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# Structural characterization and electrochemical hydrogen storage properties of $Mg_2Ni_{1-x}Mn_x(x = 0, 0.125, 0.25, 0.375)$ alloys prepared by mechanical alloying

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#### ABSTRACT

 $Mg_2Ni_{1-x}Mn_x(x = 0, 0.125, 0.25, 0.375)$  electrode alloys are prepared by mechanical alloying (MA) under argon atmosphere at room temperature using a planetary highenergy ball mill. The microstructures are characterized by XRD and SEM. XRD analysis results indicate that the substitution of Mn for Ni could inhibit the formation of  $MgNi_2$ phase with the increases of x from 0 to 0.375. Replacing Ni with Mn can also promote the formation of the amorphous phase when x increases from 0 to 0.25 for the MA alloys milled for 48 h. The new phase  $Mg_3MnNi_2$  is formed only when x = 0.375 after 48 h of milling. This new phase belongs to the face-centered cubic lattice (Fd-3m) with the lattice constant a being 1.1484 nm. Estimated from the peaks broadening, the crystallite size and lattice strain of Mg<sub>3</sub>MnNi<sub>2</sub> phase are 15.6  $\pm$  3.6 nm and 1.09  $\pm$  0.34%, respectively. Curve fit of XRD shows that amorphous and nanocrystalline Mg<sub>2</sub>Ni coexist in the Mg<sub>2</sub>Ni<sub>1-x</sub>Mn<sub>x</sub> (x = 0, 0.125, 0.25) alloys milled for 48 h. The SEM observation reveals that all the MA alloys particles are mainly flaky and show cleavage fracture morphology and these particles are agglomerates of many smaller particles, namely subparticles. Electrochemical measurements indicate that all MA alloys have excellent activation properties. The discharge capacities of MA alloys increase with the prolongation of milling time. For 16 h of milling, with the increase of Mn content, the discharge capacities of  $Mg_2Ni_{1-x}Mn_x$ (x = 0, 0.125, 0.25, 0.375) MA alloys monotonously decrease. For 24 h of milling, the discharge capacities of the  $Mg_2Ni_{1-x}Mn_x$  (x = 0, 0.125, 0.25, 0.375) alloys also show a rough tendency to decrease with the increase of Mn content except Mg<sub>2</sub>Ni<sub>0.875</sub>Mn<sub>0.125</sub> MA alloy. On the other hand, for 48 h of milling, as the rise of Mn content from x = 0.125 to 0.375, the discharge capacities increase. Mg(OH)<sub>2</sub> is formed during charge/discharge cycles in the KOH solution for all MA alloys. After 48 h of milling, the substitution of Mn for Ni for x = 0.25 improves the cycle stability at the expense of decreasing the discharge capacity. In contrast, Mg<sub>3</sub>MnNi<sub>2</sub> phase is relatively stable during charge/discharge cycles and therefore can significantly enhance the cycle stability under simultaneously maintaining a high discharge capacity.

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#### 1. Introduction

Mg-based (Mg<sub>2</sub>Ni-type) hydrogen storage alloys are considered to be promising negative electrode materials for nickelmetal hydride (Ni-MH) batteries because of their low cost, light weight, rich mineral resources and high theoretical discharge capacity [1,2]. However, the poor hydriding/dehydriding kinetics and low electrochemical discharge capacity at room temperature [3], as well as severe oxidation in alkaline solution of Mg<sub>2</sub>Ni-type electrode become the obstacle for the practical use in Ni-MH batteries. Mechanical alloying (MA) is a solid-state powder processing technique involving repeated welding, fracturing, and rewelding of powder particles in a high-energy ball mill [4]. This technique is capable of decreasing crystal size, introducing numbers of grain boundaries and defects, as well as facilitating the formation of nanostructured and amorphous phase. Therefore, MA has been widely used to prepare Mg<sub>2</sub>Ni-type alloy possessing favourable electrochemical properties [5-7]. Partial elements substitution has been proved to be appropriate for improving electrochemical properties of Mg<sub>2</sub>Ni-type alloy [8-10]. Theoretical calculation has indicated that partial substitution of alloying element M for Ni in Mg<sub>2</sub>Ni can modify the enthalpy of formation for hydride, resulting in altering the phase stability [11]. The substitution of Mn for Ni or Mg in Mg<sub>2</sub>Ni-type alloys has been reported in many literatures. Woo et al. [6] performed the substitution of Mn for Ni in Mg<sub>2</sub>Ni alloy to improve the electrochemical properties. Yang et al. [12] found that replacement of Ni in Mg<sub>2</sub>Ni by Mn lowered the decomposition plateau pressure. Jurczyk et al. [13] obtained an enhanced discharge capacity by substituting Mg with Mn in Mg<sub>2</sub>Ni alloy. Kohno et al. [14] reported that as a result of substitution of Mg with Mn, absorption of hydrogen occurred at lower temperature. Gasiorowski et al. [15] found that the partial substitution of Mg by Mn in Mg<sub>2</sub>Ni alloy leaded to an increase in discharge capacity at room temperature. It can be seen that different authors used different substitution method. Some used Mn to substitute Ni, while others used Mn to substitute Mg in Mg<sub>2</sub>Ni. Tsushio et al. [16] proposed that for designing a quaternary alloy system of Mg<sub>2</sub>Ni by substitution method, the substitution for Ni had to be considered first and then for Mg. However, none of these literatures have reported the formation of the new Mg<sub>3</sub>MnNi<sub>2</sub> phase.

Three preparing methods have been reported to synthesize the Mg<sub>3</sub>MnNi<sub>2</sub> alloy. Denys et al. [17] synthesized Mg<sub>3</sub>MnNi<sub>2</sub> intermetallic compound by high-energy ball milling in argon atmosphere with subsequent pressing and sintering. They found that the synthesized Mg<sub>3</sub>MnNi<sub>2</sub> phase exhibited an ideal electrochemical discharge curve and good cyclic stability in comparison with other magnesium alloys. Dobrovolsky et al. [18] obtained Mg<sub>3</sub>MnNi<sub>2</sub> using milling a mixture of Mg, Ni and Mn powders in hydrogen atmosphere followed by thermal decomposition of the MA product. Hsu et al. [2] prepared Mg<sub>3</sub>MnNi<sub>2</sub> alloy by the method integrating conventional melting and isothermal evaporation casting process (IECP).

In this work, the method integrating mechanical alloying and partial elements substitution is carried out to produce  $Mg_2Ni$ -type alloy. The effects of the substitution of Mn for Ni and milling time on microstructures and electrochemical properties of Mg<sub>2</sub>Ni-type alloy are investigated. It is worthy to note that the new Mg<sub>3</sub>MnNi<sub>2</sub> phase has been synthesized in this research by much simpler one-step technique which is milling elemental powders of Mg, Ni and Mn in argon atmosphere. Therefore, this one-step technique is different from the three-step technique in Ref. [17], the milling in hydrogen atmosphere followed by thermal decomposition in Ref. [18] and the method integrating conventional melting and IECP in Ref. [2]. To the best of our knowledge, this is the first time that the one-step mechanical alloying in argon atmosphere is reported to synthesize the new Mg<sub>3</sub>MnNi<sub>2</sub> phase. The influence of Mg<sub>3</sub>MnNi<sub>2</sub> phase on electrochemical properties of Mg<sub>2</sub>Ni-type alloy is also studied. Exploring new Mg-based hydrogen storage alloy is significant for developing hydrogen storage technology. Mg<sub>3</sub>MnNi<sub>2</sub> phase, as a new hydrogen storage alloy, has been proved to possess better electrochemical hydrogen storage properties. This work may provide a guide for improving the electrochemical characteristics of Mg<sub>2</sub>Ni-type alloy, especially the antioxidation property, and developing new Mg-based electrode materials.

#### 2. Experimental procedure

Starting elemental powders of Mg (purity 99.8%, particle size  $\leq$ 50  $\mu$ m, from GoodFellow), Ni (purity 99.5%, particle size  $\leq$ 250  $\mu$ m, from GoodFellow) and Mn (purity 99.3%, particle size -325 mesh, from Alfa) were mixed according to the designed composition  $Mg_2Ni_{1-x}Mn_x$  (x = 0, 0.125, 0.25, 0.375). And then the mixtures were poured into the stainless steel vials (volume 50 ml) together with two stainless steel balls (diameter 20 mm) in the glove box filled with argon. The ball to powder weight ratio is 20:1. The MA was carried out under argon atmosphere at room temperature using a planetary high-energy ball mill (Retsch PM 400) at a speed of 400rpm. The milling was performed for 4 h, 8 h, 16 h, 24 h and 48 h respectively. In order to avoid severe cold welding during high-energy milling, for 16 h, 24 h and 48 h of the milling, the ball milling was stopped every 8 h to crush the bulk materials in vials as well as scrape the powder adhered to the balls and the walls of vials in the glove box filled with argon. This also ensured that all elemental powders were fully mixed and the composition was uniform. The milling was interrupted for 30min per hour to dissipate the heat and to reduce the excessive rise of temperature.

The structures of the MA alloys with different compositions milled for different periods of time were analyzed by the Bruker D8 Advance X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) filtered by nickel. The crystallite size and lattice strain were calculated based on the approximation (Eq. (1)) that combines the Wilson formula and Scherrer formula following Williamson-Hall style plot [19].

$$\beta = 2\varepsilon \tan\theta + \frac{0.9\lambda}{d\cos\theta} \tag{1}$$

where  $\beta$  is the full-width at half maximum intensity of a Bragg reflection excluding instrumental broadening,  $\theta$  the Bragg

angle,  $\lambda$  the wavelength of the X-ray radiation,  $\varepsilon$  the effective lattice strain and *d* the average crystallite size. On rearrangement, the Eq. (1) can be written as:

$$\beta \cos\theta = 2\varepsilon \sin\theta + \frac{0.9\lambda}{d} \tag{2}$$

the  $\beta \cos\theta$  of each peak was plotted as a function of  $\sin\theta$  and a straight line can be obtained by the least squares method with the intercept as  $0.9\lambda/d$  and slope as  $2\varepsilon$  [4]. From these, the crystallite size *d* and lattice strain  $\varepsilon$  can be calculated.

The morphologies of the powdered samples were observed using the JEOL JSM-5800LV Scanning Electron Microscope.

Electrochemical charge and discharge properties were investigated using Multi-channel Battery Interface ATLAS 0461. The working electrodes were prepared by pressing (under 80kNcm<sup>-2</sup> pressure) mechanically alloyed powder and 10wt% addition of Ni to small pellet form between nickel nets, which acted as the current collector for the electrode. The electrodes were auto-activated at first three charge/discharge cycles. The electrochemical properties of electrodes were measured in an H-type shape glass cell, using NiOOH/Ni(OH)<sub>2</sub> as the counter electrode (with much larger capacity than working electrode) and Hg/HgO as the reference electrode in 6 M KOH electrolyte at room temperature. The working electrode was first charged at 20 mA g<sup>-1</sup> until hydrogen liberation and then after 60 min of rest it was discharged at 10 mA g<sup>-1</sup> with a cut-off potential set at -0.7V.

#### 3. Results and discussion

#### 3.1. Microstructures

Fig. 1 presents the X-ray diffraction patterns of the  $Mg_2Ni_{0.625}Mn_{0.375}$  alloy with different milling times. It can be seen that after 4 h of milling, the intensities of the diffraction peaks of Mg, Ni and Mn decrease and their peak widths increase as a result of the reduction of crystallite size and/or the accumulation of lattice strain during MA. When the milling time is prolonged to 8 h, the peaks of Mg and Ni disappear and simultaneously new diffraction peaks that belong to  $Mg_2Ni$  phase appear, which indicates that initial powders of Mg and Ni have transformed to  $Mg_2Ni$  phase. The peaks of  $Mg_2Ni$  become broadening and smooth with the increase of milling time from 8 h to 24 h. However, the sharp



Fig. 1 - X-ray diffraction patterns of the  $Mg_2Ni_{0.625}Mn_{0.375}$  alloy with different milling times.

diffraction peaks attributed to Mn still exist even after 24 h of milling. In addition, due to the fact that the atomic radius of Mn is larger than that of Ni, if the substitution of Mn for Ni in Mg<sub>2</sub>Ni lattice occurs, the lattice parameter of the MA alloys will be dilated and the shifts in peak positions in the X-ray diffraction patterns will appear [4]. However, we did not observe any shifts in peak positions in the XRD patterns. Therefore, Mn did not substitute Ni site in Mg<sub>2</sub>Ni lattice structure. This means that it is difficult for Mn to substitute Ni site in Mg<sub>2</sub>Ni phase, which is also reported in Ref. [6]. This phenomenon is probably explained as follows. Electronegativities of metal elements gradually increase along the sequence Mg < Mn < Ni. Therefore, due to the bigger difference of electronegativities between Ni and Mg in comparison with Mn, it is much easier for bonding between Mg and Ni. As a result, it is difficult for Mn to substitute the site of Ni in Mg<sub>2</sub>Ni lattice. It is notable that the peak of Mn at around  $52.3^{\circ}$ appears after 8 h of milling. This is because in the initial powder mixture, the peak of Ni at around 51.7° is too near to that of Mn at around  $52.3^{\circ}$  and probably the two peaks are superimposed with each other. In fact, the XRD of individual initial Mn powder was also carried out and shows the presence of the peak at around 52.3°. After 8 h of milling, Mg and Ni have transformed to Mg<sub>2</sub>Ni phase, so the interference of Ni peak disappears and then the Mn peak at around  $52.3^{\circ}$  is clearly marked. MgO is detected after 24 h of milling, which is due to periodic opening of the milling vial under argon atmosphere in order to crush the bulk materials in vials and scrape the powder adhered to the balls and the walls of vials. Varin et al. [20] also indicate that periodic opening of the milling vial in a glove box, even under highly protective atmosphere, leads somehow to the formation of MgO. There are also other reports on the formation of MgO in Ref. [18] and [21]. When the milling time is 48 h, some new peaks appear. According the index result of phase, these new peaks are confirmed to be attributed to the new phase Mg<sub>3</sub>MnNi<sub>2</sub>. This new phase belongs to the face-centered cubic lattice (Fd-3m) with ordered Ti<sub>2</sub>Ni-type structure. Its lattice constant a is calculated to be 1.1484 nm which is a little smaller than 1.1561 nm reported in Ref. [17]. Based on Eq. (2), the crystallite size and lattice strain of Mg<sub>3</sub>MnNi<sub>2</sub> phase are estimated to be 15.6  $\pm$  3.6 nm and 1.09  $\pm$  0.34%, respectively. Because of the difficulty of substitution of Mn for Ni site in Mg<sub>2</sub>Ni lattice, as well as the great difference between Mg<sub>2</sub>Ni lattice (space group P6<sub>2</sub>22 [22]) and Mg<sub>3</sub>MnNi<sub>2</sub> lattice (space group Fd-3m), the phase formation mechanism of Mg<sub>3</sub>MnNi<sub>2</sub> is probably as follows. With the increase of milling time, the lattice structure of Mg2Ni phase was destroyed and simultaneously amorphous phase was formed. And then Mg, Ni and Mn atoms rearranged to form Mg<sub>3</sub>MnNi<sub>2</sub> phase. Another peak of MgO at around 42.5° also appears in high intensity in company with its previous peak. This is because the rise of frequency of opening vials causes the increase of possibility of contacting remnant oxygen and moisture.

