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Preparation and characterization of metastable solid solution $Mg_{0.33}Al_{0.66}$ and $Mg_{0.33}Al_{0.63}Si_{0.03}$ obtained by mechanical alloying

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Mg based hydrogen storage alloy

Magnesium is the eighth most common element in the crust of earth and Mg-based intermetallic alloys are considered as good candidates for hydrogen storage applications [1].

However, its hydride has a thermodynamic problem: Mg-H binding energy is too strong H = 66-75 kJ/mol H_2 and hydrogen sorption requires high temperature activation [2].

Early purpose was investigating possible $MgAl_2$ Laves phase formation by mechanical alloying (MA) since this alloy doesn't exist in binary Mg-Al stable phase diagram [3]. This metastable phase was found by liquid-solid quenching of an Al–30 at% Mg alloy [4].

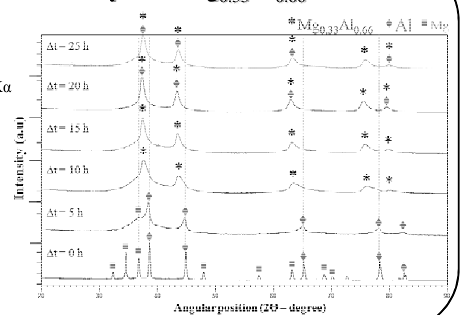
Current work in progress aims to study the thermodynamic hydrogenation properties of these metastable compounds and explore different substitution for possible adaptation in Ni-MH batteries[5-6].

X-ray diffraction analysis of $Mg_{0.33}Al_{0.66}$

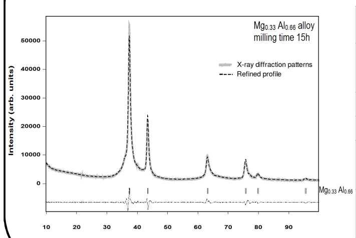
Crystallographic characterization
Panalytical XPERT PRO MPD diffractometer operating with Cu Kα radiation.

Phase identification
X'Pert HighScore Plus software connected to the Inorganic Crystal Structure Database ICSD.

Mechanical Alloying
Fritsch Pulverisette P7 planetary ball miller (Ω = 350 rpm).

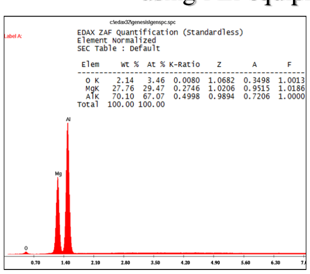


Rietveld refinement of $Mg_{0.33}Al_{0.66}$ using FullProf

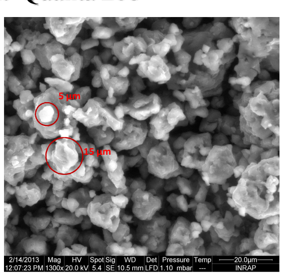


Milling time	Phase	Space group	Lattice parameters (Å)	V (Å³)	Weight fraction (%)	R_f	R_{Bragg}	χ^2
5h	Mg	P 63/m m c	a = 3.20025(1) c = 5.18064(1)	45.95	18.39	0.59	1.70	10.3
	Al	F m -3 m	a = 4.05608(1)	66.73	81.61	0.77	2.23	
10h	$Mg_{0.33}Al_{0.66}$	F m -3 m	a = 4.14423(1)	71.18	100	0.22	0.54	8.4
15h	$Mg_{0.33}Al_{0.66}$	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	

SEM Characterization of $Mg_{0.33}Al_{0.66}$ using FEI equipment Quanta 200



EDX microanalysis results



SEM micrograph in secondary electron mode of $Mg_{0.33}Al_{0.66}$
Milling time: 15h
Magnification : x1300

- Average experimental composition :

  % Mg = 30.5 at%   % Al = 69.5 at%

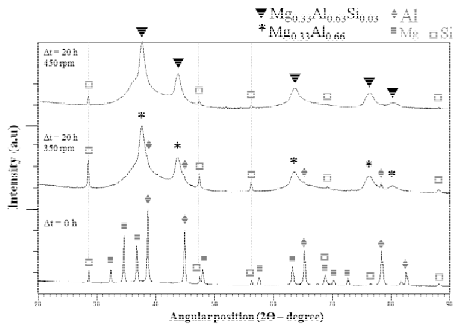
- Heterogeneous distribution of the particle size :

  few microns (2-5) to several µm (15-20)

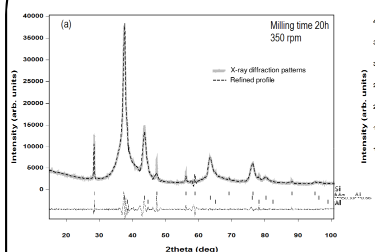
X-ray diffraction analysis of $Mg_{0.33}Al_{0.63}Si_{0.03}$

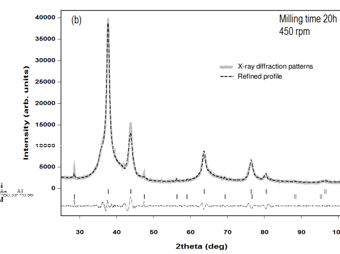
Substituted alloy
initial atomic proportions
at% Mg = 33.3%,
at% Al = 63.3%
at% Si = 3.3%

Mechanical Alloying
Same experiment and equipment testing two different disc rotation speed (Ω = 350 and 450 rpm).



Rietveld refinement of $Mg_{0.33}Al_{0.63}Si_{0.03}$ using FullProf





(a) Si diffraction peaks were still intense. Rietveld refinement converges obviously to the non-substituted alloy.

(b) Si peaks decreases indicating substantial silicon has been substituted for Al in the Al(Mg) solid solution. Rietveld Refinement converges to the substituted alloy $Mg_{0.33}Al_{0.63}Si_{0.03}$ with residual Si contribution that remains unreacted.

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	

Conclusions

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 3.1 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 6.5 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.

References

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