Properties of Mechanically Milled Nanocrystalline and Amorphous Mg–Y–Ni Electrode Alloys for Ni–MH Batteries

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Abstract Nanocrystalline and amorphous Mg₂Ni-type Mg_{20–x}Y_xNi₁₀ ($x = 0, 1, 2, 3$ and 4) electrode alloys were fabricated using mechanical milling. The effects of the Y content and milling time on the microstructures and electrochemical performances of the alloys were investigated in detail. X-ray diffraction and transmission electron microscopy analyses revealed that the substitution of Y for Mg yields an obvious change in the phase composition and micro morphology of the alloys. When the Y content $x \leq 1$, the substitution of Y for Mg does not change the major phase Mg₂Ni, but with a further increase in the Y content, the major phase of the alloys transforms into the YMgNi₄ + YMg₃ phase. A nanocrystalline and amorphous structure can be obtained by mechanical milling, and the amorphisation degree of the alloy visibly increases with increased milling time. Electrochemical measurements indicate that the discharge capacity of the alloys first increases and then decreases with increasing Y content and milling time. The substitution of Y for Mg dramatically ameliorates the cycle stability of the as-milled alloys, and the mechanical milling more or less impairs the cycle stability of the alloys. Furthermore, the high rate discharge ability, electrochemical impedance spectrum, Tafel polarisation curves and potential step measurements indicate that the electrochemical kinetic properties of the as-milled alloys first increase and then decrease with increasing Y content and milling time.

KEY WORDS: Mg₂Ni-type alloy; Y substitution for Mg; Milling time; Electrochemical performance

1 Introduction

Because of its characteristics of having an inexhaustible supply, producing zero emission of green house gases and exhibiting high energy efficiency, hydrogen has been viewed

as a promising candidate for future energy applications [1]. However, the attainment of economic, efficient and safe hydrogen storage represents a large barrier to the creation of a hydrogen economy. Solid-state hydrogen storage such as metal hydrides is considered a promising alternative, which can absorb and desorb hydrogen at relatively low pressures, offering safety and cost advantages with potentially unparalleled hydrogen storage density [2–4]. Extensive research has recently been performed in the search for hydrogen storage systems based on different metal hydrides. As a direct result of the investigations, Mg₂Ni-type metallic hydrides were observed to be one of the most promising hydrogen storage materials applied in hydrogen fuel cell vehicles or as negative electrodes in Ni–MH batteries [5] because of their major advantages, such as the theoretical gaseous hydrogen absorption capacity of 3.6 wt% and electrochemical capacity of 1000 mAh/g for Mg₂NiH₄ [6,

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7]. Most of the papers presented on the International Symposium on Metal Hydrogen System Fundamental and Applications, Manchester, UK, July 2014 (MH2014), concentrated on the investigation of Mg-based hydrogen storage alloys. However, the practical application of these alloys is seriously retarded by their relatively high H-desorption temperatures, sluggish hydriding/dehydriding kinetics and extremely poor electrochemical cycle stability, either as hydrogen storage materials for on-board use or as negative electrode materials for Ni–MH batteries. Various attempts, such as mechanical alloying (MA) [8], surface modification [9], alloying with other elements [10] and adding a catalyst [11], have been adopted to overcome these drawbacks, and there has been a remarkable improvement in the desorption kinetics [12].

It is well known that the specific capacity and hydriding/dehydriding kinetics of hydride electrode materials depend on their chemical composition and crystalline structure. In particular, nanocrystalline and amorphous Mg-based hydrogen storage alloys exhibit a higher hydrogen absorption capacity at low temperatures and ambient pressure and better kinetics of hydriding and dehydriding compared with their bulk counterparts [13]. As reported by Hima Kumar *et al.* [14], changing the structure of the Mg_2Ni alloy from polycrystalline to nanocrystalline enables its absorbing/desorbing hydrogen temperature to decrease 100 °C, namely from 300 to 200 °C. The preparation and synthesis methods are important factors that can affect the characteristics of the materials. Mechanical milling (MM), although having some insurmountable disadvantages when processing using powder metallurgy, such as the surface contamination and time-consuming nature, is considered to be an appropriate technique for producing amorphous and nanocrystalline Mg_2Ni alloys with different compositions [5]. Moreover, alloying and microstructure modification are thought to be effective approaches to improve the hydriding properties. In particular, the partial substitution of rare-earth elements (La, Ce, Pr, Nd and Y) for Mg enables the stability of the hydride to decrease and facilitate hydrogen desorption [15]. In addition, such substitution could be very effective in preventing corrosion of the materials, hence improving the cycle performance [16].