Fig. 2 shows the X-ray diffraction patterns of the  $Mg_2Ni$ alloy with different milling times. It can be seen that besides the formation of the  $Mg_2Ni$  phase, the peaks of  $MgNi_2$  phase are also detected after 8 h of milling. This is different from that in Fig. 1 where there isn't occurrence of  $MgNi_2$  phase. XRD investigation on all synthesized MA alloys shows that  $MgNi_2$ 



Fig. 2 - X-ray diffraction patterns of the Mg<sub>2</sub>Ni alloy with different milling times.

phase gradually decreases with the increase of Mn content and disappears as x achieves 0.25, which indicates that substitution of Mn for Ni could inhibit the formation of MgNi<sub>2</sub> phase. This is possibly ascribed to the change of atom ratios between Mg and Ni caused by the substitution of Mn for Ni. During mechanical alloying, since Mg is very soft and easier to adhere to the balls and walls of vials, the real content of Ni is above and near to 33 at% for x = 0 and 0.125 (smaller amount of substitution), respectively, which is corresponding to the MgNi<sub>2</sub> + Mg<sub>2</sub>Ni region in the Mg–Ni system. Therefore, Mg<sub>2</sub>Ni and small amount of MgNi<sub>2</sub> phases coexist for x = 0 and 0.125. After a large amount of substitution of Mn for Ni, Ni content is below 33 at%, which belongs to the  $Mg_2Ni + Mg$  region. As a result, MgNi<sub>2</sub> phase disappears when x = 0.25 and 0.375. With the rise of milling time from 8 h to 24 h, the peaks of Mg<sub>2</sub>Ni phase and MgNi<sub>2</sub> phase get broadening, implying the reduction of crystallite size and/or the accumulation of lattice strain. When the milling time reaches 48 h, the peaks of Mg<sub>2</sub>Ni phase become smooth and diffusing at around 18°-22° and  $38^{\circ}-50^{\circ}$ , which is the typical feature of amorphous phase. In order to identify the amorphous phase more clearly, the fitted and experimental XRD are presented in Fig. 3. The error of fit is 2.36%. It can be observed that the majority of Mg<sub>2</sub>Ni phase has transformed to amorphous state and the sharp peaks of MgO are superimposed on the broad amorphous peaks at around 42.5°. There are also residual nanocrystalline phase of Mg<sub>2</sub>Ni. Estimated from the peaks broadening of Mg<sub>2</sub>Ni phase in Fig. 3,



Fig. 3 – Experimental and fitted X-ray diffraction patterns of the Mg<sub>2</sub>Ni alloy with a fixed milling time of 48 h.



Fig. 4 – Experimental and fitted X-ray diffraction patterns of the  $Mg_2Ni_{0.875}Mn_{0.125}$  alloy with a fixed milling time of 48 h.

the crystallite size of Mg<sub>2</sub>Ni phase is 7.6  $\pm$  1.6 nm. Therefore, there coexist amorphous and nanocrystalline phases and it is probable that the nanocrystallites are embedded in the amorphous matrix in the Mg<sub>2</sub>Ni MA alloy. This phenomenon has also been reported in Ref. [23]. For x = 0.125 and 0.25, the curve fit of experimental XRD shown in Figs. 4 and 5 also reveals that the amorphous and nanocrystalline phases coexist in these MA alloys. By comparing Fig. 2 with Fig. 1, it is found that MgO begins to appear after 16 h and 24 h of milling for Mg<sub>2</sub>Ni and Mg<sub>2</sub>Ni<sub>0.625</sub>Mn<sub>0.375</sub> alloys, respectively, which implies that the substitution of Mn for Ni in Mg<sub>2</sub>Ni can more or less inhibit the oxidation of powder.

Fig. 6 presents X-ray diffraction patterns of the  $Mg_2Ni_{1-x}Mn_x$  alloys with a fixed milling time of 48 h: (a) x = 0, (b) x = 0.125, (c) x = 0.25 and (d) x = 0.375. It can be observed that the diffusing peaks of amorphous phase become smoother and lower with the rise of Mn content from x = 0 to x = 0.25, which implies that the content of amorphous phase increases. For x = 0.375, as mentioned above, the phase formation of  $Mg_3MnNi_2$  is probably related to the amorphous phase. Therefore, in the middle of this process, the substitution of Mn for Ni may also play a role of promoting the formation of Mn for Ni is favourable for the formation of the



Fig. 5 – Experimental and fitted X-ray diffraction patterns of the  $Mg_2Ni_{0.75}Mn_{0.25}$  alloy with a fixed milling time of 48 h.



Fig. 6 – X-ray diffraction patterns of the  $Mg_2Ni_{1-x}Mn_x$ alloys with a fixed milling time of 48 h: (a) x = 0 (b) x = 0.125 (c) x = 0.25 and (d) x = 0.375.

amorphous phase can be obtained. This can be ascribed to two reasons. Firstly, with the increase of Mn content, the alloy composition shifts to the  $Mg_2Ni$  + Mg region in the Mg-Ni system. The increase of Mg content in the composition is favourable to the formation of amorphous phase [1]. Secondly, Ni is malleable and ductile, while Mn is hard and brittle. With the increase of substitution amount of Mn for Ni, the hardness and brittleness of MA powders substantially increase, which is favourable for the MA powders to get work hardened and can cause more intensive collisions among powders. As a result, more intensive collisions promote the more generations of a variety of defect structures (dislocations, vacancies, grain boundaries, etc.). These defect structures destabilize the ordered nature of the lattice and promote the formation of a disordered amorphous phase [4]. Based on the two reasons mentioned above, after long milling time of 48 h, the substitution of Mn for Ni could promote the formation of the amorphous phase. For the other milling time, such as 8 h, 16 h and 24 h, the amorphous phase is not found according to the results of XRD analysis. Because the Mg reacted with Ni to form Mg<sub>2</sub>Ni phase for shorter milling time (8 h, 16 h, 24 h). The peaks of residual crystal phase of Mg2Ni become more broadening. It is worthy to note that the main characteristic peaks of Mg<sub>3</sub>MnNi<sub>2</sub> phase appear only when x = 0.375, which can be explained as follows. The ratios of Mg, Ni, Mn atom for Mg<sub>3</sub>MnNi<sub>2</sub> phase and Mg<sub>2</sub>Ni<sub>1-x</sub>Mn<sub>x</sub> alloys when x = 0.125, 0.25and 0.375 are 9:6:3, 48:21:3, 24:9:3 and 16:5:3, respectively. The schematic equations below are constructed artificially (These equations are not the real reactions and the product of  $Mg_3MnNi_2$  on the right of the schematic Eq. (3), (4) and (5) does not indicate its real formation.):

$$9 \text{ Mg}+6\text{Ni}+3\text{Mn} \rightarrow 3\text{Mg}_3\text{MnNi}_2 \tag{3}$$

 $48 \text{ Mg} + 21\text{Ni} + 3\text{Mn} \rightarrow 3\text{Mg}_3\text{MnNi}_2 + 39 \text{ Mg} + 15\text{Ni}$  (4)

 $24 \text{ Mg}+9\text{Ni}+3\text{Mn} \rightarrow 3\text{Mg}_3\text{MnNi}_2 + 15 \text{ Mg}+3\text{Ni}$ (5)

$$16 \text{ Mg}+5\text{Ni}+3\text{Mn} \rightarrow 5/2 \text{ Mg}_3\text{MnNi}_2 + 17/2 \text{ Mg} + 1/2\text{Mn}$$
 (6)



Fig. 7 – X-ray diffraction patterns of the  $Mg_2Ni_{0.625}Mn_{0.375}$ alloys with a fixed milling time of 48 h: (a) initially after milling (b) after 12 charge/discharge cycles.

In all the schematic equations above, the Mn content is fixed at 3 on the left, the contents of Mg and Ni are adjusted according to the content of Mn. For the schematic Eq. (3), (4) (x = 0.125) and (5) (x = 0.25), 3Mn are completely consumed to form  $3Mg_3MnNi_2$ , whereas for schematic Eq. (6) (x = 0.375), 3Mn can not be exhausted to form  $3Mg_3MnNi_2$ and only produces 5/2Mg<sub>3</sub>MnNi<sub>2</sub>, resulting in the remnant of 1/2Mn. For Eqs. (4) and (5), the Mg and Ni remain existing in the products, indicating that they are excess. However, for Eq. (6), Mn and Mg are excess. Considering Mg is always excess in Eqs. (4-6), the reason why there is the formation of Mg<sub>3</sub>MnNi<sub>2</sub> phase only when x = 0.375 is that the content of Mn is excess relative to the ratio 9:6:3 in Mg<sub>3</sub>MnNi<sub>2</sub> phase. This provides a guide to synthesize Mg<sub>3</sub>MnNi<sub>2</sub> phase. Woo et al. [6] did not find the Mg<sub>3</sub>MnNi<sub>2</sub> phase even after 120 h of milling for Mg<sub>2</sub>Ni<sub>0.9</sub>Mn<sub>0.1</sub> alloy, which can be explained as that the Mn content of  $Mg_2Ni_{0.9}Mn_{0.1}$  alloy is not excess compared with the ratio of 9:6:3 in Mg<sub>3</sub>MnNi<sub>2</sub> phase.

The XRD patterns of  $Mg_2Ni_{0.625}Mn_{0.375}$  alloys before and after electrochemical cycle are shown in Fig. 7. After 12 charge/discharge cycles, the peaks of  $Mg(OH)_2$  appear, confirming that the oxidation of MA alloys occurs in KOH solution during charge/discharge cycles. The sharp peaks of Ni are attributed to the decomposition of MA alloy and the addition of Ni for preparing electrode. This result is in good agreement with that obtained by Liu et al. [24]. It is noteworthy that the peaks of  $Mg_3MnNi_2$  phase remain existing after 12 charge/ discharge cycles, which indicates that the  $Mg_3MnNi_2$  phase is relatively stable during charge/discharge cycles. Because of the small solubility of MgO in KOH solution and the slow reaction of MgO and  $H_2O$ , MgO is still present after 12 charge/ discharge cycles. Lei et al. [25] have also reported the formation of MgO during cycling.

The SEM morphologies of  $Mg_2Ni_{0.625}Mn_{0.375}$  alloys milled for 8 h and 48 h are shown in Fig. 8. It can be seen that most of the particles (in fact, they are clusters of smaller particles) are smaller than 20 µm in size after 8 h of milling in Fig. 8a. However, further milling (48 h of milling in Fig. 8b) does not dramatically decrease the particle size of  $Mg_2Ni_{0.625}Mn_{0.375}$  alloys, which indicates that a steady–state equilibrium between fracturing (tending to decrease the particle size) and welding (tending to increase particle size) is attained. Fig. 9 shows the SEM



Fig. 8 – SEM morphologies of the Mg<sub>2</sub>Ni<sub>0.625</sub>Mn<sub>0.375</sub> alloys with different milling time: (a) 8 h (b) 48 h.

morphologies of  $Mg_2Ni_{1-x}Mn_x$  (x = 0, 0.125, 0.25, 0.375) alloys with a fixed milling time of 48 h at higher magnification. It is observed that the powder particles in all the compositions are mainly flaky and show cleavage fracture morphology, which is in agreement with that observed in Ref. [15] and [26]. The powder particles are agglomerates of many smaller particles, namely subparticles with the size of several micrometres. The SEM morphology of Mg<sub>2</sub>Ni<sub>0.625</sub>Mn<sub>0.375</sub> alloys milled for 8 h at higher magnification also shows the similar structure. The reason for this phenomenon is that a large amount of energy of balling is transferred to subparticles, resulting in high concentration of defects and decrease of subparticles size. As a result, the surface free energy of subparticles substantially rises. In order to decrease the total energy of subparticles, they agglomerate together to form large clusters (particles mentioned above) to reduce the surface area for lowering surface free energy.

