Mechanical alloying processing of solid solution $Mg_{0.33}Al_{0.66}$ and its substituted compound $Mg_{0.33}Al_{0.63}Si_{0.03}$

Hassen Jaafar*, Aymen Ayedi, Mohieddine Abdellaoui

Laboratoire des Matériaux Utiles, Institut National de Recherche et d'Analyse Physico-chimique, BiotechPole Sidi Thabet, 2020 Ariana, Tunisia

(Received: 12 September 2017, accepted: 15 December 2018)

Abstract: Optimization of mechanical alloying process for the synthesis of $Mg_{0.33}Al_{0.66}$ and $Mg_{0.33}Al_{0.63}Si_{0.03}$ solid solution is carried out in this paper. These alloys are usually having a metastable character; we have done X-ray diffraction analysis (XRD) was for both synthesized compounds. In order to characterize and verify the morphology and the particles size, only the non-substituted alloy is analyzed by scanning electron microscopy (SEM).

Keywords: Mechanical alloying, solid solution, Mg-Al alloys, Al substitution, Si insertion.

INTRODUCTION

Mg-based intermetallic alloys are very good candidates for hydrogen storage purpose furthermore Magnesium is abundant and prevalent element in earth [1].

On the other hand, its controversy that Mg-hydride highlights some limitations due to the strong Mg-H binding energy about DH = 66-75 kJ/mol H_2 and the requirement of high temperature activation during the hydrogen sorption process [2].

In the beginning of this study, we started investigating the possibility of obtaining $MgAl_2$ Laves phase by mechanical alloying (MA) given that this alloy is not outlined in binary Mg-Al stable phase diagram [3]. In fact, a liquid-solid quenching of an Al–30 at% Mg alloy seems to be necessary to form this metastable phase [4].

During the last decade, several studies have been done on the mechanical alloying in different compositional range of Mg-Al compounds and their hydrogenation properties [5-8]. Solid-gaz hydrogenation properties of Al(Mg) solid solutions was studied by Bouaricha et al. [5] where they noticed two sloping plateau at 11 and 20 atmospheres for Mg:Al (58:42) at 350°C. However the hydrogen sorption in Mg:Al (37:63) is being negligible [5]. Another study was done by Andreason [6] on the hydrogenation of Mg_2Al_3 compound; a simple extrapolation of the Van't Hoff curve for ambient temperature gives very low hydrogen equilibrium pressure about 3. 10^{-4} bar.

Recent stage research in our group turned to the development of AB_3 type alloys [9] combining AB_5 and AB_2 alloys in 1:2 proportion. $LaNi_5$ is known to have relatively high hydrogen equilibrium pressure at room temperature (~ 2 bar) [10]. Therefore in order to have the appropriate properties for reasonable hydrogen storage AB_3 material, a selection of suitable AB_2 system is very important.

A series of Mg-based intermetallics's structural and electrochemical properties like Mg_xNi_{100-x} obtained by mechanical alloying has been widely investigated previously: correlation between the microstructural state and the electrochemical properties was established, we also studied kinetics of hydrogen desorption and relationship between the mechanical alloying conditions and the microstructural state of end products [11-15].

We report in this paper on the optimization of mechanical alloying process for the synthesis of $Mg_{0.33}Al_{0.66}$ and $Mg_{0.33}Al_{0.63}Si_{0.03}$ solid solution.

* Corresponding author, e-mail address : hassen.jaafar@inrap.rnrt.tn

EXPERIMENTALS DETAILS

For non-substituted alloy, 1g mixture of elemental Mg (VWR, 99.8 %) and Al (VWR, 99.9 %), with an atomic ratio of 1:2, was sealed into a stainless steel vial (45 cm^3 in volume) with 5 stainless steel balls (12 mm in diameter and 7.16 g in mass) in a glove box filled with purified argon gas. The ball-to-powder weight ratio was equal to 36:1.

The MA experiments were performed at room temperature using a Fritsch "Pulverisette P7" planetary ball miller. The disc and vial rotation speed were equal to 350 and 700 rpm, respectively.