Our previously published works have reported that a series of Mg_2Ni -type alloys were fabricated by melt spinning, and their structures and electrochemical performances were investigated [17, 18]. In this paper, Mg_2Ni -type $\text{Mg}_{20-x}\text{Y}_x\text{Ni}_{10}$ ($x = 0-4$) alloys were prepared by mechanical milling, and the effects of the Y content and milling time on the structures and electrochemical performances of the alloys were investigated in detail.

2 Experimental

Alloys with chemical compositions of the $\text{Mg}_{20-x}\text{Y}_x\text{Ni}_{10}$ ($x = 0-4$) were prepared using a vacuum induction furnace in a helium atmosphere at a pressure of 0.04 MPa to prevent Mg from volatilising. The molten alloy was poured into a copper mould cooled by water, thus producing a cast ingot. The chemical composition analysis indicates that the volatilisation amount of magnesium was less than 6%. A part of the as-cast alloys was mechanically crushed into powder with a diameter of approximately 50 μm . Then, the prepared powder was mechanically milled using a planetary-type mill in an argon atmosphere to prevent the powders from being oxidised during ball milling. The samples were handled in a glove box under Ar atmosphere. Cr–Ni stainless steel balls and the powders with a weight ratio of 35:1 were placed together into Cr–Ni stainless steel vials. The milling speed was 135 r/min, and the durations were 10, 30, 50 and 70 h. The alloys were labelled by their Y contents of $x = 0, 1, 2, 3$ and 4 as $\text{Y}_0, \text{Y}_1, \text{Y}_2, \text{Y}_3$ and Y_4 , respectively.

The phase structures of the as-cast and as-milled alloys were determined by X-ray diffraction (XRD) (D/max/2400). The diffraction, with the experimental parameters of 160 mA, 40 kV and 10°/min, respectively, was performed with CuK_α radiation filtered by graphite. The powder samples of the as-milled alloys were observed using a high-resolution transmission electron microscope (HRTEM) (JEM-2100F, operated at 200 kV), and their crystalline states were ascertained by electron diffraction (ED).

The mixture of the alloy powder and carbonyl nickel powder in a weight ratio of 1:4 was cold-pressed under a pressure of 35 MPa into round electrode pellets that were 15 mm in diameter and with a total weight of 1 g. The electrochemical performances were measured at 30 °C using a tri-electrode open cell consisting of a working electrode (the metal hydride electrode), a sintered $\text{Ni}(\text{OH})_2/\text{NiOOH}$ counter electrode and a Hg/HgO reference electrode, which were immersed in a 6 mol/L KOH electrolyte. The voltage between the negative electrode and reference electrode was defined as the discharge voltage. In every cycle, the alloy electrode was first charged with a constant current density; after resting for 15 min, the electrode was discharged at the same current density to a cut-off voltage of -500 mV.

To determine the electrochemical kinetics of the alloy electrodes, the electrochemical impedance spectra (EIS) and Tafel polarisation curves of the alloys were measured at 30 °C using an electrochemical workstation (PARSTAT 2273). Before the measurements, several electrochemical charging and discharging cycles were performed to activate the materials. The fresh electrodes were fully charged and then rested for 2 h up to the stabilisation of the open-circuit

potential. The EIS of the alloy electrodes were measured at 50% depth of discharge (DOD) in the frequency range from 10 kHz to 5 mHz, with a 5-mV potentiostatic signal amplitude or galvanostatic measurements and 60 points per decade of frequencies. The Tafel polarisation curves were measured in the potential range of -1.2 to $+1.0$ V (vs. Hg/HgO) with a scan rate of 5 mV/s. For the potentiostatic discharge, the test electrodes in the fully charged state were discharged at 500 mV potential steps for 5000 s on an electrochemical workstation (PARSTAT 2273) using an electrochemistry corrosion software (CorrWare).