#### 3.2. Electrochemical hydrogen storage properties

Discharge capacity as a function of cycle number for  $Mg_2Ni_{1-x}Mn_x$  (x = 0, 0.125, 0.25, 0.375) alloys with a fixed milling time of 48 h is shown in Fig. 10. As can be seen, all alloys achieve their maximum discharge capacities at first charge/discharge cycle including  $Mg_3MnNi_2$  phase, indicating that these alloys have excellent activation property. Whereas the  $Mg_3MnNi_2$  alloy prepared by Hsu et al. [2] attains its maximum discharge capacity after 3 cycles. This difference is because of the different preparing methods. Obviously, in comparison with the method integrating conventional melting and IECP used in Ref. [2], mechanical alloying performed here can create more fresh surfaces and defects which are favourable for the diffusion of hydrogen. In addition, the crystallite size and lattice strain of  $Mg_3MnNi_2$  phase are estimated to be 15.6  $\pm$  3.6 nm and 1.09  $\pm$  0.34%, respectively. The



Fig. 9 – SEM morphologies of the Mg<sub>2</sub>Ni<sub>1-x</sub>Mn<sub>x</sub> alloys with a fixed milling time of 48 h: (a) x = 0 (b) x = 0.125 (c) x = 0.25 and (d) x = 0.375.



Fig. 10 – Discharge capacity as a function of cycle number for  $Mg_2Ni_{1-x}Mn_x(x = 0, 0.125, 0.25, 0.375)$  alloys with a fixed milling time of 48 h.

smaller nanograins with larger lattice strain may enhance the activation performance [27]. Therefore, the improved activation property is obtained by MA in this study. With the increase of Mn from x = 0.125 to x = 0.375, the maximum discharge capacity grows monotonously from 42mAh/g to 82 mAh/g. The discharge capacity of Mg<sub>3</sub>MnNi<sub>2</sub> alloy is a little lower than that reported by Hsu et al. [2]. Two reasons are responsible for the lower discharge capacity. Firstly, it is due to the formation of MgO. The MgO may deplete the reacting powder of Mg required for synthesizing Mg-based hydrogen storage alloys. Secondly, the structure of alloy phases is another main reason for the poor discharge capacity. On the one hand, mechanical alloying can substantially decrease crystal size to nanoscale, introduce large numbers of grain boundaries and defects. The nanostructured phase can avoid the long-range diffusion of hydrogen atoms through the already formed hydride phase [28]. At the same time, quantities of microstrains introduced by the defects and grain boundaries can accelerate the hydrogen absorbing/desorbing process [27]. Therefore, MA can improve the discharge capacity of the alloys. On the other hand, the grain refining weakens the anti-corrosion capability of the MA alloy due to the inevitable inter-nanocrystalline corrosion [1], which consequently accelerates the corrosion of MA alloys in alkaline solution and result in the formation of Mg(OH)<sub>2</sub>. The layers of Mg(OH)<sub>2</sub> are not transparent to hydrogen so that these layers prevent hydrogen from further penetrating into the alloys [29]. As a result, the discharge capacity of the MA alloy is considerably reduced.

Discharge capacities of  $Mg_2Ni_{1-x}Mn_x$  (x = 0, 0.125, 0.25, 0.375) alloys with milling time and content of Mn are listed in Table 1. As can be seen, both milling time and Mn content can significantly influence the discharge capacities. Firstly, the discharge capacities increase with the increase of milling time. The explanation for this phenomenon is as below. With the prolongation of milling time, the microstructures of MA alloys experience the structural transformation process as follows:

Microcrystalline (0 h of milling)  $\rightarrow$  Nanocrystalline (8 h, 16 h, 24 h of milling)  $\rightarrow$  Amorphous with nanocrystalline (48 h of milling)

For nanocrystalline alloys, because of the reduction of crystallite size, the large number of interfaces and grain boundaries are produced, which can enhance the solubility and provide easier channel for the diffusion of hydrogen atoms. As a result, the faster kinetics (excellent activation property) and higher discharge capacity are obtained with the increase of milling time from 16 h to 24 h. With further prolongation of milling time to 48 h, the amorphous phase is formed with the residual nanocrystallites embedded in it. The formation of amorphous phase significantly increases the disordered degree, resulting in the wide energy distribution of the available site for hydrogen atom in the amorphous structure. Orimo et al. [30] reported that the maximum hydrogen concentrations of the three regions had been experimentally determined to be 0.3% in the grain region of nanocrystalline Mg<sub>2</sub>Ni, 4.0% in the interface between Mg<sub>2</sub>Ni grains and 2.2% in the amorphous region. For the nanocrystalline/amorphous composite MA alloys that possess a great number of interfaces, the amorphous phase has larger capacity of hydrogen than nanograins. In addition, the amorphous region around nanocrytallites provides an easier access of hydrogen into the nanograins. As a result, the synergic effect between nanocrystalline and amorphous phase can significantly improve the kinetic properties (activation property) and increase the discharge capacity of MA alloys. Therefore, due to the structural transformation, the discharge capacities increase with the prolongation of milling time.

Secondly, as listed in Table 1, the discharge capacity of  $Mg_2Ni_{1-x}Mn_x$  (x = 0, 0.125, 0.25, 0.375) MA alloys monotonously decreases with the increase of Mn content for 16 h of milling, which is presumably caused by the unreacted element Mn in the MA alloys [6]. It is possible that the

Table 1 – Discharge capacities of $Mg_2Ni_{1-x}Mn_x$ (x = 0, 0.125, 0.25, 0.375) alloys with milling time and the content of Mn.							
Milling time (h)		Discharge capacity (mAh/g)					
	Mg <sub>2</sub> Ni	$Mg_2Ni_{0.875}Mn_{0.125}$	$Mg_2Ni_{0.75}Mn_{0.25}$	Mg <sub>2</sub> Ni <sub>0.625</sub> Mn <sub>0.375</sub>			
16	17	10	8	5			
24	28	8	21	19			
48	90	42	64	82			

existence of Mn could inhibit the absorption and penetration of hydrogen on the surface of MA alloys and consequently set up an obstacle for hydriding. Therefore, the discharge capacities decrease with the increase of Mn content. For the  $Mg_2Ni_{1-x}Mn_x$  (x = 0, 0.125, 0.25, 0.375) alloys milled for 24 h, the discharge capacities also shows a rough tendency to decrease with the increase of Mn content except Mg<sub>2</sub>Ni<sub>0.875</sub>Mn<sub>0.125</sub> MA alloy. The reason for this phenomenon is similar as that for 16 h of milling. The exception for  $Mg_2Ni_{0.875}Mn_{0.125}$  MA alloy milled for 24 h can be explained as follows. There exist Mn and MgNi2 simultaneously in  $Mg_2Ni_{0.875}Mn_{0.125}$  MA alloy. Although the phase composition is the same for Mg<sub>2</sub>Ni<sub>0.875</sub>Mn<sub>0.125</sub> MA alloy milled for 16 h and 24 h, the prolongation of milling time from 16 h to 24 h causes a better dispersion of Mn and MgNi2 phase in MA alloy. In contrast to Mg<sub>2</sub>Ni, the MgNi<sub>2</sub> phase does not interact with hydrogen [31]. Therefore, Mn and MgNi<sub>2</sub> phase further hinder the absorption and penetration of hydrogen on the surface of Mg<sub>2</sub>Ni<sub>0.875</sub>Mn<sub>0.125</sub> MA alloy. As a result, the discharge capacity of  $Mg_2Ni_{0.875}Mn_{0.125}$  MA alloy is lowest among all MA alloys milled for 24 h and even lower than its discharge capacity for 16 h of milling. For 16 h and 24 h of milling, there also exists MgNi<sub>2</sub> phase in Mg<sub>2</sub>Ni MA alloy, whereas the unreacted Mn is present in other MA alloys and Mn is possible to be dominant in terms of hindering the absorption and penetration of hydrogen on the surface of MA alloys compared with MgNi<sub>2</sub> phase. Therefore, the Mg<sub>2</sub>Ni MA alloy shows the highest discharge capacity among all the MA alloys milled for 16 h or 24 h. The reason why the Mg<sub>2</sub>Ni<sub>0.875</sub>Mn<sub>0.125</sub> MA alloy milled for 16 h does not show the lowest discharge capacity among all MA alloys milled for 16 h is that the MgNi<sub>2</sub> phase is not dispersed sufficiently. As a result, the inhibiting effects of Mn on absorption and penetration of hydrogen on the surface of MA alloys is dominant for 16 h of milling. Therefore, the discharge capacities of  $Mg_2Ni_{1-x}Mn_x$  (x = 0, 0.125, 0.25, 0.375) MA alloys monotonously decrease with the increase of Mn content for 16 h of milling as mentioned above.

As can be obtained in Table 1, for 48 h of milling, the Mg<sub>2</sub>Ni MA alloy shows the highest discharge capacity among all MA alloys at the first cycle, which is due to its high content of Mg<sub>2</sub>Ni nanocrystallites and numbers of interfaces between nanocrystallites. With the rise of Mn content from x = 0.125 to 0.375, the discharge capacities gradually increase. It can be seen in Fig. 6 that, the peaks become smoother and lower from x = 0.125 to 0.25, which reveals the increase of disordered degree and amorphous phase proportion. Therefore, the substitution of Mn for Ni enhances the amorphous phase forming ability of the MA alloys, leading to a higher discharge capacity of  $Mg_2Ni_{0.75}Mn_{0.25}$  alloy than  $Mg_2Ni_{0.875}Mn_{0.125}$  alloy. Huang et al. [32] also indicate that the increase of discharge capacity is strongly influenced by the amorphous phase proportion in the alloys. The formation of new phase Mg<sub>3</sub>MnNi<sub>2</sub> is responsible for the high discharge capacity of Mg<sub>2</sub>Ni<sub>0.625</sub>Mn<sub>0.375</sub> alloy. As shown in Fig. 10, in spite of the fact that the Mg<sub>2</sub>Ni MA alloy has the highest discharge capacity among all MA alloys at the first cycle, the discharge capacity of Mg<sub>2</sub>NiO<sub>.625</sub>Mn<sub>0.375</sub> MA alloy begins to overtake that of it from the second cycle because of the formation of the new phase Mg<sub>3</sub>MnNi<sub>2</sub>. Hsu et al. [2] also reported that Mg<sub>3</sub>MnNi<sub>2</sub> phase could effectively improve the reaction activity of the electrode



Fig. 11 – Evolution of the capacity retaining rate of the  $Mg_2Ni_{1-x}Mn_x$  (x = 0, 0.125, 0.25, 0.375) alloys milled for 48 h with the cycle number.

alloys and the discharge capacity of electrode alloys increases with the increase of  $Mg_3MnNi_2$  phase content. Therefore, the discharge capacity of  $Mg_2Ni0_{.625}Mn_{0.375}$  MA alloy is enhanced due to the formation of new phase  $Mg_3MnNi_2$ .

Cycle stability can be evaluated by capacity retaining rate (R<sub>h</sub>) as that introduced in Ref. [1].  $R_h = C_n/C_{max} \times 100\%$ , where  $C_n$ and C<sub>max</sub> are the discharge capacity of the nth cycle and the maximum discharge capacity, respectively. The evolution of the capacity retaining rate of the  $Mg_2Ni_{1-x}Mn_x$  (x = 0, 0.125, 0.25, 0.375) alloys milled for 48 h with the cycle number is illustrated in Fig. 11. All MA alloys show the tendency of capacity degradation. As shown in Fig. 7, the peaks of Mg(OH)<sub>2</sub> are identified after 12 charge/discharge cycles. In fact, all MA alloys show the formation of Mg(OH)2 during charge/ discharge cycles. Mg(OH)<sub>2</sub> not only consumes the MA alloys, but also increases the resistance of electrodes, resulting in inhibiting the charge transfer. Therefore it can be inferred that the discharge capacity degradation of MA alloys is mainly attributed to Mg(OH)<sub>2</sub>. After 10 cycles, the R<sub>h</sub> of Mg<sub>2</sub>Ni and  $Mg_2Ni_{0.875}Mn_{0.125}$  MA alloys fall to 22% and 10% respectively, implying the poor cycle stability. Whereas, for Mg<sub>2</sub>Ni<sub>0.75</sub>Mn<sub>0.25</sub> and  $Mg_2Ni_{0.625}Mn_{0.375}$  MA alloys, the values of  $R_h$  are 52% and 44%, respectively, showing the improved cycle stability compared with Mg<sub>2</sub>Ni MA alloy. It is obvious that the proper substitution of Mn for Ni could improve the cycle stability of MA alloys. For  $Mg_2Ni_{0.875}Mn_{0.125}$  and  $Mg_2Ni_{0.75}Mn_{0.25}$  MA alloys, the amorphous and nanocrystalline phases coexist in them as shown in Figs. 4 and 5. Zhang et al. [8] reported that the formation of amorphous phase was responsible for the enhanced cycle stability. On the other hand, the grain refining weakens the anti-corrosion capability of the alloy due to the inevitable inter-nanocrystalline corrosion [1]. These two factors function together to influence the cycle stability of MA alloys. For Mg<sub>2</sub>Ni MA alloys, due to high content of Mg<sub>2</sub>Ni nanocrystallites and numbers of interfaces between nanocrystallites (fewer amorphous phase compared with x = 0.125and 0.25), it is oxidized more easily and its discharge capacity decreases more rapidly with the increase of cycle number. For

Mg<sub>2</sub>Ni<sub>0.75</sub>Mn<sub>0.25</sub> MA alloy, its significantly improved amorphous phase forming ability is dominant, therefore its cycle stability is enhanced. Whereas for Mg<sub>2</sub>Ni<sub>0.875</sub>Mn<sub>0.125</sub> MA alloy, the latter factor is dominant, as a result, its cycle stability is weakened. The improvement of cycle stability of Mg<sub>2</sub>Ni<sub>0.625</sub>Mn<sub>0.375</sub> MA alloy is due to the formation of the new phase Mg<sub>3</sub>MnNi<sub>2</sub>. As shown in Fig. 7, the Mg<sub>3</sub>MnNi<sub>2</sub> phase remains existing after 12 charge/discharge cycles, which indicates that Mg<sub>3</sub>MnNi<sub>2</sub> phase is relatively stable. Hsu et al. [2] also indicated that Mg<sub>3</sub>MnNi<sub>2</sub> phase could enhance the anti-corrosive performance and possesses a positive effect on the retardation of cycling capacity degradation rate of the electrode alloys. The improved cycle stability of  $Mg_2Ni_{0.75}Mn_{0.25}$  alloy is at the expense of the reduction of the discharge capacity. In contrast, the Mg<sub>3</sub>MnNi<sub>2</sub> phase can significantly improve the cycle stability under maintaining a relative high discharge capacity compared with other substituted MA alloys.