For substituted alloy, 1g mixture of elemental Mg, Al and Si (VWR, 99%) was introduced under the same previous conditions with the following atomic proportions at% Mg = 33.3%, at% Al = 63.3% and at% Si = 3.3%.

Same MA experiments were tested with disc rotation speed equal to 350 and 450 rpm.

Crystallographic characterization of synthesized powders was carried out by XRD using a (θ – 2θ) Panalytical XPERT PRO MPD diffractometer operating with Cu Kα radiation (λ = 0.15406 nm).

Phase identification was carried out using the X'Pert HighScore Plus software connected to the Inorganic Crystal Structure Database ICSD [16].

XRD diffractogram refinement was done using Rietveld method through FullProf Suite Program (2.05) [17]. Powder morphology was characterized using an FEI equipment the Quanta 200 environmental scanning electron microscope.

RESULTS AND DISCUSSION

1. Non-substituted alloy characterization

XRD patterns of mechanical alloyed samples for different milling time are shown in Figure 1. The diffractogram of the initial mixture before milling (Δt = 0h) is also given in Figure 1 for comparison. After 5h milling, it seems that no reaction occurred and the diffractogram shows the peaks corresponding to initial face-centered cubic Al and hexagonal Mg that certain portion obviously changed from crystalline to amorphous state.

After 10h milling time, a new phase was observed. Identification by HighScore connected to ICSD data base shows that this phase corresponds to the Al(Mg) solid solution where Mg is incorporated in Al unit cell. This phase seems to be stable even for longer milling time and we have here lock-encapsulation of amorphous Magnesium inside the Aluminum Matrix.

Refinement of XRD pattern of the sample obtained after 15h milling time is shown in Figure 2 where the values of state of occupation of Mg and Al are corrected to consider the atomic ratio of the two initial elementary metals (1:2). This phase is refined in the cubic Fm-3m space group and the vertical markers correspond to the allowed Bragg reflections for $Mg_{0.33}Al_{0.66}$.

All refinement results including cell parameters, mass fraction and Rietveld refinement reliability factors are shown in Table I. Theoretical weight fractions before milling are respectively 31.03% and 68.96% for Mg and Al.

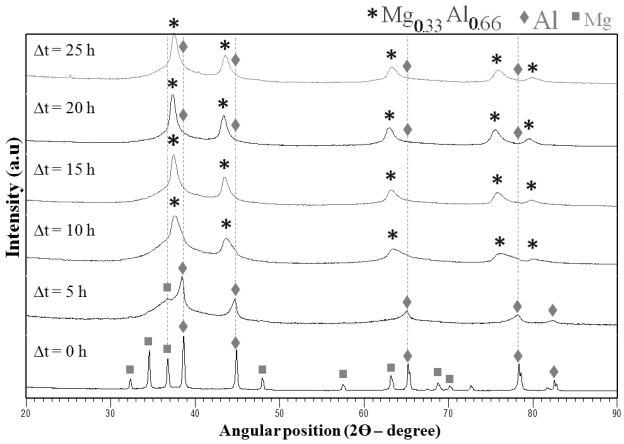

Figure 1: XRD patterns of the mechanical alloyed Mg-Al mixture after different milling time

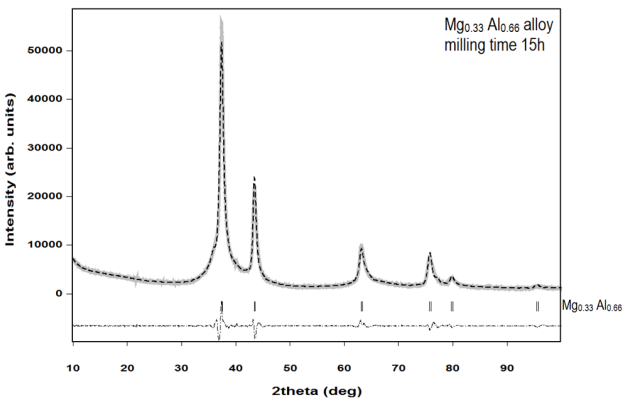

Figure 2: Calculated (dashed line) and observed (gray line) X-ray diffraction patterns for the $Mg_{0.33}Al_{0.66}$ alloy obtained after 15h milling time

Table I: Refinement results for obtained XRD patterns.