3 Results

3.1 Microstructural Characteristics

The phase components and structure characteristics of the as-cast and as-milled $\text{Mg}_{20-x}\text{Y}_x\text{Ni}_{10}$ ($x = 0-4$) alloys were subjected to XRD detections, as illustrated in Fig. 1. Here, it is observed that mechanical milling causes the diffraction peaks of the alloys to merge and dramatically broaden, which can be ascribed to the changes in the crystal grain size and heterogeneous strain. Moreover, it is also observed that the substitution of Y for Mg yields an obvious change in the phase composition of the as-milled alloys. When the Y content $x = 1$, the major phase of the alloy remains the Mg_2Ni phase; however, the secondary phases YMgNi_4 and YMg_3 also appear. With increasing Y content, the major phase of the as-milled alloys changes from Mg_2Ni to

$\text{YMgNi}_4 + \text{YMg}_3$. This result was consistent with previously published studies [19]. It is also noted that with increasing milling time, the intensity of the diffraction peaks of the Y_2 alloy decreases and their width clearly increases, indicating that the powder sizes become much smaller and that the strain energy is stored.

The structural characteristics of the as-milled $\text{Mg}_{20-x}\text{Y}_x\text{Ni}_{10}$ ($x = 0-4$) alloys were inspected by HRTEM, as shown in Fig. 2. For the 10-h milling time, the alloy particles clearly agglomerate with increasing Y content. The locally amplified morphologies of the as-milled (10 h) alloys reveal that the Y_0 alloy has a nearly completely nanocrystalline structure, and the Y_3 alloy exhibits an obvious nanocrystalline and amorphous structure, indicating that the substitution of Y for Mg facilitates the glass forming of the Mg_2Ni alloy, which is supported by examining the Debye–Scherrer rings. A similar conclusion was reported by Teresiak *et al.* [15]. In addition, it can be found that upon increasing the milling time from 10 to 70 h, the alloy particles agglomerate heavily. The grain size of the Y_2 alloy markedly decreases, and the disordered degree of its microstructure clearly increases, indicating that a large amount of strain energy is stored, which leads to non-stabilisation of the lattice, yielding the fine grain sizes. As stated by Northwood *et al.* [20], the stored internal strain grows with increasing milling time. Longer milling times result in the introduction of more defects. Moreover, after careful verification, it is found that when the milling time reaches 30 h, an amorphous phase clearly appears which is confirmed by examining the Debye–Scherrer rings.

Fig. 1 XRD profiles of the $\text{Mg}_{20-x}\text{Y}_x\text{Ni}_{10}$ ($x = 0-4$) alloys milled for 10 h **a** and as-cast and as-milled Y_2 alloy **b**

Fig. 2 HRTEM micrographs and ED patterns of the as-milled $\text{Mg}_{20-x}\text{Y}_x\text{Ni}_{10}$ ($x = 0-4$) alloys: **a** Y_0 alloy, milled for 10 h; **b** Y_1 alloy, milled for 10 h; **c** Y_3 alloy, milled for 10 h; **d** Y_2 alloy, milled for 10 h; **e** Y_2 alloy, milled for 30 h; **f** Y_2 alloy, milled for 70 h

Fig. 3 Discharge potential curves of the $\text{Mg}_{20-x}\text{Y}_x\text{Ni}_{10}$ ($x = 0-4$) alloys milled for 10 h **a** and as-cast and as-milled Y_2 alloy **b**

3.2 Electrochemical Performances

3.2.1 Discharge Potential and Discharge Capacity

The discharge potential curves of the as-cast and as-milled $\text{Mg}_{20-x}\text{Y}_x\text{Ni}_{10}$ ($x = 0-4$) alloy electrodes are shown in

Fig. 3 with a current density of 40 mA/g at the first charging/discharging cycle because all the alloys can be easily activated to reach the maximum capacity during the first cycle. The discharge potential characteristic, which directly determines the stability of the output power, is a very important performance indicator of the alloy electrode

Fig. 4 Evolutions of the discharge capacity of the $\text{Mg}_{20-x}\text{Y}_x\text{Ni}_{10}$ ($x = 0-4$) alloys milled for 10 h **a** and as-cast and as-milled Y_2 alloy **b**

Fig. 5 Evolution of S_n values of the $\text{Mg}_{20-x}\text{Y}_x\text{Ni}_{10}$ ($x = 0-4$) alloys milled for 10 h **a** and as-cast and as-milled Y_2 alloy **b**

and is characterised by the potential plateau of the discharge curve of the alloy. A longer and more horizontal discharge curve potential plateau indicates better discharge potential characteristics of the alloy. It is noted that both the substitution of Y for Mg and the mechanical milling markedly improve the discharge potential characteristics of the alloys, enhancing the discharge potential and lengthening the discharge plateau. In addition, Y substitution for Mg and mechanical milling clearly affect the discharge capacity of the alloys, as demonstrated in Fig. 4. It is observed that the discharge capacities of the alloys first increase and then decline with increasing Y content and milling time. Specifically, when the Y content increases from 0 to 4, the discharge capacity of the as-milled (10 h) alloys increases from 105.5 ($x = 0$) to 352.8 mAh/g ($x = 3$) and then declines to 341.5 mAh/g ($x = 4$). Additionally, when the milling time increases from 0 h (the as-cast condition is defined as a milling time of 0 h) to 70 h, the discharge capacity of the Y_2 alloy increases from 149.7 (0 h) to 379.6 mAh/g (30 h) and then decreases to 302.5 mAh/g (70 h).

