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Original research article

Dispersion of niquel on the microstructure in magnesium based alloys for hydrogen storage

A.A. Zaldívar-Cadena [a,*], I. Díaz-Peña [a], J.G. Cabañas-Moreno [b]

[a] *Universidad Autónoma de Nuevo León, Av. Universidad s/n, Facultad de Ingeniería Civil, San Nicolás de los Garza N.L. C.P.66451, Mexico*
[b] *Instituto Politécnico Nacional, UPALM, Col. Lindavista, C.P.07338 México D.F., Mexico*

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Abstract

Mg−Xwt.%Ni ($X = 5$ and 20) alloys have been prepared by mechanical alloying using milling times of 15 and 30 h in a planetary ball milling to know the effects of magnesium with the addition of Ni as catalyst, dispersion on the microstructure, area surface and the efficiency of hydrogen storage. SEM-EDS, XRD and ImageJ® software have been used to characterize the microstructure and chemical composition of the alloys. Hydriding experiments were performed as batch-type tests at 200, 250 and 300 °C under 2 MPa H_2 pressure during 30 min. These experiments resulted in varying amounts of MgH_2 in the hydrided powders depending on composition and hydriding conditions. The best results point to an optimum Ni dispersion, which in turn depends on Ni content and milling time.

Keywords: Hydrogen storage; Magnesium; Niquel; Alloy; Characterization

1. Introduction

Magnesium hydride is one of the most important materials for hydrogen storage because its high storage capacity of 7.6 wt.% [1]. However, its hydriding and dehydriding kinetics is very slow because diffusion of hydrogen atoms through the hydride is slow and hydrogen atoms are bonded with the magnesium atoms because the enthalpy of formation of the hydride is large and needs both high temperature and pressure to be released as hydrogen gas [1,2]. Some studies have been reported with the aim to improve the reaction kinetics of magnesium with hydrogen adding nickel as catalyst in form of dispersed particles by mechanical alloying [2−5]. The use of nickel dispersed by mechanical alloying can improve the dissociation rate of hydrogen molecules by reduction the activation energy and creation of nucleation sites and defects [1,2,4,5]. In addition, the diffusion distance and mobility of hydrogen, which influences the growth rate of the magnesium hydride, can be decreased by mechanical alloying of magnesium with niquel, thereby reducing the magnesium particles sizes and introducing cracks and defects being more advantageous for hydrogen absorption [6,7]. Song MY et al. [2,4,8,9] reported that addition of Ni to Mg by mechanical alloying improved the hydriding and dehydriding kinetics in particular the hydrogen desorption.

The aim of this work is to study the effect of addition of nickel as catalyst in form of particles dispersed into the matrix of magnesium by mechanical alloying. The effect of particle size and occupied area % by nickel phase on the microstructure is related both with surface area and hydrogen storage efficiency.

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* Corresponding author. Tel.: +52 81 8329 4000x7229.
E-mail addresses: azaldiva70@hotmail.com, azaldiva70@gmail.com (A.A. Zaldívar-Cadena).

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2. Experimental

2.1. Mg−Ni alloys preparation

Magnesium in powder mesh −20 + 100 at 99.8% pure with a particle size of 150 μm and nickel powder mesh −325 at 99.8% pure with a particle size of 44 μm were used as alloying materials and both products were supplied by Alfa Aesar.

Powder mixtures (total weight = 30 g of magnesium and niquel with 3 ml of ethanol) were mixed and synthesized in a stainless steel container (volume of 250 ml) from a Pulverisette 6 planetary ball milling from FRITSH at a rotating speed of 350 r/min and balls-weight ratio of 11:1. All sample handling was performed in a glove box under Ar in order to prevent oxidation. Once the milling time was completed, milled powders were exposed to controlled air during 24 h for avoiding ignition.

2.2. Mg−Ni alloys hydriding

For each one of the Mg−5wt.%Ni and Mg−20wt.%Ni alloys samples, three 5-min of hydrogen injection and 5-min of vacuum activations were applied and after they were hydrided during 30 min at 2 Mpa of hydrogen pressure. The samples were hydrided at 200, 250 and 300 °C in a Parr reactor and the hydrogen storage efficiency was obtained by DTA/TGA equipment from TA Instruments.