Milling time	Phase	Space group	Lattice parameters (Å)	V (Å^3)	Weight fraction (%)	R_f	R_{Bragg}	χ^2
5h	Mg	P 63/mmc	a = 3.20025(1) c = 5.18064(1)	45.95	18.39	0.59	1.70	10.3
	Al	F m -3 m	a = 4.05608(1)	66.73	81.61	0.77	2.23	
10h	$Mg_{0.33}Al_{0.66}$	F m -3 m	a = 4.14423(1)	71.18	100	0.22	0.54	8.4
15h	$Mg_{0.33}Al_{0.66}$	F m -3 m	a = 4.16294(1)	72.14	100	0.93	1.91	13.0
20h	$Mg_{0.33}Al_{0.66}$	F m -3 m	a = 4.17662(1)	72.86	98.87	1.09	2.56	10.9
	Al	F m -3 m	a = 4.03261(1)	65.58	1.13	1.23	2.08	
25h	$Mg_{0.33}Al_{0.66}$	F m -3 m	a = 4.16993(1)	72.51	90.54	1.56	3.00	9.7
	Al	F m -3 m	a = 4.026(2)	65.27	9.46	0.32	0.53	

Weight fractions given for 5 hours MA are 18.39% and 81.61% for respectively Mg and Al. This is far from experimental values and can be basically explained by substantial magnesium amorphization phenomenon while the expected phase is not yet formed.

Amorphization process is enhanced by several factors specifically the defects density which accelerates interdiffusion between the elemental powders and also dissymmetry between diffusion coefficients [18].

According to the refinement results, optimal milling time for the formation of the Al(Mg) solid solution ranges between 10 and 15h.

For samples synthesized during 20h and 25h, the XRD refinement shows the precipitation of crystalline Al from Al(Mg) solid solution.

After 10 hours mechanical alloying, the system reaches its equilibrium state and we have stabilization of the new phase $Mg_{0.33}Al_{0.66}$.

Previous physical and mechanical study shows that after prolonged time of MA, defects quantity increases

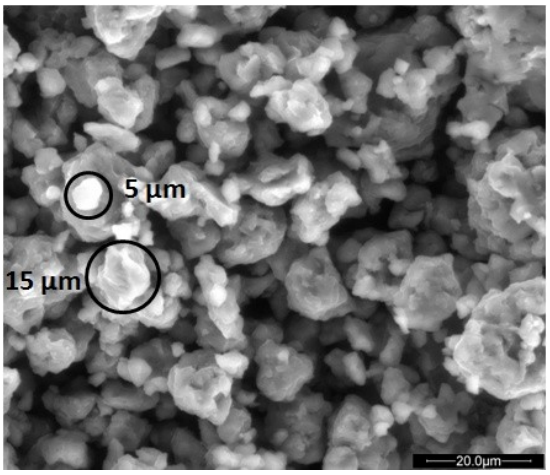

Figure 3: SEM micrograph in secondary electron mode of $Mg_{0.33}Al_{0.66}$ alloy obtained after 15h milling time

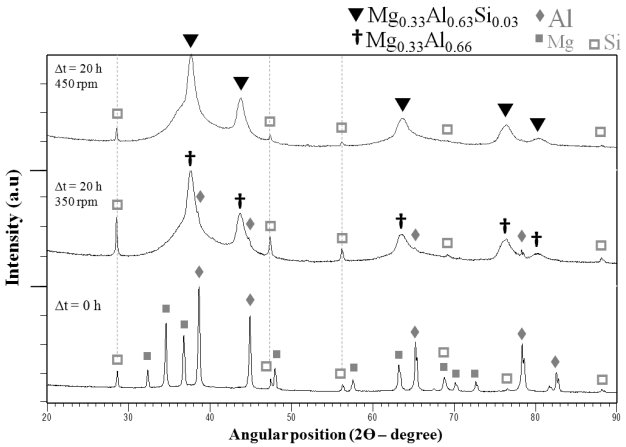

Figure 4: XRD patterns of the mechanically alloyed Mg-Al-Si samples obtained after 20h milling time at 350 and 450 rpm disc rotation speed