3.2.2 Electrochemical Cycle Stability

The cyclic stability of a hydrogen storage alloy is one of the major performance indicators used to evaluate whether an alloy can be applied as a negative electrode material. This property is characterised by the capacity retaining rate (S_n), which is defined as $S_n = C_n/C_{\max} \times 100\%$, where $C_{\max}$ is the maximum discharge capacity and C_n is the discharge capacity of the n th charge–discharge cycle at a current density of 40 mA/g. If an alloy electrode can maintain a higher capacity retention rate after repeated charge–discharge cycles, we say it exhibits superior electrochemical cyclic stability and is more appropriate to act as a negative electrode material for Ni/MH batteries. The variations in the S_n values of the as-cast and as-milled $\text{Mg}_{20-x}\text{Y}_x\text{Ni}_{10}$ ($x = 0-4$) alloys with cycle number is described in Fig. 5, from which the degradation process of the discharge capacity of the alloys can be clearly observed. Evidently, the degradation rate of the discharge capacity of the as-milled alloys dramatically decreases with increasing Y content, suggesting that the substitution of Y

Fig. 6 Evolutions of the S_{20} values of the $Mg_{20-x}Y_xNi_{10}$ ($x = 0-4$) alloys milled for 10 h **a** and as-cast and as-milled Y_2 alloy **b**

Fig. 7 Evolution of the HRDs of the $Mg_{20-x}Y_xNi_{10}$ ($x = 0-4$) alloys milled for 10 h **a** and as-cast and as-milled Y_2 alloy **b**

for Mg makes a positive contribution to the cycle stability. Furthermore, we can see that the degradation rate of the discharge capacity of the Y_2 alloy clearly increases with increasing milling time. To directly demonstrate the effects of the Y content and milling time on the cycle stability of the alloys, the relationships between the S_{20} ($n = 20$) value of the alloy and the Y content and between the S_{20} value and the milling time are illustrated in Fig. 6. Evidently, the S_{20} value considerably increases with increasing Y content but clearly decreases with increasing milling time prolonging. More specifically, the S_{20} value of the as-milled (10 h) alloy is enhanced from 38.3 to 80.2% by increasing the Y content from $x = 0$ to $x = 4$, while prolonging the milling time from 0 to 70 h results in a decrease in the S_{20} value of the Y_2 alloy from 80.9 to 60.8%.

3.2.3 Electrochemical Kinetics

In general, the electrochemical kinetics of an alloy electrode is symbolised by its high rate discharge ability (HRD), which is defined as $HRD = C_i/C_{40} \times 100\%$,

where C_i and C_{40} are the maximum discharge capacities of the alloy electrode charged–discharged at a current density of i and 40 mA/g, respectively. The evolutions of the HRDs of the as-cast and as-milled $Mg_{20-x}Y_xNi_{10}$ ($x = 0-4$) alloys with discharge current density are depicted in Fig. 7. It is unavoidable that the discharge capacity of an electrode alloy more or less decreases with increasing current density. However, maintaining a high discharge capacity during the process of charge–discharge cycles with a large current density is important for practical applications of an alloy electrode in Ni–MH batteries and, in particular, in power batteries. We observe that Y substitution for Mg and mechanical milling significantly affect the HRD of the alloys. Based on the data in Fig. 7 at a current density of 200 mA/g ($i = 200$ mA/g), the relationships between the HRD of the as-milled (10 h) alloys and the Y content and between the HRD of the Y_2 alloy and the milling time can be established, as shown in Fig. 7a, b, respectively. When the Y content (x) increases from 0 to 4, the HRD of the as-milled (10 h) alloys increases from 50.8% ($x = 0$) to 75.2% ($x = 2$) and then

Fig. 8 Semilogarithmic curves of anodic current versus time responses of the $\text{Mg}_{20-x}\text{Y}_x\text{Ni}_{10}$ ($x = 0-4$) alloys milled for 10 h **a** and as-cast and as-milled Y_2 alloy **b**

Fig. 9 Tafel polarisation curves of the $\text{Mg}_{20-x}\text{Y}_x\text{Ni}_{10}$ ($x = 0-4$) alloys milled for 10 h **a** and as-cast and as-milled Y_2 alloy **b**

decreases to 70.7% ($x = 4$). In addition, when the milling time increases from 0 to 70 h, the HRD of the Y_2 alloy increases from 73.4% (0 h) to 77.4% (30 h) and then decreases to 63.5% (70 h).