#### 4. Conclusions

The structure and electrochemical hydrogen storage properties of  $Mg_2Ni_{1-x}Mn_x$  (x = 0, 0.125, 0.25, 0.375) alloys prepared by mechanical alloying have been investigated. Based on this study, the following conclusions can be obtained: (1) it is difficult for Mn to substitute Ni site in Mg<sub>2</sub>Ni lattice structure. The substitution of Mn for Ni could inhibit the formation of MgNi<sub>2</sub> phase with the increases of x from 0 to 0.375. After 48 h of milling, the results of XRD analysis indicates that the substitution of Mn for Ni could promote the formation of the amorphous phase when x increases from 0 to 0.25. The amorphous and nanocrystalline Mg<sub>2</sub>Ni coexist in the  $Mg_2Ni_{1-x}Mn_x(x = 0, 0.125, 0.25)$  alloys milled for 48 h with nanocrystallites embedded in the amorphous matrix. (2) The new phase Mg<sub>3</sub>MnNi<sub>2</sub> is synthesized only when x = 0.375 after 48 h of milling. To the best of our knowledge, this is the first time that the one-step mechanical alloying in argon atmosphere is reported to synthesize the new Mg<sub>3</sub>MnNi<sub>2</sub> phase. This new phase belongs to the face-centered cubic lattice (Fd-3m) with the lattice constant a being 1.1484 nm. Estimated from the peaks broadening, the crystallite size and lattice strain of Mg<sub>3</sub>MnNi<sub>2</sub> phase are 15.6  $\pm$  3.6 nm and 1.09  $\pm$  0.34%, respectively. The phase formation mechanism of Mg<sub>3</sub>MnNi<sub>2</sub> is probably that with the increase of milling time, the lattice structure of Mg<sub>2</sub>Ni phase was destroyed and simultaneously amorphous phase was formed. And then Mg, Ni and Mn atoms rearranged to form Mg<sub>3</sub>MnNi<sub>2</sub> phase. In the middle of this process, the substitution of Mn for Ni may also play a role of promoting the formation of amorphous phase. It is suggested that in order to synthesize Mg<sub>3</sub>MnNi<sub>2</sub>, the content of Mn should be excess relative to the ratio 9:6:3 of Mg, Ni and Mn in Mg<sub>3</sub>MnNi<sub>2</sub> phase. (3) The SEM observation reveals that all the MA alloys particles are mainly flaky and show cleavage fracture morphology and these particles are agglomerates of many smaller particles, namely subparticles. (4) All MA alloys have excellent activation properties. With the increase of milling time, the discharge capacities of MA alloys rise. The discharge capacities of  $Mg_2Ni_{1-x}Mn_x$  (x = 0, 0.125, 0.25, 0.375) MA alloys monotonously decrease with the increase of Mn

content for 16 h of milling, which is presumably caused by the unreacted element Mn in the MA alloys. It is possible that the existence of Mn could inhibit the absorption and penetration of hydrogen on the surface of MA alloys and consequently set up an obstacle for hydriding. For the  $Mg_2Ni_{1-x}Mn_x$  (x = 0, 0.125, 0.25, 0.375) alloys milled for 24 h, the discharge capacities also show a rough tendency to decrease with the increase of Mn content except  $Mg_2Ni_{0.875}Mn_{0.125}$  MA alloy. For the  $Mg_2Ni_{1-x}Mn_x$  (x = 0.125, 0.25, 0.375) MA alloys with a fixed milling time of 48 h, the discharge capacities rise with the increase of substitution of Mn for Ni. From x = 0.125 to 0.25, the substitution of Mn for Ni enhances the amorphous phase forming ability of MA alloys and consequently improves the discharge capacity.  $Mg_2Ni_{0.625}Mn_{0.375}$  MA alloy shows the highest discharge capacity among these three MA alloys due to the formation of new phase Mg<sub>3</sub>MnNi<sub>2</sub>. The appearance of MgO in MA alloys is one reason for causing a poor discharge capacity. Furthermore, nanocrystallites and numbers of interfaces between nanocrystallites introduced by mechanical alloying cause an easier inter-nanocrystalline corrosion, which also results in a lower discharge capacity and a poor cycle stability. Reducing the formation of MgO and improving the inter-nanocrystalline corrosion is the next aim of research. Mg(OH)<sub>2</sub> is produced during charge/discharge cycle in all MA alloys, which leads to the degradation of discharge capacity. Amorphous phase is favourable for improving cycle stability. Mg<sub>3</sub>MnNi<sub>2</sub> phase is relatively stable during charge/ discharge cycles and therefore can significantly enhance the cycle stability under simultaneously maintaining a high discharge capacity.

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# **ANNEXE 4**

Huang LW, Elkedim O, Hamzaoui R. First principles investigation of the substitutional doping of Mn in Mg<sub>2</sub>Ni phase and the electronic structure of Mg<sub>3</sub>MnNi<sub>2</sub> phase. Journal of Alloys and Compounds 2011; 509 : S328–33.

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# First principles investigation of the substitutional doping of Mn in $Mg_2Ni$ phase and the electronic structure of $Mg_3MnNi_2$ phase

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#### ABSTRACT

The substitutional doping of Mn in Mg<sub>2</sub>Ni phase and the electronic structure of Mg<sub>3</sub>MnNi<sub>2</sub> phase have been investigated by first principles density functional theory calculations. The calculation of enthalpy of formation shows that among the four different lattice sites of Mg(6f), Mg(6i), Ni(3b) and Ni(3d) in Mg<sub>2</sub>Ni unit cell, the most preferable site of substitution of Mn in Mg<sub>2</sub>Ni lattice has been confirmed to be Mg(6i) lattice site. The constructed Mg<sub>9</sub>Mn<sub>3Mg(6i)</sub>Ni<sub>6</sub> structure by replacing 3 Mg atoms at Mg(6i) lattice sites with 3 Mn atoms in the Mg<sub>2</sub>Ni unit cell is less stable. In contrast, the cubic Mg<sub>3</sub>MnNi<sub>2</sub> phase that has the same composition as that of Mg<sub>9</sub>Mn<sub>3Mg(6i)</sub>Ni<sub>6</sub> structure possesses good stability. Analysis of density of states (DOS) indicates that there is a strong hybridization between Mg s, Mg p and Ni d electrons, which is dominant in controlling the structural stability of pure and Mn-doped Mg<sub>2</sub>Ni phases. The Mnsubstitution in Mg<sub>2</sub>Ni unit cell weakens the interaction between Mg s, Mg p and Ni d electrons, especially for Mg<sub>9</sub>Mn<sub>3Mg(6i)</sub>Ni<sub>6</sub> phase. The cubic Mg<sub>3</sub>MnNi<sub>2</sub> phase possesses a strong hybridization between Mn and Mg, Ni atomic orbits under simultaneously retaining the strong bonding among Mg s, Mg p and Ni d electrons. Based on the calculated results, the stability of phases gradually decreases along the sequence pure Mg<sub>2</sub>Ni phase > Mg<sub>3</sub>MnNi<sub>2</sub> phase > Mn-substitution doped Mg<sub>2</sub>Ni phase.

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AND COMPOUNDS

#### 1. Introduction

Mg<sub>2</sub>Ni is considered to be one of the most promising hydrogen storage alloys, because of its lightweight, low cost and high theoretical gravimetric hydrogen storage capacity (3.6 mass%, assuming the formation of Mg<sub>2</sub>NiH<sub>4</sub>). Besides, it can absorb and desorb hydrogen at moderate temperatures and pressures. However, the poor hydriding/dehydriding kinetics and high thermodynamical stability of Mg<sub>2</sub>NiH<sub>4</sub> (requiring 280 °C for 1 bar hydrogen [1]) become the obstacle for the practical use for hydrogen storage. Mn, as a ternary element, has been experimentally added into Mg<sub>2</sub>Ni for improving its hydrogen storage properties. Different literatures reported different substitution methods. Some authors used Mn to substitute Ni [2–3], while others used Mn to substitute Mg in  $Mg_2Ni$  [4–5]. However, these literatures only focus on the nominal change of initial elemental composition after Mn-substitution, which does not mean that the real substitution of lattice sites of atoms (Mg or Ni) in Mg<sub>2</sub>Ni alloy is generated. In theoretical aspect, Jurczyk et al. [6] carried out the total energy calculations for  $Mg_{11/6}Mn_{1/6}Ni$ and indicated that the impurity atoms Mn preferred Mg(6i) position. However, the total energy calculations of the substitution of Ni by Mn were not reported and not compared with that of Mg, too. Therefore, whether Mn prefers to substitute Ni or Mg lattice sites in Mg<sub>2</sub>Ni as well as the specific position of substitution is not clear. Many works have been dedicated to the investigation of electronic and structural properties of high temperature (HT)-Mg<sub>2</sub>NiH<sub>4</sub> (cubic) [7–8] and low temperature (LT)-Mg<sub>2</sub>NiH<sub>4</sub> (monoclinic) [8–10]. Takahashi et al. [11] studied the electronic structure of Mg<sub>2</sub>Ni intermetallic hydride containing a variety of alloying elements (V, Cr, Fe, Co, Cu, Zn) by the DV-X $\alpha$  cluster method. van Setten et al. [12] investigated the effects of transition metal (Fe, Co, Cu) doping of Mg<sub>2</sub>NiH<sub>4</sub> by first principles density functional theory calculations. However, there are very few reports on the theoretical calculation on the substitutional doping of Mn in Mg<sub>2</sub>Ni phase and this subject needs to be further studied.

We have reported the synthesis of the new nanocrystalline  $Mg_3MnNi_2$  phase by the one-step mechanical alloying in argon atmosphere [13]. This phase, as a new hydrogen storage alloy, has been proved to possess better electrochemical hydrogen storage properties. To the best of our knowledge, the electronic structure investigation on  $Mg_3MnNi_2$  phase has not been reported.

In this work, we study the substitutional doping of Mn in Mg<sub>2</sub>Ni phase as well as the electronic structure of Mg<sub>3</sub>MnNi<sub>2</sub> phase by first principles density functional theory calculations. The preferable site of substitution of Mn in Mg<sub>2</sub>Ni lattice has been determined by total energy calculation, which provides a guide for using the method of elemental substitution to improve the hydrogen storage

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 $\textbf{Fig. 1.} Models of the unit cell of Mg_2Ni (a), Mg_{11}Mn_{Mg(6f)}Ni_6 (b), Mg_{11}Mn_{Mg(6i)}Ni_6 (c), Mg_{12}Mn_{Ni(3b)}Ni_5 (d), Mg_{12}Mn_{Ni(3d)}Ni_5 (e) and Mg_3Mn_{3Mg(6i)}Ni_6 (f). Mg_{12}Mn_{Ni(3b)}Ni_5 (d), Mg_{12}Mn_{Ni(3b)}Ni_5 (e) and Mg_3Mn_{3Mg(6i)}Ni_6 (f). Mg_{12}Mn_{Ni(3b)}Ni_5 (e) and Mg_3Mn_{3Mg(6i)}Ni_6 (f) and Mg_$ 

properties of  $Mg_2Ni$  intermetallic compound. Furthermore, the change of structural stability from the Mn-substitution doped  $Mg_2Ni$  phase to  $Mg_3MnNi_2$  phase is studied for explaining the formation process of  $Mg_3MnNi_2$  phase.

#### 2. Computational models and method

The structure of Mg<sub>2</sub>Ni phase is shown in Fig. 1a. Its unit cell belongs to the space group  $P6_222$  with lattice parameters a = 5.216(6) Å, c = 13.20(6) Å [14]. The Mg<sub>2</sub>Ni unit cell contains 6 formula units, which can be expressed as Mg<sub>12</sub>Ni<sub>6</sub>. The 12 Mg atoms occupy 6f and 6i lattice sites, while 6 Ni atoms occupy 3b and 3d lattice sites. The different lattice sites are denoted by the balls in different colors as shown in Fig. 1a. To investigate the effects of substitutional doping, a Mn atom is introduced into the Mg<sub>2</sub>Ni unit cell to substitute the atom at Mg(6f), Mg(6i), Ni(3b) and Ni(3d) lattice sites, respectively. The corresponding doped unit cells are presented in Fig. 1b–e (In Fig. 1d, only one fourth of each Mn atom located at the edges of lattice belongs to the doped unit cell).