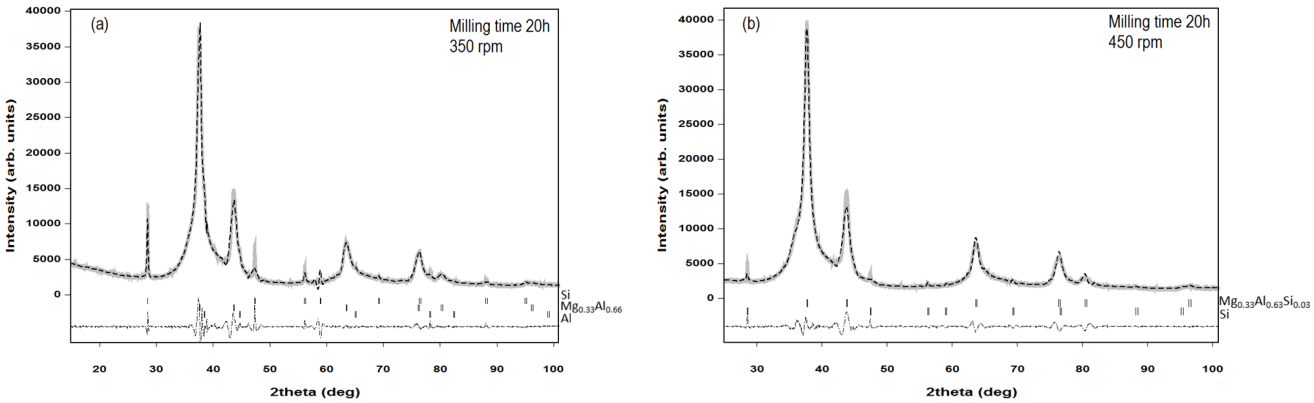

Figure 5: Calculated (dashed line) and observed (gray line) X-ray diffraction patterns of the mechanical alloyed Mg-Al-Si sample after 20h milling time at 350 rpm (a) and 450 rpm (b)

until reaching a steady state which is not able to be destabilized into another structural state [19].

SEM image in secondary electron mode is given in Figure 3 showing morphology of $Mg_{0.33}Al_{0.66}$ solid solution obtained after 15h of MA.

The alloyed particles (formed by an assembly of nanocrystalline grains, which size is equal to the coherence domain size given by the XRD patterns analyses) showed heterogeneous distributions. Their sizes varied from a few µm (3–5) to many µm (15–20).

2. Aluminum substitution for silicon

Figure 4 gives XRD patterns corresponding to the mechanically alloyed $Mg_{0.33}Al_{0.63}Si_{0.03}$ sample. Diffractogram of initial Mg-Al-Si mixture before milling (Δt = 0h) is also given for comparison.

At first, the disc rotation speed was kept unchanged (350 rpm) and the mechanical alloying duration fixed to 20 hours.

In this case, we observed that Si diffraction peaks were still intense. Rietveld refinement on this sample converges obviously to the non-substituted alloy.

Figure 5 shows Rietveld refinement of XRD patterns of $Mg_{0.33}Al_{0.63}Si_{0.03}$ MA samples. Table II gives the XRD patterns refinement results.

When increasing disc rotation speed to 450 rpm, the intensity of Si peaks decreases enough indicating that substantial silicon has been substituted for Al in the Al(Mg) solid solution.

The XRD pattern refinement shows a likely substituted alloy $Mg_{0.33}Al_{0.63}Si_{0.03}$ with residual Si contribution that remains unreacted.

Table II: Results of Mg-Al-Si XRD patterns refinement.

Disc rotation speed	Phase	a (Å)	Weight fraction (%)	R_f	R_{Bragg}	χ^2
350 rpm	Si (F d -3 m)	5.43193(1)	3.66	3.33	5.34	22
	$Mg_{0.33}Al_{0.66}$ (F m -3 m)	4.14398(1)	94.75	0.78	0.95	
	Al (F m -3 m)	4.05326(1)	1.59	2.78	2.33	
450 rpm	$Mg_{0.33}Al_{0.63}Si_{0.03}$ (F m -3 m)	4.13524(1)	98.14	0.64	0.93	11
	Si (F d -3 m)	5.42154(1)	1.86	3.85	9.70	

CONCLUSION

The use of mechanical alloying in this work leads to a solid solution $Mg_{0.33}Al_{0.66}$ instead of Laves phase $MgAl_2$.