2.3. Microstructural characterization of Mg−Ni alloys

The characterization of microstructure of hydrided and non-hydrided samples was made by Brunauer−Emmett−Teller analysis (BET) for the determination of surface area, X-ray diffraction (XRD) for determining the corresponding phases and scanning electron microscopy (SEM) for the morphology study and elemental chemistry analysis (EDS).

2.3.1. Surface area analysis (BET)

Surface area analysis was made in a BET NOVA 2000e by Quantachrome Instruments. Samples were degasificated at 100 °C during an hour to assure all moisture has been removed and it was proceeded to simultaneously analyze both samples during 90 min.

2.3.2. X-ray diffraction (XRD)

X-ray diffraction (XRD) analysis was made to samples of hydrided and non-hydrided alloys in a X-ray diffractometer D8 Advance from Bruker with Vantec detector under the following conditions such as an excitation voltage 40 kV, current of 40 mA, scan rate of 0.05 (2θ/s) at an initial and final angle between 10° and 70°, respectively.

2.3.3. Microstructure characterization of Mg−Ni alloys

Samples were mounted and polished by standard metallography using SiC sandpapers of numbers 600 and 2400 for hard and fine finish, respectively. After, the samples were submerged in acetone bath during 3 min in ultrasound device and between each polish step with the purpose to remove pollutants or impurities. Finally, the samples were polished with colloidal silica on a microcloth and covered with a thin layer of gold to make it more conductive and obtain better resolution in the SEM. The microstructure was analyzed in a Scanning Electron Microscope JSM-6490LV by JEOL coupled with an X-ray Energy Dispersion Spectrometer (EDS) of Oxford.

2.3.3.1. Ni quantification on microstructure. For quantification of % area and particle size of nickel on the surface it was required to take 10 micrographs with the signal of backscattered electrons (BSE) at a magnification of 1000× and maximum contrast to differentiate nickel from magnesium matrix. Furthermore, for quantification of particle size of nickel it was required to take 5 measurements in each of previously taken 10 micrographs giving 50 measurements of nickel particles. The measurements both % area and particle size were made using Image J® software.

2.3.4. TGA analysis

Hydrided samples of the Mg−*X*wt.%Ni ($X = 5$ and 20) alloys were dehydrided in a DTA/TGA of TA Instruments to know the weight loss (wt.%) or hydrogen storage efficiency.

The conditions used during dehydriding tests with DTA/TGA were heating sample at rate of 10 °C/min in platinum melting pot up to 50 °C and one hour rest with the purpose to remove moisture, heating at rate 10 °C/min up to dehydriding temperatures of 200, 250, 300 and 350 °C and further cooling. It is worth to mention that to avoid oxidation these tests were performed at nitrogen inert atmosphere.

3. Results and discussion

3.1. Morphology of Mg−Ni alloys

In Fig. 1a and c are shown the morphologies of Mg−5wt.%Ni and Mg−20wt.%Ni alloys with 15 h of milling and where it can be seen particle agglomerates distributed both in a non-uniform shape and size. In Fig. 1b and d are shown better homogeneous distribution and particle sizes, less than 10 μm, in both Mg−5wt.%Ni and Mg−20wt.%Ni alloys with 30 h of milling. In general, it can be noted that using a milling time of 30 h are obtained a well distribution and smaller particle size.

3.2. Hydriding of Mg−Ni alloys

Fig. 2 shows the X-ray patterns of Mg−5wt.%Ni alloy hydrided at 200 °C, 250 °C and 300 °C with 15 and 30 h of milling. The X-ray analysis shows diffraction peaks of MgH_2 with the most intensity in samples hydrided at 200 and 250 °C with 30 h of milling. The formation of MgH_2 results in the decrease of the amount of Mg, so the intensity of Mg peaks reduces, but the intensity of Ni peaks does not change markedly. XRD analysis reveals increasing the milling time from 15 to 30 h is obtained a greater intensity of magnesium hydride (MgH_2) peaks. This is likely due to the formation of a large amount of defects in the microstructure in which the hydrogen atoms can be more easily bonded [4,8−14]. It is worth to