The unit cell of Mg<sub>3</sub>MnNi<sub>2</sub> phase is shown in Fig. 2a. It has a cubic symmetry (space group *Fd*-3*m*) with lattice parameter a = 11.564 Å

[15]. Each unit cell contains 16 formula units of Mg<sub>3</sub>MnNi<sub>2</sub>, namely Mg<sub>48</sub>Mn<sub>16</sub>Ni<sub>32</sub>. 48 Mg atoms, 16 Mn atoms and 32 Ni atoms occupy Mg(48f), Mn(16d) and Ni(32e) lattice sites, respectively. In order to increase the computational efficiency, the primitive cell shown in Fig. 2b is used in the calculation. It has 12 Mg atoms, 4 Mn atoms and 8 Ni atoms, namely Mg<sub>12</sub>Mn<sub>4</sub>Ni<sub>8</sub>. By replacing 3 Mg atoms with 3 Mn atoms in the Mg<sub>2</sub>Ni unit cell (shown in Fig. 1f), the corresponding chemistry formula Mg9Mn3Ni6 is obtained, namely 3 formula units of Mg<sub>3</sub>MnNi<sub>2</sub>, which shows the same composition as that of the new Mg<sub>3</sub>MnNi<sub>2</sub> phase. Because of the difference between Mg<sub>2</sub>Ni lattice (space group P6<sub>2</sub>22 [14]) and Mg<sub>3</sub>MnNi<sub>2</sub> lattice (space group Fd-3m [15]), the size of Mg<sub>9</sub>Mn<sub>3</sub>Ni<sub>6</sub> phase (based on Mg<sub>2</sub>Ni unit cell) is different from that of the primitive cell of Mg<sub>3</sub>MnNi<sub>2</sub> phase. However, their same chemical composition makes it possible to compare the stability of different structures (This has a similarity with the allotropy).

The calculation in this work has been carried out using the CASTEP programme [16], which is a first principles quantum mechanical code based on the density functional theory. It employs plane-wave basis sets to treat valence electrons and pseudopotentials to approximate the potential field of ionic cores (including nuclei and tightly bond core electrons) [17]. The Perdew–Burke–Ernzerhof (PBE) [18] generalized gradient approxL.W. Huang et al. / Journal of Alloys and Compounds 509S (2011) S328-S333



Fig. 2. Models of the unit cell (a) and primitive cell (b) of Mg<sub>3</sub>MnNi<sub>2</sub> phase.

#### Table 1

Experimental and calculated structural parameters of Mg<sub>2</sub>Ni and Mg<sub>3</sub>MnNi<sub>2</sub> phase.

Compound	Lattice constants (Å)		Atom site	Fractional coordinates						
		Experimental	Calculated		Experimental		Calculated			
Mg <sub>2</sub> Ni (P6 <sub>2</sub> 22)	a c	5.216(6) [14] 13.20(6)	5.218 13.246	Mg(6f) Mg(6i) Ni(3b) Ni(3d)	0.5 0.1635(6) 0 0.5	0 0.327 0 0	0.1149(2) [14] 0 0.5 0.5	0.5 0.1642 0 0.5	0 0.3284 0 0	0.1163 0 0.5 0.5
Mg <sub>3</sub> MnNi <sub>2</sub> ( <i>Fd</i> -3 <i>m</i> )	а	11.564 [15]	11.549	Mg(48f) Mn(16d) Ni(32e)	0.3239 0.5 0.70529	0.125 0.5 0.70529	0.125 [15] 0.5 0.70529	0.3245 0.5 0.70534	0.125 0.5 0.70534	0.125 0.5 0.70534

The digits in parentheses for experimental lattice constants and fractional coordinates are standard deviations.

imation (GGA) exchange and correlation potential was used in the calculations. The transition metals (Ni, Mn) were treated by spin polarized calculation. Ultrasoft pseudopotentials [17] in reciprocal space were used to replace the core electrons. We have tested the dependence of the total energy on the energy cutoff values and the *k*-point sets. For example, for Mg<sub>2</sub>Ni unit cell, when the energy cutoff is higher than 380 eV and the *k*-point sets are beyond  $6 \times 6 \times 2$ , the change in total energy is less than 1.64 meV/atom. In consideration of computational cost, all the geometry optimization calculations were performed with a 380 eV energy cutoff. The corresponding *k*-point sets are  $6 \times 6 \times 2$  for pure and Mn-doped Mg<sub>2</sub>Ni unit cell and  $4 \times 4 \times 4$  for Mg<sub>3</sub>MnNi<sub>2</sub> primitive cell, respectively. The convergence criteria were set at  $5.0 \times 10^{-6}$  eV/atom for energy change, 0.01 eV/Å for maximum force, 0.02 GPa for maximum stress and  $5.0 \times 10^{-4}$  Å for maximum displacement.

The enthalpy of formation of a compound can be defined as the difference between its total energy and the energies of its constituent elements in their stable states (referred to the elementary substances). The zero-point energy (ZPE) contributions are significant in reactions where hydrogen molecules are adsorbed or desorbed [12]. The reactions investigated in this work do not include hydrogen. Thus, the ZPE contributions are not considered in this study. Therefore, for a lattice containing *x* Mg atoms, *y* Mn atoms and *z* Ni atoms, the enthalpy of formation is given by:

$$\Delta_f H = E_{\text{tot}}(\text{Mg}_x \text{Mn}_y \text{Ni}_z) - [xE(\text{Mg}) + yE(\text{Mn}) + zE(\text{Ni})]$$
(1)

where  $\Delta_f H$  and  $E_{tot}$  refer to the enthalpy of formation and total energy of the compound, respectively. E(Mg), E(Mn) and E(Ni) are the single atomic energies of the hcp-Mg,  $\alpha$ -Mn and fcc-Ni in the solid state, respectively. The enthalpy of formation can be used to demonstrate whether and how much a compound structure is favored over its constituent elements in thermodynamics.

#### 3. Results and discussion

#### 3.1. Enthalpy of formation

At first, calculations of both Mg<sub>2</sub>Ni and Mg<sub>3</sub>MnNi<sub>2</sub> crystals were performed with full optimization of both the lattice parameters and the coordinates of all atoms based on the experimentally confirmed structure. The calculated values are listed in Table 1 and compared with the experimental data. This table shows that the difference between calculated and experimental values is below 1.3% for all results, which indicates that present calculations are in good agreement with the experimental results. As shown in Table 2, the

Table 2	
Total energy and enthalpy of formation of calculated models	s.

	Total energy (eV)	Total energy (eV)		Enthalpy of formation (eV)			
	Unit cell	Primitive cell	Unit cell	Per Mg <sub>3</sub> MnNi <sub>2</sub> formula unit	Per atom		
Mg <sub>2</sub> Ni	-19817.2794		-3.2691		-0.1816		
Mg <sub>11</sub> Mn <sub>Mg(6f)</sub> Ni <sub>6</sub>	-19496.4273		-2.7273		-0.1515		
Mg <sub>11</sub> Mn <sub>Mg(6i)</sub> Ni <sub>6</sub>	-19496.4777		-2.7777		-0.1543		
Mg <sub>12</sub> Mn <sub>Ni(3b)</sub> Ni <sub>5</sub>	-19115.3243		-2.1059		-0.1170		
Mg <sub>12</sub> Mn <sub>Ni(3d)</sub> Ni <sub>5</sub>	-19115.3679		-2.1495		-0.1194		
Mg <sub>3</sub> MnNi <sub>2</sub>		-25141.5880		-1.0372	-0.1729		
$Mg_9Mn_{3Mg(6i)}Ni_6$	-18854.7660			-0.5622	-0.0937		

calculated enthalpy of formation of  $Mg_2Ni$  unit cell is -3.2691 eV, which can be transferred into  $-52.57 \text{ kJ/mol} Mg_2Ni$  formula unit. This value is close to -51.9 kJ/mol reported in Ref. [19].

In order to study the effects of substitutional doping of Mn in Mg<sub>2</sub>Ni phase, a Mn atom is added into Mg<sub>2</sub>Ni unit cell to substitute a Mg (or Ni) atom at the positions 6f and 6i (or 3b and 3d), respectively. As shown in Table 2, the chemical formulae of the Mn-doped Mg<sub>2</sub>Ni unit cells are expressed as Mg<sub>11</sub>Mn<sub>Mg(6f)</sub>Ni<sub>6</sub>, Mg<sub>11</sub>Mn<sub>Mg(6i)</sub>Ni<sub>6</sub>, Mg<sub>12</sub>Mn<sub>Ni(3b)</sub>Ni<sub>5</sub> and Mg<sub>12</sub>Mn<sub>Ni(3d)</sub>Ni<sub>5</sub>, respectively. The enthalpy of formation is fundamental for evaluating the structural stability. The calculated enthalpies of formation per unit cell of the pure and Mn-doped Mg<sub>2</sub>Ni unit cell are also tabulated in Table 2. It can be obtained that Mg<sub>2</sub>Ni has the most negative enthalpy of formation, indicating that it is the most stable structure in thermodynamics. However, the Mn-substitutions for Mg or Ni atom in Mg<sub>2</sub>Ni phase decrease the stability of Mg<sub>2</sub>Ni phase because of the less negative enthalpies of formation in comparison with pure Mg<sub>2</sub>Ni phase. We have reported that during the mechanical alloying of elemental powders of Mg, Ni and Mn, the first appearing phase was Mg<sub>2</sub>Ni and it was difficult for Mn to substitute Ni site in Mg<sub>2</sub>Ni lattice structure [13]. The present calculated enthalpy of formation shows that pure Mg<sub>2</sub>Ni phase is more favored in thermodynamics than the Mn-doped phases, which is in good agreement with the phenomenon found in Ref. [13]. In addition, the enthalpies of formation of Mg<sub>11</sub>Mn<sub>Mg(6f)</sub>Ni<sub>6</sub> and Mg<sub>11</sub>Mn<sub>Mg(6i)</sub>Ni<sub>6</sub> are -2.7273 eV and -2.7777 eV, respectively, both of which are more negative than those of  $Mg_{12}Mn_{Ni(3b)}Ni_5$  (-2.1059 eV) and  $Mg_{12}Mn_{Ni(3d)}Ni_5$  (-2.1495 eV). Therefore, the Mn atom prefers to substitute Mg in Mg<sub>2</sub>Ni lattice in comparison with Ni. Furthermore, between Mg(6f) and Mg(6i) lattice sites, it is more favorable for Mn atom to replace the Mg(6i) position due to the most negative enthalpy of formation of -2.7777 eV for Mg<sub>11</sub>Mn<sub>Mg(6i)</sub>Ni<sub>6</sub> among the four Mn-doped phases. As a result, the calculated enthalpy of formation confirms that the most preferable site of substitution of Mn in Mg<sub>2</sub>Ni lattice is Mg(6i) position. This can provide a guide for using the method of elemental substitution to improve the hydrogen storage properties of Mg<sub>2</sub>Ni intermetallic compound. Takahashi et al. [11] reported that both the Ni-H and the Ni-Mg atomic interactions were found to affect directly the phase stability of the hydride. As mentioned above, the Mn-substitutions for Mg or Ni atom in Mg<sub>2</sub>Ni phase decrease the stability of Mg<sub>2</sub>Ni phase, which indicates that the Ni-Mg atomic interactions are weakened (Electronic structure calculation to be introduced in Section 3.2 will also further confirm this.). Therefore, Mn-substitutions for Mg or Ni atom in Mg<sub>2</sub>Ni phase are probably favorable for decreasing the stability of the hydride. Yang et al. [3] found that replacement of Ni in Mg<sub>2</sub>Ni by Mn lowered the decomposition plateau pressure. Jurczyk et al. [6] obtained an enhanced discharge capacity by substituting Mg with Mn in Mg<sub>2</sub>Ni alloy. Kohno and Kanda [4] reported that as a result of substitution of Mg with Mn, absorption of hydrogen occurred at lower temperature, which indicates that substituting Mg with Mn can overcome the poor hydriding/dehydriding performance of Mg<sub>2</sub>Ni alloy. As a result, the hydrogen storage properties can be tailored by appropriate designing of Mn-substitution.

In order to study the change of structural stability from the Mnsubstitution doped Mg<sub>2</sub>Ni phase to Mg<sub>3</sub>MnNi<sub>2</sub> phase for explaining the formation process of Mg<sub>3</sub>MnNi<sub>2</sub> phase, 3 Mn atoms substitute 3 Mg atoms at Mg(6i) position in the Mg<sub>2</sub>Ni unit cell. And then the corresponding chemistry formula Mg<sub>9</sub>Mn<sub>3Mg(6i)</sub>Ni<sub>6</sub> is obtained, namely 3 formula units of Mg<sub>3</sub>MnNi<sub>2</sub>, which shows the same composition as that of the new Mg<sub>3</sub>MnNi<sub>2</sub> phase (As mentioned above, the most preferable site of substitution of Mn is Mg(6i). Thus the Mg<sub>9</sub>Mn<sub>3Mg(6i)</sub>Ni<sub>6</sub> structure is preferred. For other possible configurations, such as Mg<sub>9</sub>Mn<sub>2Mg(6i)</sub>Mn<sub>Mg(6f)</sub>Ni<sub>6</sub>, Mg<sub>9</sub>Mn<sub>Mg(6i)</sub>Mn<sub>2Mg(6f)</sub>Ni<sub>6</sub> and Mg<sub>9</sub>Mn<sub>3Mg(6f)</sub>Ni<sub>6</sub> their structures have also been calculated and show less negative enthalpies of formation than Mg9Mn3Mg(6i)Ni6, which further confirms that the Mg9Mn3Mg(6i)Ni6 is more stable. The increase of substitution amount of Mn atom for Mg atom at Mg(6f) position weakens the structural stability. Therefore, the Mg9Mn3Mg(6i)Ni6 structure is selected to compare with the new Mg<sub>3</sub>MnNi<sub>2</sub> phase). The enthalpies of formation per Mg3MnNi2 formula unit for Mg9Mn3Mg(6i)Ni6 phase and Mg3MnNi2 phase are listed in Table 2. It can be seen that the enthalpy of formation of Mg3MnNi2 phase (-1.0372 eV) is far below than that of Mg<sub>9</sub>Mn<sub>3Mg(6i)</sub>Ni<sub>6</sub> phase (-0.5622 eV), which indicates that the Mg<sub>3</sub>MnNi<sub>2</sub> phase is more stable than  $Mg_9Mn_{3Mg(6i)}Ni_6$  phase. This is the reason why Mg<sub>3</sub>MnNi<sub>2</sub> phase appeared after long time of milling rather than Mg9Mn3Mg(6i)Ni6 phase [13]. The enthalpies of formation per atom for all structures in Table 2 show that the stability of phase gradually decreases along the sequence pure Mg<sub>2</sub>Ni phase > Mg<sub>3</sub>MnNi<sub>2</sub> phase > Mn-substitution doped Mg<sub>2</sub>Ni phase, which is consistent with the experimental results (During the mechanical alloying of elemental powders of Mg, Ni and Mn, at first, the Mg<sub>2</sub>Ni phase appeared, and then Mg<sub>3</sub>MnNi<sub>2</sub> phase. No Mn-substitution doped Mg<sub>2</sub>Ni phase was observed) in Ref. [13].