$Mg_{0.33}Al_{0.66}$ solid solution can be synthesized in quasi-quantitatif yield after only 10 hours of mechanical alloying at 3.0826 W/g injected shock power.

Monosubstituted alloy $Mg_{0.33}Al_{0.63}Si_{0.03}$ was obtained in good yield after 20 hours mechanical alloying with higher shock power of 6.5532 W/g.

Ongoing efforts in the laboratory concern the setup of AB_3 alloy combining $LaNi_5$ with magnesium based alloys in the prospective of hydrogen storage under ambient conditions.

Acknowledgments: We would like to thank the Service de Diffraction des Rayons X and the Service de Microscopie Electronique à Balayage of INRAP.

REFERENCES

[1] L. Wang, Y. Wang and H. Yuan: *J. Mater. Sci. Technol.*, **2001**, 17, 590-596.
[2] J. Yang, A. Sudik, C. Wolvertonb and D. J. Siegel: *Chem. Soc. Rev.*, **2010**, 39, 656-675.
[3] P. Zhang, Correlation of the Microstructure and Creep Behavior of Die Cast Mg-Al-base Alloys, **2005**, 5, Cuvillier Verlag, Göttingen.
[4] S. H. Ghaderi, A. Mori and K. Hokamoto: *Mater. Trans.*, **2008**, 49, 1142-1147.
[5] S. Bouaricha, J.P. Dodelet, D. Guay, J. Huot, S. Boily and R. Schulz: *J. Alloy. Compd.*, **2000**, 297, 282-293.
[6] A. Andreasen: *Int. J. Hydrog. Energy*, **2008**, 33, 7489-7497.
[7] S. Scudino, M. Sakaliyska, K.B. Surreddi and J. Eckert: *J. Alloy. Compd.*, **2009**, 483, 2-7.
[8] J.-C. Crivello, T. Nobuki, T. Kuji: *Int. J. Hydrog. Energy*, **2009**, 34, 1937-1943.
[9] M. Elghali, M. Abdellaoui, V. Paul-Boncour and M. Latroche: *Intermetallics*, **2013**, 41, 76-81.
[10] J. Lamloumi, C. Lartique, A. Percheron-Guegan, J. C. Achard, G. Jehanno, The Rare Earths in Modern Science and Technology, **1982**, 487, Plenum Press, New York.
[11] M. Abdellaoui, D. Cracco and A. Percheron-Guégan: *J. Alloy. Compd.*, **1998**, 268, 233-240.
[12] M. Abdellaoui, D. Cracco and A. Percheron-Guégan: *J. Alloy. Compd.*, **1999**, 293-395, 501-507.
[13] M. Abdellaoui, S. Mokbli, F. Cuevas, M. Latroche, A. Percheron-Guégan and H. Zarrouk: J. Alloy. Compd., **2003**, 356-357, 557-561.
[14] M. Abdellaoui, S. Mokbli, F. Cuevas, M. Latroche, A. Percheron Guégan and H. Zarrouk: *Int. J. Hydrog. Energy*, **2006**, 31, 247-250.
[15] S. Mokbli, M. Abdellaoui, H. Zarrouk, M. Latroche and A. Percheron Guégan: *J. Alloy. Compd.*, **2008**, 460, 432-439.
[16] A. Belsky, M. Hellenbrandt, V. L. Karen and P. Luksch: *Acta Cryst.*, **2002**, B58, 364-369.
[17] J. Rodriguez-Carvajal, FullProf: A Program for Rietveld Refinement and Pattern Matching Analysis, **1990**, 127, Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, Toulouse.
[18] J.S. Benjamin, *Metall. Trans.*, **1970**, 1, 2943-2951.
[19] M. Abdellaoui and E. Gaffet: *Acta Metall. Mater.*, **1995**, 43, 1087-1098.