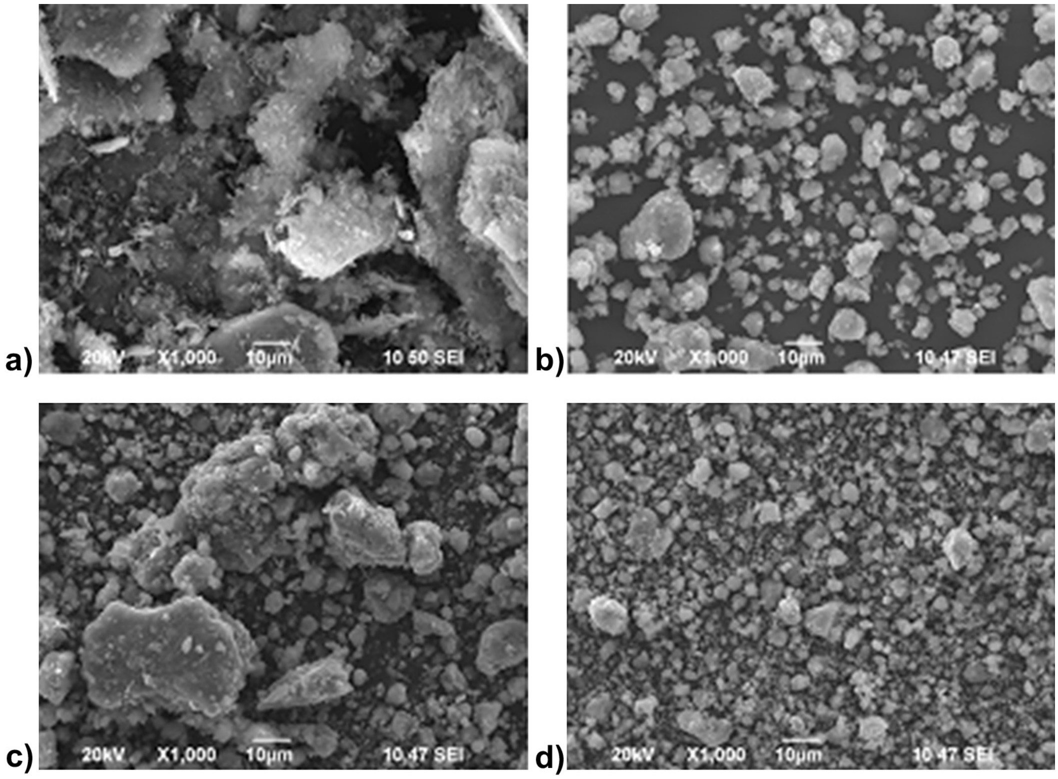

Fig. 1. (a) Mg–5wt.%Ni (15 h), b) Mg–5wt.%Ni (30 h), (c) Mg–20wt.%Ni (15 h) and (d) Mg–20wt.%Ni (30 h).

mention that there were not detected peaks of magnesium oxide (MgO) and magnesium hydroxide $Mg(OH)_2$ that could have formed during process and manipulation of powders mixture.

In Fig. 3 are shown the X-ray diffractograms of Mg–20wt.% Ni alloy at 15 and 30 h of milling hydrided at 200 °C, 250 °C and 300 °C. The most intense peaks of magnesium hydrides MgH_2 could be detected at 250 °C and 300 °C with 15 and 30 h of milling time, respectively. The Mg_2Ni phase shows a small signal in the XRD analysis, being this phase the main precursor of magnesium hydrides, is also considered to increase the hydriding and dehydriding rates of the alloy [15].

3.3. Dispersion and nickel particle size in hydrided samples

Fig. 4 shows the effect of milling time on the occupied area % by nickel catalysts and where it can be observed that increasing milling time from 15 to 30 h reduces considerably the occupied area % by Ni, also homogeneous particle can be obtained. In the samples with 20% of Ni it can be noted that occupied area % by Ni increases significantly as consequence of greater Ni concentration. Some authors have reported the addition of catalysts as niquel in form of powders processed by

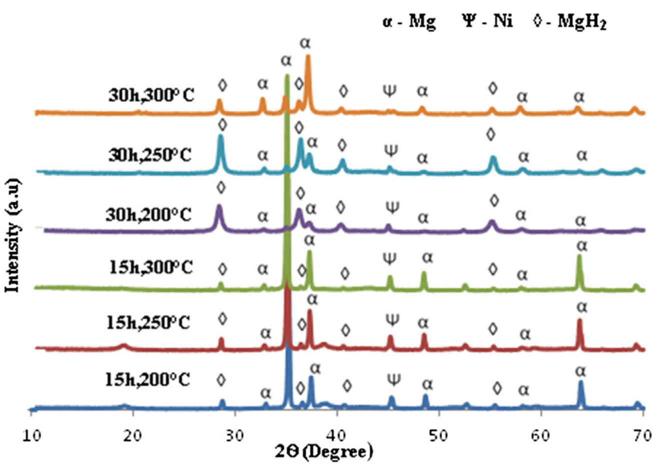

Fig. 2. X-ray diffractograms of the Mg–5wt.%Ni alloy with 15 and 30 h of milling hydrided at 200 °C, 250 °C and 300 °C.