#### 3.2. Electronic structure

Analysis of total and partial density of states (DOS and PDOS) of the pure and doped phase has been performed to study the electronic structure mechanism on the change of structural stability. Fig. 3a exhibits the DOS and PDOS of pure Mg<sub>2</sub>Ni phase. It can be seen that the main bonding peaks are located at the energy range between -7.8 eV and Fermi level  $E_F$ . The highest peak at -1.4 eVis mainly contributed by the Ni d, the main part, Mg s, Mg p and a few Ni p electrons. The bonding peaks between -6 eV and -4 eV originate from the contribution of the electrons of Mg s, Mg p and Ni s, Ni p orbits. The bonding peaks from -7.8 eV to -6 eV are dominated by Mg s and a few Ni s electrons. This indicates that there is a wide hybridization between Mg and Ni atomic orbits, among which, the strong bonding between Mg s, Mg p and Ni d electrons is dominant and controls the structural stability of Mg<sub>2</sub>Ni phase. The DOS of  $Mg_{11}Mn_{Mg(6f)}Ni_6$  and  $Mg_{11}Mn_{Mg(6i)}Ni_6$  are nearly the same (The DOS of Mg<sub>12</sub>Mn<sub>Ni(3b)</sub>Ni<sub>5</sub> and Mg<sub>12</sub>Mn<sub>Ni(3d)</sub>Ni<sub>5</sub> are also nearly the same.), which is consistent with the little difference of the enthalpies of formation between them as calculated above. Therefore, only the DOS for the preferable Mg(6i) and Ni(3d) position for the substitution of Mn for Mg and Ni, respectively, are chosen to be shown in Fig. 3b and c for comparison. For Mn-doped Mg<sub>2</sub>Ni unit cells, the differences of DOS shown in Fig. 3b and c can be seen: (1) compared with the pure  $Mg_2Ni$  unit cell, the altitude of the bonding peaks of Mg s, Mg p and Ni d decreases between  $-4.0 \,\text{eV}$ and  $E_F$  for Mg<sub>11</sub>Mn<sub>Mg(6i)</sub>Ni<sub>6</sub> and Mg<sub>12</sub>Mn<sub>Ni(3d)</sub>Ni<sub>5</sub>; (2) Due to the Mn-substitution, the Mn s, Mn p and Mn d orbits participate in bonding with Ni and Mg atomic orbits in the energy region -4.0 to 0 eV. The first difference indicates that the interaction among Mg s, Mg p and Ni d orbits is weakened, which will destabilize the unit cells. The Mg-Ni atomic interaction is the most dominant, because it supports the structural framework of unit cell. Therefore, though there is a bonding among Mg, Ni and Mn atoms, the decrease of Mg-Ni atomic interaction lowers the stability of Mn-doped phases, which is consistent with the calculated results of enthalpy of formation. Fig. 3f shows the spin-resolved DOS for Mn d states. Red and green curves denote up spin and down spin, respectively. It can be seen that because of spin polarization, the Mn d states are mainly located below and above  $E_{\rm F}$  for the up spin and down spin, respectively. However, the highest bonding peak of Mn d up spin state for  $Mg_{11}Mn_{Mg(6i)}Ni_6$  is pushed to a lower energy (-2.95 eV) than that (-2.65 eV) of Mg<sub>12</sub>Mn<sub>Ni(3d)</sub>Ni<sub>5</sub>. The hybridization among Mg, Ni and Mn at lower energy region is favorable for the struc-



**Fig. 3.** Total and partial density of states of  $Mg_2Ni$  (a),  $Mg_{11}Mn_{Mg(6i)}Ni_6$  (b),  $Mg_{12}Mn_{Ni(3d)}Ni_5$  (c),  $Mg_9Mn_{3Mg(6i)}Ni_6$  (d),  $Mg_3MnNi_2$  (e) and spin-resolved DOS for Mn d states (f). The vertical dashed line represents the Fermi level  $E_F$ .

tural stability. As a result,  $Mg_{11}Mn_{Mg(6i)}Ni_6$  unit cell is more stable than  $Mg_{12}Mn_{Ni(3d)}Ni_5$  unit cell, which is in agreement with the calculated results of enthalpy of formation. After increasing the amount of substitution of Mn, the DOS of  $Mg_9Mn_{3Mg(6i)}Ni_6$  unit cell is obtained as shown in Fig. 3d. Compared with Fig. 3a-c, its altitude of the bonding peaks of Mg s, Mg p and Ni d significantly decreases between -4.0 eV and  $E_F$ . Furthermore, as shown in Fig. 3f, there are lots of Mn d down spin states above E<sub>F</sub>. Therefore, Mg<sub>9</sub>Mn<sub>3Mg(6i)</sub>Ni<sub>6</sub> unit cell is the least stable among the Mn-doped phases. In contrast, the cubic Mg<sub>3</sub>MnNi<sub>2</sub> phase that has the same composition with  $Mg_9Mn_{3Mg(6i)}Ni_6$  unit cell is rather stable. As shown in Fig. 3e: (1) its altitude of the bonding peaks of Mg s, Mg p and Ni d is nearly the same with that of pure Mg<sub>2</sub>Ni phase; (2) majority of Mn d states are below  $E_{\rm F}$ , which is beneficial for making a strong bonding with Mg and Ni atoms; (3) the main and high bonding peaks of Mg p, Ni d and Mn d electrons are superimposed with each other very well below  $E_{\rm F}$ , which implies a strong interaction. Therefore, Mg<sub>3</sub>MnNi<sub>2</sub> phase possesses high stability, which is in agreement with the result obtained in the calculation of enthalpy of formation.

#### 4. Conclusions

The substitutional doping of Mn in Mg<sub>2</sub>Ni phase and the electronic structure of Mg<sub>3</sub>MnNi<sub>2</sub> phase have been investigated by first principles density functional theory calculations. Based on this study, the following conclusions can be obtained: (1) The calculated lattice parameters and atomic coordinates are in good agreement with the experimental results. The calculation of enthalpy of formation shows that pure Mg<sub>2</sub>Ni phase is more favored in thermodynamics than the Mn-dope phases. The possibility of the site of Mn-substitution in Mg<sub>2</sub>Ni lattice has been confirmed to be Mg(6i)>Mg(6f)>Ni(3d)>Ni(3b) positions. The constructed Mg<sub>9</sub>Mn<sub>3Mg(6i)</sub>Ni<sub>6</sub> unit cell is proved to be less stable. In contrast, the cubic Mg<sub>3</sub>MnNi<sub>2</sub> phase that has the same composition as that of Mg9Mn3Mg(6i)Ni6 structure possesses good stability. The stability of phases gradually decreases along the sequence pure Mg<sub>2</sub>Ni phase > Mg<sub>3</sub>MnNi<sub>2</sub> phase > Mn-substitution doped Mg<sub>2</sub>Ni phase, which is consistent with the experimental results; (2) Analysis of density of states (DOS) indicates that the strong hybridization between Mg s, Mg p and Ni d electrons is dominant in controlling the structural stability of pure and Mn-doped Mg<sub>2</sub>Ni phases. The

Mn-substitution for Mg and Ni atoms in Mg<sub>2</sub>Ni unit cell weakens the interaction between Mg s, Mg p and Ni d electrons. The Mn d states in Mn-doped phases and Mg<sub>3</sub>MnNi<sub>2</sub> phase are mainly located below and above  $E_{\rm F}$  for the up spin and down spin, respectively. The bonding among Ni d and Mg s, Mg p electrons in Mg9Mn3Mg(6i)Ni6 phase is significantly decreased. The cubic Mg<sub>3</sub>MnNi<sub>2</sub> phase possesses a strong hybridization between Mn and Mg, Ni atomic orbits under simultaneously retaining the strong bonding between Mg s, Mg p and Ni d electrons. The results of analysis of DOS are in agreement with that of calculation of enthalpies of formation.

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# ANNEXE 5

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# Synergistic effects of multiwalled carbon nanotubes and Al on the electrochemical hydrogen storage properties of Mg<sub>2</sub>Ni-type alloy prepared by mechanical alloying

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#### ABSTRACT

 $Mg_{2-x}Al_xNi$  (x = 0, 0.25) electrode alloys with and without multiwalled carbon nanotubes (MWCNTs) have been prepared by mechanical alloying (MA) under argon atmosphere at room temperature using a planetary high-energy ball mill. The microstructures of synthesized alloys are characterized by XRD, SEM and TEM. XRD analysis results indicate that Al substitution results in the formation of AlNi-type solid solution that can interstitially dissolve hydrogen atoms. In contrast, the addition of MWCNTs hardly affects the XRD patterns. SEM observations show that after co-milling with 5 wt. % MWCNTs, the particle sizes of both Mg2Ni and Mg1.75Al0.25Ni milled alloys are decreased explicitly. The TEM images reveal that ball milling is a good method to cut long MWCNTs into short ones. These MWCNTs aggregate along the boundaries and surfaces of milled alloy particles and play a role of lubricant to weaken the adhesion of alloy particles. The majority of MWCNTs retain their tubular structure after ball milling except a few MWCNTs whose tubular structure is destroyed. Electrochemical measurements indicate that all milled alloys have excellent activation properties. The Mg<sub>1.75</sub>Al<sub>0.25</sub>Ni-MWCNTs composite shows the highest discharge capacity due to the synergistic effects of MWCNTs and Al on the electrochemical hydrogen storage properties of Mg<sub>2</sub>Ni-type alloy. However, the improvement on the electrode cycle stability by adding MWCNTs is unsatisfactory.

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#### 1. Introduction

Mg-based hydrogen storage alloys have attracted great attention as negative electrode materials for nickel-metal hydride (Ni-MH) batteries because of their low cost, light weight, rich mineral resources and high theoretical discharge capacity [1,2]. For example, theoretical gravimetric storage hydrogen capacity of  $Mg_2Ni$  alloy, assuming the formation of  $Mg_2NiH_4$ , is 3.6 mass% (equivalent to 999 mAh/g for the discharge capacity), which is approximately 2.7 times as large as that of  $LaNi_5$ . However, the practical applications of  $Mg_2Ni$ -type alloy for Ni-MH batteries are full of challenges because of

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its sluggish hydriding/dehydriding kinetics [1], low electrochemical discharge capacity relative to the theoretical value at room temperature [3] and poor cycle stability in alkaline solution. Partial elements substitution has been proved to be appropriate for improving electrochemical properties of Mg<sub>2</sub>Ni-type alloy [4–6]. In experimental aspect, the substitution of Al for Mg in Mg<sub>2</sub>Ni-type alloy has been intensively studied [7–10] and shows an improvement on electrochemical properties of Mg<sub>2</sub>Ni-type alloy. In theoretical aspect, the firstprinciples calculations revealed that partial component substitution of Mg by Al resulted in a destabilization of the hydride of Mg<sub>2</sub>Ni (namely Mg<sub>2</sub>NiH<sub>4</sub>) [11], which also indicates an amelioration on hydrogen storage properties of Mg<sub>2</sub>Ni-type alloy due to the Al replacement.

Carbon materials exhibit certain properties that make them in combination with metal hydrides more suitable compared to other potential supports or additives [12]. Generally speaking, all of the carbon allotropes, such as graphite, fullerene, activated carbon, carbon black and carbon nanotubes (CNTs), show positive effects on the hydrogen storage properties of Mg-based systems. It has been reported that the addition of graphite, fullerene or Vulcan carbon black in small amounts (5 wt.%) to nanocrystalline Mg<sub>2</sub>Ni could increase the desorption kinetics of Mg<sub>2</sub>Ni [13]. Wu et al. [14] have studied the effect of various carbon additives and noncarbon materials on hydrogen capacity and dehydriding/ hydriding kinetics of Mg. Interestingly, all the carbon additives exhibited prominent advantage over the noncarbon additives and among the various carbon additives, purified SWCNTs exhibited the most prominent "catalytic" effect on improving hydrogen capacity and absorption/desorption kinetics of Mg. Quite recently, Amirkhiz et al. [15] reported that the coupled additions of SWCNTs and metallic nanoparticles could catalyze the desorption of hydrogen for MgH<sub>2</sub> powders. This research group [16] also studied the hydrogen sorption cycling performance of SWCNTs-Mg hydride nanocomposites and indicated that the nanocomposites displayed much improved kinetic stability relative to MgH2. Besides SWCNTs, multiwalled carbon nanotubes (MWCNTs) have also been reported to be excellent additive for improving hydrogen storage properties of Mg-based systems. Pandey et al. [17] investigated the admixing of MWCNTs in Mg<sub>2</sub>Ni and Aminorroaya et al. [18] studied the co-milling of MWCNTs and Mg-6 wt% Ni alloy. They indicated that MWCNTs were very effective at promoting the desorption kinetics and increasing the hydrogen capacity of these alloys. Recently, Verón et al. [19] reported that coupled addition of Co and MWCNTs showed synergetic effect on hydrogen sorption properties of MgH<sub>2</sub>. Based on the reported results above, it is desirable to integrate the advantages of both Al substitution and MWCNTs addition to further improve electrochemical hydrogen storage properties of Mg<sub>2</sub>Ni-type alloy.

