimen disturbs the growth of binary the Mg_2Ti compound. After 30 h of milling the mass fractions of the Mg, Ti, TiH_2 and Mg_2Ti phases are 5.26 tw%, 1.25 wt%, 62.90 wt% and 30.60 wt% respectively. After hydriding at 300 ^oC, the specimen is transformed into Mg_2TiH_4, TiH_2 and γ-MgH_2 phases with mass the fraction of 25.48 wt%, 64.0 wt%, and 10.53 wt%. The growth of the TiH_2 peaks and the formation of new peaks the γ-MgH_2 and Mg_2TiH_4 support the view that the longer milling time will result in the higher the hydrogen capacity of the specimen. Microstructure analyses reveal that due to the diffusion process, the particles of the specimen change from polygonal shape into irregular one. To be promoted as a hydrogen storage material, further examination on the Mg-Ti alloy is being conducted in the form of hydrogen capacity measurements and hydriding-dehydriding properties.

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