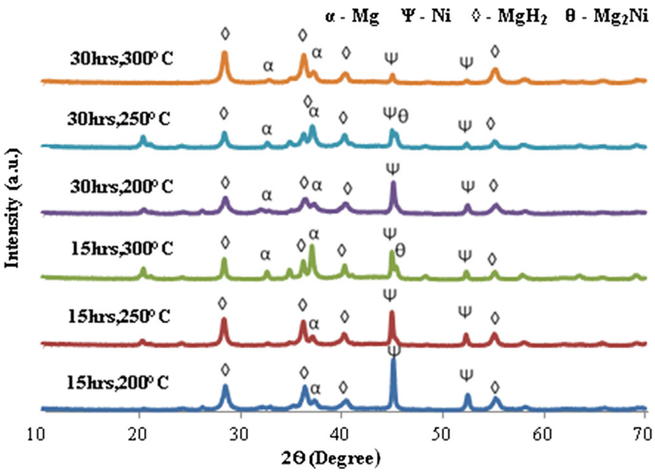

Fig. 3. XRD analysis of Mg–20wt.%Ni alloys with 15 and 30 h of milling hydrided at 200 °C, 250 °C and 300 °C.

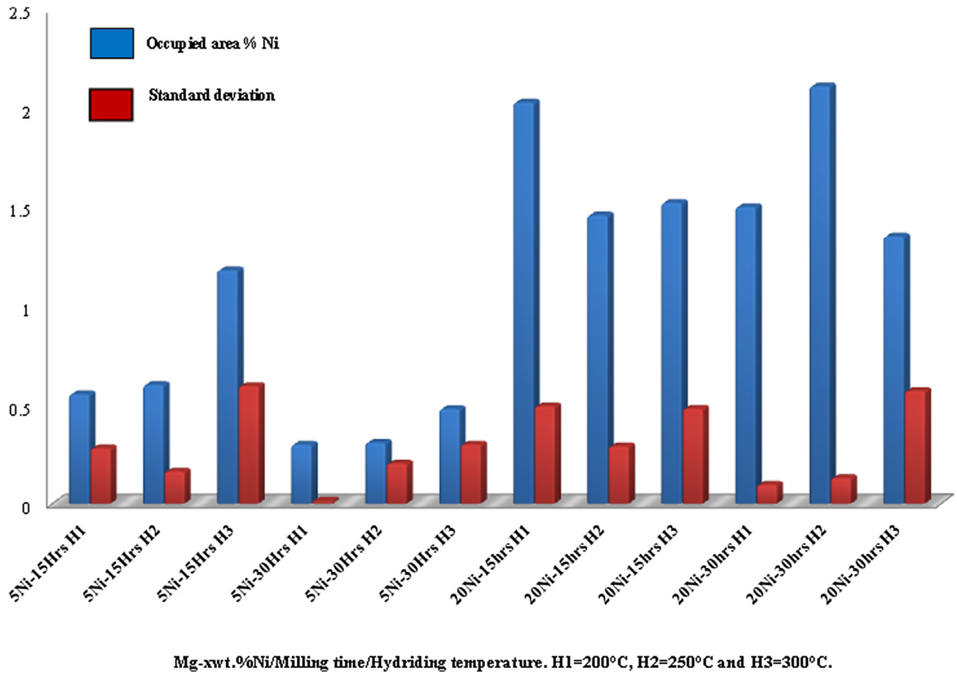

Fig. 4. Occupied area % by Ni as function of the nickel concentration, milling time and hydriding temperature.

mechanical milling to produce high density of crystal defects and a fine dispersion of particles on the microstructure increasing the reaction kinetics and reducing the decomposition temperature of magnesium hydride [16,17].