To the best of our knowledge, there are no reports on combining Al substitution with MWCNTs addition to ameliorate electrochemical hydrogen storage properties of Mg<sub>2</sub>Nitype alloy. Therefore, in this work, the influences of Al substitution and MWCNTs addition on microstructures and electrochemical properties of Mg<sub>2</sub>Ni-type alloy are investigated. The synergistic functions of MWCNTs and Al are presented and discussed. The obtained new results are expected to provide a guide for further designing and developing  $Mg_2Ni$ -type alloy with better electrochemical hydrogen storage properties.

#### 2. Experimental procedure

In the first step, the purchased (from GoodFellow) elemental powders of Mg (purity 99.8%, particle size  $\leq$  50  $\mu$ m), Ni (purity 99.5%, particle size  $\leq$  250  $\mu$ m) and Al (purity 99.9%, particle size  $\leq$ 60  $\mu$ m) were mixed according to the designed composition  $Mg_{2-x}Al_xNi$  (x = 0, 0.25). And then the mixtures were poured into the stainless steel vials (volume 50 ml) together with two stainless steel balls (diameter 20 mm). The ball to powder weight ratio is 10:1. The MA was carried out under argon atmosphere at room temperature using a planetary highenergy ball mill (Retsch PM 400) at a speed of 400 rpm. The milling was performed for 20 h. In order to avoid severe cold welding during high-energy milling, the ball milling was stopped every 10 h to crush the bulk materials in vials as well as scrape the powder adhered to the balls and the walls of vials. This also ensured that all elemental powders were fully mixed and the composition was uniform. The milling was interrupted for 15 min after every 30 min of milling for dissipating the heat and reducing the excessive rise of temperature. In the last step, the as-milled powders were mixed with 5.0 wt. % MWCNTs (GRAPHISTRENGTH C100, purity > 90%, supplied by Arkema France. The rest compositions are  $Al_2O_3$   $\leq$  7% and  $Fe_2O_3$   $\leq$  5%. Because the added amount of MWCNTs is only 5.0 wt. %, the introduced  $Al_2O_3$  and  $Fe_2O_3$  will be rather few. Moreover, we have not found these two impurity phases by XRD and TEM. Therefore, the MWCNTs are responsible for all the properties in this work) and then these mixtures were further milled for another 2 h at a speed of 200 rpm. For purpose of brevity, in this study, these milled mixtures containing MWCNTs are expressed as Mg<sub>2</sub>Ni-MWCNTs and Mg<sub>1.75</sub>Al<sub>0.25</sub>Ni-MWCNTs, respectively. All handling of the powders was performed in a glove box filled with argon.

The X-ray diffraction (XRD) patterns of the MA alloys were obtained by the Bruker D8 Advance X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.15418$  nm) filtered by nickel. The crystallite size and lattice strain were calculated based on the approximation (Eq. (1)) that combines the Wilson formula and Scherrer formula following Williamson-Hall style plot [20].

$$\beta = 2\varepsilon \tan \theta + \frac{0.9\lambda}{d\cos \theta} \tag{1}$$

Where  $\beta$  is the full-width at half maximum intensity of a Bragg reflection excluding instrumental broadening,  $\theta$  the Bragg angle,  $\lambda$  the wavelength of the X-ray radiation,  $\varepsilon$  the effective lattice strain and d the average crystallite size. The  $\beta \cos \theta$  of each peak was plotted as a function of  $\sin \theta$  and a straight line can be obtained by the least squares method with the intercept as  $0.9\lambda/d$  and slope as  $2\varepsilon$  [21]. From these, the crystallite size d and lattice strain  $\varepsilon$  can be calculated.

The morphologies and microstructure of the powdered samples were characterized by scanning electron microscopy (SEM, JEOL JSM-5800LV) and transmission electron microscopy (TEM, JEOL JEM-2100 operating at 200 kV accelerating voltage). Electrochemical charge and discharge properties were investigated using Multi-channel Battery Interface ATLAS 0461. The working electrodes were prepared by compressing (under a pressure of 325 MPa) the milled powder and 10wt% addition of Ni powder to form a small pellet between nickel nets acting as the current collector. The electrochemical properties of electrodes were measured in an H-type shape glass cell, using NiOOH/Ni(OH)<sub>2</sub> as the counter electrode (with much larger capacity than working electrode) and Hg/HgO as the reference electrode in 6 M KOH electrolyte at room temperature. The working electrode was first charged at a current density of 20 mAg<sup>-1</sup> until hydrogen liberation and then after 1 h of rest it was discharged at the same current density to a cut-off potential of -0.7 V vs. the reference electrode.

#### 3. Results and discussion

#### 3.1. Microstructures

The XRD patterns of as-milled samples are shown in Fig. 1. From Fig. 1a, it can be seen that after 20 h of milling, the initial elemental powders of Mg and Ni have transformed to Mg<sub>2</sub>Ni phase and a small quantity of MgNi<sub>2</sub> phase. As we have reported in Ref. [22], the coexistence of these two phases is due to the fact that during mechanical alloying, since Mg is very soft and easier to adhere to the balls and walls of vials relative to Ni, the real content of Mg is below 67 at%, which is corresponding to the  $Mg_2Ni + MgNi_2$  region in the Mg-Ni system. Therefore, Mg<sub>2</sub>Ni and small amount of MgNi<sub>2</sub> phases are simultaneously identified. Because the MgNi<sub>2</sub> phase does not react with hydrogen [23] and only traces of this phase appear, we mainly focus on the hydrogen storage phase Mg<sub>2</sub>Ni. The peaks of Mg<sub>2</sub>Ni show a broadening and smooth feature, implying the reduction of crystallite size and/or the accumulation of lattice strain. Based on the Eq. (1), the crystallite size and lattice strain of Mg<sub>2</sub>Ni are estimated to be 7.5 nm and 0.65%, respectively. The XRD pattern of Mg<sub>2</sub>Ni-MWCNTs co-milled powder is shown in Fig. 1b. It can be observed that



Fig. 1 – XRD patterns of as-milled samples: (a)  $Mg_2Ni$ (b)  $Mg_2Ni$ -MWCNTs (c)  $Mg_{1.75}Al_{0.25}Ni$  and (d)  $Mg_{1.75}Al_{0.25}Ni$ -MWCNTs. The vertical blue lines denote the standard peak positions of AlNi alloy. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

there is not significant difference between Fig. 1b and a. Thus we may conclude that the addition of MWCNTs does not affect the diffraction patterns in an appreciable way. Additionally, neither characteristic peaks of MWCNTs nor peaks of new phase formed between MWCNTs and milled alloys are detected. This could be explained as follows: the amount of MWCNTs additive is too low to generate sufficient diffraction intensity and MWCNTs are not expected to get incorporated in Mg<sub>2</sub>Ni lattice structure to form solid solution [17,18]. In fact, MWCNTs do exist in the as-milled samples, which will be revealed in the subsequent TEM analysis section. Fig. 1c displays the XRD pattern of milled  $Mg_{1.75}Al_{0.25}Ni$  sample. In comparison with Fig. 1a, it can be found that because of the partial substitution of Mg by Al in Mg<sub>2</sub>Ni alloy, the XRD pattern of Mg<sub>1.75</sub>Al<sub>0.25</sub>Ni alloy shows an apparent difference, namely appearance of several new diffraction peaks. The vertical blue lines in Fig. 1 denote the standard peak positions of AlNi alloy with a space group Pm-3m and lattice parameter a = 2.881 Å (PDF 65-5171). As the main feature, all the peak positions of (1 0 0), (1 1 0), (1 1 1) etc have shifted to smaller  $2\theta$  angles, which is a typical character of formation of solid solution [21]. The peaks of elemental Al are not identified in Fig. 1c, which also indicates that Al has participated in forming solid solution. The lattice constant a of AlNi-type structure synthesized in this study is calculated to be 2.948 Å, which is larger than the standard value 2.881 Å (PDF 65–5171) and is in agreement with the value of the same solid solution reported in Ref. [24]. Because the atomic size of Mg is larger than that of Al, the substitution of Al by Mg in AlNi lattice will make the lattice expand, resulting in an increase in lattice constant a. The XRD pattern of Mg<sub>1.75</sub>Al<sub>0.25</sub>Ni-MWCNTs composite is illustrated Fig. 1d. According to the broadening of diffraction peaks of AlNi-type solid solution, its crystallite size and lattice strain are estimated to be 6.8 nm and 0.85%, respectively. The addition of MWCNTs hardly influences the diffraction patterns of  $Mg_{1.75}Al_{0.25}Ni$  alloy, which is similar to the result obtained in Mg<sub>2</sub>Ni alloy mentioned in Fig. 1a and b. There also exist MWCNTs in the milled Mg<sub>1.75</sub>Al<sub>0.25</sub>Ni-MWCNTs powder and these tubular MWCNTs (unlike the graphite carbon that can be incorporated into Mg<sub>2</sub>Ni crystal structure during the milling process [25]) most likely aggregate along the particle boundaries of Mg<sub>1.75</sub>Al<sub>0.25</sub>Ni alloy, which will be exhibited in the subsequent TEM analysis section.

SEM images of all milled samples are shown in Fig. 2. It can be observed from Fig. 2a and c that the powder particles are mainly flaky and show cleavage fracture morphology, which is in agreement with that observed in Ref. [8,22,26]. The powders are composed of irregular particles with the size distribution varying from less than 1 µm to several micrometers. The SEM image of Mg<sub>1.75</sub>Al<sub>0.25</sub>Ni alloy displayed in Fig. 2c shows that the substitution of Mg by Al does not affect significantly the morphology of powder particles in comparison with Fig. 2a except a slight reduction of average particle sizes. It is worthy to note that after co-milling with 5 wt. % MWCNTs, the particle sizes of both Mg<sub>2</sub>Ni and Mg<sub>1.75</sub>Al<sub>0.25</sub>Ni milled alloys are decreased explicitly as shown in Fig. 2b and d. Due to the limit of resolution of SEM used in this study, the MWCNTs can not be clearly seen. In fact, based on TEM to be presented in the following section, the added MWCNTs aggregate along the boundaries and surfaces of milled alloy





Fig. 2 – SEM micrographs of as-milled samples: (a)  $Mg_2Ni$  (b)  $Mg_2Ni$ -MWCNTs (c)  $Mg_{1.75}Al_{0.25}Ni$  and (d)  $Mg_{1.75}Al_{0.25}Ni$ -MWCNTs.

particles and play a role of lubricant to weaken the adhesion of alloy particles, which results in a smaller particle size, less agglomeration and better dispersion [27]. Amirkhiz et al. [15] indicated that the addition of SWCNTs had the effect of deagglomerating the powders during the milling process. Yao et al. [28] also indicated that carbon materials have high catalytic dispersion and activity, and thus they could facilitate the ball milling of ductile metals to obtain finer particles. Therefore, the surface area of particles is significantly increased, which is expected to promote the absorption of hydrogen on the surface of milled alloys and improve their hydrogen storage properties.

The typical microstructure of as-received MWCNTs is shown in Fig. 3. Fig. 3a indicates that the length of MWCNTs is about hundreds of nanometers and even reaches the level of micrometer. In fact, the MWCNTs are too long to fit in a single TEM image, and their length ranges from 0.1 to 10  $\mu$ m. The typical high resolution TEM (HRTEM) image of an MWCNT in Fig. 3b shows the number of walls and large central hollow. The large central hollow of MWCNTs could provide an easy channel for the transport of hydrogen [17,27,28]. Amirkhiz et al. [15] indicated that SWCNTs could penetrate the thin hydroxide shell on the surface of MgH<sub>2</sub> and act as "hydrogen pumps" to move the atoms to the surface. The similar function is also expected for MWCNTs. Additionally, MWCNTs are characterized by their unique tubular structure built from rolled-up sheets of graphite. Ruffieux et al. [29] reported that the hydrogen adsorption energy barrier decreased with increasing curvatures of carbon network, and thus the curved carbon surfaces of MWCNTs are more favorable for the adsorption and diffusion of H atoms than graphite. In general, the unique and novel microstructure of MWCNTs is responsible for the positive effects on the transport of hydrogen.

The dark and bright field TEM images of milled Mg<sub>2</sub>Ni alloy are illustrated in Fig. 4a and b, respectively. From the dark field TEM image, one can infer that the crystallite sizes of Mg<sub>2</sub>Ni alloy (bright dots) range from about 5 to 9 nm. The average crystallite size is close to the calculated value (7.5 nm) based on peaks broadening in XRD analysis section, indicating a good agreement between XRD and TEM characterizations. Fig. 4c shows the corresponding selected area electron diffraction (SAED) pattern. Debye-Scherrer rings of Mg2Ni appear in the SAED pattern, which indicates a feature of nanocrystalline phase. Additionally, this electron diffraction pattern also exhibits broad halos, confirming the presence of the amorphous phase. Therefore, there coexist nanocrystalline and amorphous phases and the nanocrystallites are embedded in the amorphous matrix, which can be observed directly by the HRTEM image shown in Fig. 4d. Fig. 5 shows a bright field TEM micrograph that illustrates the dispersion of MWCNTs on the  $Mg_{1.75}Al_{0.25}Ni$  alloy surfaces. It can be observed that after 20 h of milling, the MWCNTs are cut to be



Fig. 3 – TEM micrographs of as-received MWCNTs: (a) bright field TEM image (b) HRTEM image.

shorter than their initial ones due to the collision between balls and MWCNTs. Pierard et al. [30] also reported the same behavior. The shortening of MWCNTs is beneficial for accelerating the passage of hydrogen in their central hollow. Additionally, a large number of MWCNTs aggregate along the boundaries and surfaces of milled  $Mg_{1.75}Al_{0.25}Ni$  alloy particles. Due to this special microstructure, these MWCNTs prevent the as-milled alloys from adhering effectively and



Fig. 4 – TEM micrographs of milled  $Mg_2Ni$  alloy: (a) dark field TEM image (b) bright field TEM image (c) corresponding SAED pattern (d) HRTEM image.



Fig. 5 – Bright field TEM image of milled  $Mg_{1.75}Al_{0.25}Ni-MWCNTs$  composite.

stabilize the smaller powder particles. This also explains why the average particle size of milled alloys is reduced due to the addition of MWCNTs in SEM analysis mentioned above. Though the majority of MWCNTs retain their tubular structure after ball milling, there also exist a few MWCNTs whose tubular structure is destroyed. As shown in Fig. 6a, the residual graphite walls are disordered and deformed, which indicates a feature of poor crystallinity. A typical crystal grain of AlNi-type solid solution denoted in Fig. 6a shows a crystallite size of approximate 7 nm. The calculation of crystallite size based on peaks broadening in XRD also gets a similar value (6.8 nm). Fig. 6b shows the HRTEM image of a spherical carbon onion-like particle. This particle possesses a large inner hollow space and is irregularly closed at some sites of shells (indicated with a black arrow), which is consistent with the results reported in Ref. [31,32]. The research carried out by Yao et al. [28] indicated that at low temperature (150 °*C*), the CNT additives could improve the hydrogen absorption properties of Mg better than graphite due to the fact that the tubular structure of CNTs could facilitate the moving of hydrogen atoms through the hollow tubes. Therefore, the destruction of tubular structure will damage the channels of hydrogen diffusion and this is undesirable. The typical retained tubular MWCNT is also exhibited in Fig. 6b.

#### 3.2. Electrochemical hydrogen storage properties

Discharge capacity as a function of cycle number for all milled alloys is shown in Fig. 7. As can be seen, all alloys achieve their maximum discharge capacities at first charge/discharge cycle, indicating that these alloys have good activation property. After the Al substitution for Mg in Mg2Ni, the formed Mg<sub>1.75</sub>Al<sub>0.25</sub>Ni alloy shows a higher maximum discharge capacity than Mg<sub>2</sub>Ni. It has been reported that the electrochemical capacity of Mg<sub>1.8</sub>Al<sub>0.2</sub>Ni alloy is higher than that of Mg<sub>2</sub>Ni alloy [7], which also indicates that the addition of Al could improve maximum discharge capacities of alloys. Whereas the Mg<sub>1.8</sub>Al<sub>0.2</sub>Ni alloy synthesized by diffusion method in Ref. [7] attains its maximum discharge capacity at the 3rd cycle. Obviously, in comparison with the diffusion method in Ref. [7], mechanical alloying performed in this work can create more fresh surfaces and defects which are favorable for the diffusion of hydrogen and therefore results in a better activation property. The authors in Ref. [7] ascribed the improvement of discharge capacity to the formation of a new phase Mg<sub>3</sub>AlNi<sub>2</sub>. However, in this study, no Mg<sub>3</sub>AlNi<sub>2</sub> phase is formed. Alternatively, we have synthesized AlNi-type solid solution by substituting Mg with Al in Mg<sub>2</sub>Ni alloy. Firstly, the crystalline phase of this solid solution can interstitially dissolve hydrogen atoms and possesses good stability [9]. Additionally, the addition of Al (resulting in the formation of AlNi-type solid solution) could improve the anti-corrosion behavior of the alloys to a certain extent in KOH solution [7]. As a result, Mg<sub>1.75</sub>Al<sub>0.25</sub>Ni alloy shows a higher maximum discharge capacity than Mg<sub>2</sub>Ni alloy.



Fig. 6 – HRTEM image of milled  $Mg_{1.75}Al_{0.25}Ni$ -MWCNTs composite.



Fig. 7 – Discharge capacity as a function of cycle number for all milled samples. The inset shows the enlarged curves for  $Mg_2Ni$  and  $Mg_2Ni$ -MWCNTs.

After the addition of 5 wt.% MWCNTs, both Mg2Ni-MWCNTs and Mg<sub>1.75</sub>Al<sub>0.25</sub>Ni-MWCNTs composites show enhanced maximum discharge capacities in comparison with those of Mg<sub>2</sub>Ni and Mg<sub>1.75</sub>Al<sub>0.25</sub>Ni milled alloys, respectively. This phenomenon could be explained as follows: (1) As observed in SEM, due to the lubricant function of MWCNTs, the alloy particles show smaller particle sizes, less agglomeration and better dispersion. Smaller particles could shorten the diffusion distance of hydrogen and therefore facilitate access of hydrogen to inner parts of alloy particles. Additionally, the surface area of alloy particles is also enlarged significantly, which is favorable for alloy particles to absorb hydrogen. (2) It is shown in TEM and HRTEM images that majority of MWCNTs retain their tubular structure during ball milling and surround the alloy particles. Even after 11 cycles, as illustrated in Fig. 8, the MWCNTs still preserve their tubular structure, which indicates their stability. These MWCNTs with specific tubular structure provide good channels for easy passage of hydrogen. Based on these two reasons, we may get a conclusion that the addition of 5 wt.% MWCNTs could enhance the electrochemical hydrogen storage capacity of milled alloys. It is worthy to note that though the Mg<sub>2</sub>Ni-MWCNTs sample exhibits a higher maximum discharge capacity than Mg<sub>2</sub>Ni alloy, this discharge capacity is still below that of Mg<sub>1.75</sub>Al<sub>0.25</sub>Ni alloy. Therefore, adding MWCNTs individually is less effective than adding Al for improving discharge capacity, which is because of the fact that the addition of Al changes the phase composition of milled alloy and leads to the formation of AlNi-type solid solution that can also incorporate hydrogen atoms. When Al and MWCNTs are added simultaneously, the highest discharge capacity is obtained for Mg1.75Al0.25Ni-MWCNTs composite, which implies that MWCNTs and Al have synergistic effects on electrochemical hydrogen storage capacity of milled alloys. All milled alloys show the tendency of capacity degradation, which is because of their oxidation in alkaline solution. The improvement on the electrode cycle stability by adding MWCNTs is unsatisfactory, which is similar to the results reported in



Fig. 8 – HRTEM image of electrode powder of Mg<sub>1.75</sub>Al<sub>0.25</sub>Ni-MWCNTs composite after 11 charge/discharge cycles.

Ref. [33]. The reason is probably like this: On the one hand, the alloy particles refining increases the discharge capacity. On the other hand, this refining weakens the anti-corrosion capability of milled alloys due to the exposure of more surfaces of alloy particles to the KOH solution. Besides, we have found a few MWCNTs at the bottom of the H-type shape glass cell during charge/discharge cycles in our experiment, indicating that some MWCNTs have flaked away from the working electrode. As a result, the electrode cycle stability has not been improved satisfactorily.

#### 4. Conclusions

 $Mg_{2-x}Al_xNi$  (x = 0, 0.25) electrode alloys with and without MWCNTs have been prepared by mechanical alloying under argon atmosphere at room temperature using a planetary high-energy ball mill. Based on this study, the following conclusions can be obtained: (1) Al substitution for Mg in Mg<sub>2</sub>Ni-type alloys results in the formation of AlNi-type solid solution that can interstitially dissolve hydrogen atoms. In contrast, the addition of MWCNTs hardly affects the phase compositions. (2) After co-milling with 5 wt. % MWCNTs, the particle sizes of both  $Mg_2Ni$  and  $Mg_{1.75}Al_{0.25}Ni$  milled alloys are decreased explicitly. The long MWCNTs were cut into short ones during ball milling. These MWCNTs aggregate along the boundaries and surfaces of milled alloy particles and play a role of lubricant to weaken the adhesion of alloy particles. As a result, the milled alloy particles show smaller particle sizes, less agglomeration and better dispersion. The majority of MWCNTs retain their tubular structure after ball milling except a few MWCNTs whose tubular structure is destroyed. (3) All milled alloys exhibit excellent activation properties. The Mg<sub>1.75</sub>Al<sub>0.25</sub>Ni-MWCNTs composite shows the highest

discharge capacity due to the synergistic effects of MWCNTs and Al on the electrochemical hydrogen storage properties of Mg<sub>2</sub>Ni-type alloy. However, the improvement on the electrode cycle stability by adding MWCNTs is unsatisfactory.

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#### **RESUMÉ**:

L'utilisation des combustibles fossiles (énergies non renouvelables) est responsable de l'augmentation de la concentration en gaz à effet de serre dans l'atmosphère. Parmi les solutions de remplacement envisagées, l'hydrogène apparaît comme le vecteur énergétique le plus séduisant. Son stockage dans des intermétalliques permet d'obtenir des capacités massiques et volumiques (e.g. 140 g/L) supérieures à celles obtenues en voie liquide ou sous pression (respectivement 71 et 40 g/L). Dans les accumulateurs Nickel-Métal Hydrure (Ni-MH), l'électrode négative est constituée d'un composé intermétallique qui absorbe l'hydrogène de façon réversible dans des conditions normales de pression et de température.

Ce travail de thèse vise d'une part, à synthétiser les alliages  $Mg_2Ni_{1-x}Mn_x$  (x =0, 0.125, 0.25, 0.375) et les alliages  $Mg_{2-x}Al_xNi$  (x = 0, 0.25) avec ou sans nanotubes de carbone (MWCNTs) par mécanosynthèse et d'autre part, d'étudier les effets des substitutions/additions sur la composition et la microstructure des alliages  $Mg_2Ni$  afin d'améliorer leurs propriétés de stockage d'hydrogène.

Les résultats obtenus montrent que les capacités de décharge des alliages  $Mg_2Ni_{1-x}Mn_x(x = 0, 0.125, 0.25, 0.375)$  augmentent avec le temps de broyage. Pour l'alliage  $Mg_2Ni_{0.625}Mn_{0.375}$  broyé durant 48 h, nous avons mis en évidence la formation d'une nouvelle phase  $Mg_3MnNi_2$  qui est relativement stable. Par conséquent,  $Mg_3MnNi_2$  est capable d'améliorer de manière significative la stabilité des cycles tout en maintenant une capacité de décharge relativement élevée.

Les résultats obtenus par la théorie de la fonctionnelle de la densité (DFT) en utilisant le programme CASTEP montrent d'une part, que les paramètres de maille et les coordinations atomiques sont en parfait accord avec les résultats expérimentaux. D'autre part, que la stabilité des phases décroit graduellement selon l'ordre suivant : Mg<sub>2</sub>Ni sans aucune substitution >Mg<sub>3</sub>MnNi<sub>2</sub> > Mg<sub>2</sub>Ni avec substitution par Mn.

L'addition de nanotubes de carbone et de Al ont des effets synergétiques sur la capacité de stockage d'hydrogène électrochimique dans le cas des alliages  $Mg_{2-x}Al_xNi$  (x = 0, 0.25) + 5 wt.% MWCNTs.

<u>MOTS CLÉS</u> : Intermétalliques de type  $Mg_2Ni$ ; Stockage d'hydrogène électrochimique; Mécanosynthèse; Substitution partielle; DFT; MWCNTs

#### **ABSTRACT:**

The use of fossil fuels (non-renewable energy) is responsible for increasing the concentration of greenhouse gases in the atmosphere. Among the considered alternatives, hydrogen is seen as the most attractive energy vector. The storage in intermetallics makes it possible to obtain mass and volume capacities (e.g. 140 g/L) higher than those obtained by liquid form or under pressure (respectively 71 and 40 g/L). The negative electrode of Nickel-Metal Hydride (NiMH) batteries, is constituted by an intermetallic compound which is able to reversibly absorb hydrogen under normal conditions.

In this work, on the one hand,  $Mg_2Ni_{1-x}Mn_x(x=0, 0.125, 0.25, 0.375)$  and  $Mg_{2-x}Al_xNi$  (x = 0, 0.25) electrode alloys with and without multiwalled carbon nanotubes (MWCNTs) have been prepared by Mechanical Alloying. On the other hand, influence of the partial elements substitution on the microstructure and electrochemical hydrogen storage properties of  $Mg_2Ni$ -type alloy has been studied.

The results show that the discharge capacities of  $Mg_2Ni_{1-x}Mn_x$  (x =0, 0.125, 0.25, 0.375) alloys increase with the prolongation of milling time. The new phase  $Mg_3MnNi_2$  is formed only when x=0.375 after 48 h of milling.  $Mg_3MnNi_2$  phase is relatively stable during charge/discharge cycles and therefore can significantly enhance the cycle stability under simultaneously maintaining a high discharge capacity.

Based on the calculated results of first principles, the lattice parameters and atomic coordinates are in good agreement with the experimental results and the stability of phases gradually decreases along the sequence pure  $Mg_2Ni$  phase >  $Mg_3MnNi_2$  phase > Mn-substitution doped  $Mg_2Ni$  phase.

When Al and MWCNTs are added simultaneously, the highest discharge capacity is obtained for  $Mg_{1.75}Al_{0.25}Ni$ -MWCNTs composite, which implies that MWCNTs and Al have synergistic effects on electrochemical hydrogen storage capacity of milled alloys.

**<u>KEY WORDS</u>** : *Mg*<sub>2</sub>*Ni-type intermetallics; Electrochemical hydrogen storage; Mechanical alloying; Partial elements substitution; DFT; MWCNTs*