In Fig. 5 is shown the effect of milling time on the particle size of the nickel catalyst embedded on the magnesium matrix in the Mg–5wt.%Ni and Mg–20wt.%Ni alloys. The results show that 30 h of mechanical alloying there is a considerable reduction in the nickel particle size with a mean particle size of 2.5 microns in the Mg–5wt.%Ni alloy. Furthermore, a better Ni particles dispersion is obtained on the microstructure. In the samples of the Mg–20wt.%Ni alloy could be noted that Ni particle size is increased significantly as consequence of greater Ni concentration.

3.4. Hydrogen storage efficiency

In Table 1 are shown the weight loss or hydrogen storage efficiency and surface area results of Mg–5wt.%Ni and Mg–20wt.%Ni alloys hydrided at 200, 250 and 300 °C in a Parr reactor and dehydrided by TGA analysis. Hydrogen storage efficiencies up to 5 wt.% were obtained in both

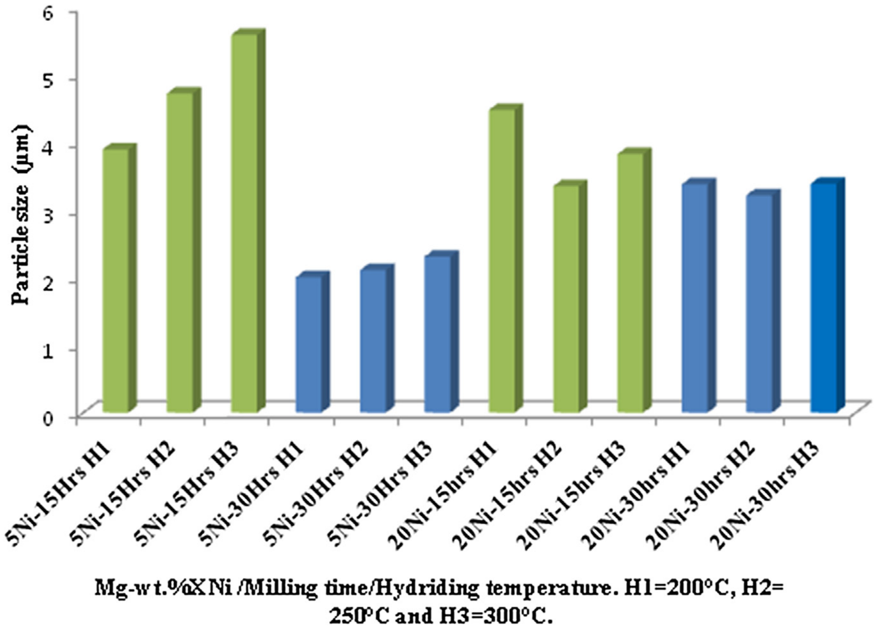

Fig. 5. Nickel particle size as function of the nickel concentration, milling time and hydriding temperature.

Table 1
Hydrogen storage in the Mg–Xwt.%Ni ($X = 5$ and 20) alloys.

Alloy	Milling time (h)	Surface area (BET) (m^2/gr)	Hydriding temperature (°C)	Dehydriding temperature			
				50 °C	200 °C	250 °C	300 °C
Unmilled Mg	–	3.30		Hydrogen storage (wt.%)			
Mg–5wt.%Ni	15	6.20	200	0.65	3.72	3.98	4.8
			250	1.02	3.65	3.82	4.82
			300	0.97	2.01	2.87	3.05
	30	7.23	200	1.03	4.2	4.43	5.44
			250	0.89	3.3	3.63	5.11
			300	0.54	2.28	2.54	3.46
Mg–20wt.%Ni	15	6.80	200	0.56	0.88	1.06	2.67
			250	0.86	2.94	3.26	4.8
			300	0.61	2.27	2.77	4.06
	30	7.30	200	0.79	3.18	3.74	5.47
			250	0.14	0.19	0.62	1.67
			300	0.53	2.62	3.12	4.22

Mg–5wt.%Ni and Mg–20wt.%Ni alloys using 30 h of milling and hydriding and dehydriding temperatures between 200 and 250 °C and 300 °C, respectively.

Surface area analysis results of Mg–5wt.%Ni and Mg–20wt.%Ni alloys at 15 and 30 h of mechanical alloying in which can be observed that pure unmilled magnesium from Alfa Aesar has a surface area of 3.30 m^2/gr. As shown in Table 1, a greater surface area is obtained when milling time is increased. Some authors have reported that using niquel as catalysts and mechanical alloying can improve the microstructure and reaction surface by creating nucleation sites and defects on the surface and interior of the magnesium structure where the hydrides could nucleate and growth [1,6,9].

This can be corroborated with diffractograms of hydrided Mg–5wt.%Ni and Mg–20wt.%Ni alloys on which more intense peaks of de MgH_2 can be detected. It can be summarized that at milling times of 30 h greater surface area is obtained and in consequence greater hydrides formation.

The previous results were confirmed by TGA analysis concluding that weight loss percentages in the Mg–5wt.%Ni and Mg–20wt.%Ni systems with 30 h of milling showed better surface areas and hydrogen storage efficiencies in comparison with alloys at 15 h of milling time. Also, it was possible to detect a slight increase in the surface area at greater nickel concentrations.

4. Conclusions

The synthesis by mechanical alloying of studied alloys shows that it significantly reduces particle size. Also, by means of scanning electron microscopy and ImageJ® software it was found that samples synthesized at 30 h of mechanical milling have better Ni particle distribution and size on the microstructure. The surface analysis results show that at milling times of 30 h there is better reaction surface giving as result higher formation of hydrides due presence of more sites for reaction where hydride can nucleate and growth. By means of thermogravimetric analysis technique (TGA) it was detected that best hydrogen storage efficiencies were obtained in both Mg–5wt.%Ni and Mg–20wt.%Ni alloys at 30 h of mechanical milling. It is worth to mention that at greater nickel concentrations there could be a decrease in the nucleation sites and growth of magnesium hydrides. The best hydriding and dehydriding temperatures for both alloys were of 200 °C and 300 °C, respectively.

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References

[1] E. David, J. Mater. Process. Technol. 162–163 (2005) 169–177.
[2] Myoung Youp Song, Sung Nam Kwon, Hye Ryoung Park, Seong-Hyeon Hong, Int. J. Hydrogen Energy 36 (2011) 13587–13594.
[3] I.P. Jain, Chhagan Lal, Ankur Jain, Int. J. Hydrogen Energy 35 (10) (2010) 5133–5144.
[4] Myoung Youp Song, Int. J. Hydrogen Energy 20 (3) (1995) 221–227.
[5] Che-Wei Hsu, Sheng-Long Lee, Fu-Kai Hsu, Jing-Chie Lin, Int. J. Hydrogen Energy 36 (9) (2011) 5383–5387.
[6] A. Zaluska, L. Zalusky, J.O. Ström Olsen, J. Alloys Compd. 288 (1999) 217–225.
[7] B. Vigeholm, J. Kjoller, B. Larsen, A.S. Pedersen, J. Less Common. Met. 89 (1) (1983) 135–144.
[8] Myoung Youp Song, Sung Hwan Baek, Jean-Louis Bobet, Sung Nam Kwon, Seong-Hyeon Hong, J. Mater. Sci. 44 (18) (2009) 4827–4833.
[9] Myoung Youp Song, J. Mater. Sci. 30 (1995) 1343–1351.
[10] R.L. Holtz, M.A. Imam, J. Mater. Sci. 34 (11) (1999) 2655–2663.
[11] J.L. Bobet, B. Chevalier, J. Mater. Sci. 39 (16–17) (2004) 5243–5246.
[12] Y.Q. Hu, Haifeng Zhang, Cheng Yan, Lin Ye, B.Z. Ding, Z.Q. Hu, J. Mater. Sci. 39 (4) (2004) 1455–1457.
[13] G. Liang, R. Schulz, J. Mater. Sci. 38 (2003) 1179–1184.
[14] F. Delogu, G. Mulas, Int. J. Hydrogen Energy 34 (7) (2009) 3026–3031.
[15] Myoung Youp Song, Young Jun Kwak, Hye Ryoung Park, Daniel R. Mumm, Mater. Res. Bull. 46 (2011) 1887–1891.
[16] A.M. Wang, B.Z. Ding, H.F. Zhang, Z.Q. Hu, J. Mater. Sci. Lett. 19 (2000) 1089–1091.
[17] Marco Vittori Antisari, Amelia Montone, Annalisa Aurora, M. Rita Mancini, Daniele Mirabile Gattia, Luciano Pilloni, Intermetallics 17 (2009) 596–602.