It is well known that the HRD of an alloy electrode is primarily dominated by the hydrogen diffusion capability in the bulk alloy and the charge-transfer rate on the alloy electrode surface [21]. Hence, it is necessary to investigate the effects of Y substitution for Mg and the milling time on the diffusion ability of hydrogen atoms and the charge-transfer rate to reveal the mechanism of the electrochemical kinetics of the alloy affected by increasing the Y content and milling time.

The hydrogen diffusion ability is characterised by the hydrogen diffusion coefficient, which can be derived using the semilogarithmic curves of anodic current versus working duration of an alloy electrode, as demonstrated in Fig. 8. Based on White's model [22], the diffusion coefficient of the hydrogen atoms in the bulk of the alloy could be easily calculated using the slope of the linear region of

the corresponding plots according to the following formulae:

$$\log i = \log \left(\pm \frac{6FD}{a^2} (C_0 - C_s) \right) - \frac{\pi^2 D}{2.303 a^2} t, \quad (1)$$

$$D = - \frac{2.303 a^2 d \log i}{\pi^2 dt}, \quad (2)$$

where i is the diffusion current density (A/g), D is the hydrogen diffusion coefficient (cm^2/s), C_0 is the initial hydrogen concentration in the bulk of the alloy (mol/cm^3), C_s is the hydrogen concentration on the surface of the alloy particles (mol/cm^3), a is the alloy particle radius (cm), d is the density of the hydrogen storage alloy (g/cm^3), and t is the discharge time (s). The evolutions of the D values of the alloys can be derived using Eq. (2) with Y content and milling time, as shown in Fig. 8a and b, respectively. Clearly, the D values of the alloys first increase and then decrease with increasing Y content and milling time, which is similar to the variation trends of the HRDs of the alloys, indicating that the diffusion ability of hydrogen atoms is a

very important factor in the electrochemical kinetics of the alloy.

The limiting current density (i_L), which is another important electrochemical kinetic parameter associated with diffusion rate of hydrogen, can be obtained by measuring the Tafel polarisation curve, as depicted in Fig. 9. In all cases, each anodic polarisation curve has a clear inflection point, namely the existence of a critical value, which is termed the i_L . This inflection point is viewed as being the result of an oxidation reaction occurring on the surface of the alloy electrode, and the oxidation layer hinders hydrogen atoms from further penetrating [21]. Thus, the i_L can be regarded as a critical current density for passivating. According to the data provided in Fig. 9, the relationships between the i_L values of the alloys and the Y content and between the i_L values with the milling time can be established, as demonstrated in Fig. 9a and b, respectively. Apparently, the alloys have maximum i_L values with varying Y content and milling time.

The charge-transfer capability can be qualitatively evaluated by its EIS in consideration of Kuriyama's model [23]. In Fig. 10, the EIS curves of the as-cast and as-milled $\text{Mg}_{20-x}\text{Y}_x\text{Ni}_{10}$ ($x = 0-4$) alloys are presented, from which it can be observed that each EIS has two distorted capacitive loops in the high- and middle-frequency regions separately as well as a line in the low-frequency region, which very well expresses the electrochemical process of the alloy electrode. The smaller semicircle in the high-frequency region is regarded as reflecting the contact resistance between the alloy powder and conductive material, and the larger one in the middle-frequency region corresponds to the charge-transfer resistance on the alloy surface, whereas the straight line in the low-frequency region represents the atomic hydrogen diffusion in the alloy. In such cases, the charge-transfer capability can be easily estimated; namely, a larger radius of the semicircle in the

middle-frequency region indicates a higher charge-transfer resistance of the alloy electrode. Figure 10 clearly demonstrates that the radii of the large semicircles of the alloys in the middle-frequency region first shrink and then expand with increasing Y content and milling time, implying that the charge-transfer ability of the alloy electrode first increases and then decreases, which is very similar to the evolutions of the HRDs of the alloys, suggesting that the charge-transfer ability of the surface of the alloy electrode is also an important factor affecting the electrochemical kinetics of the alloy.

4 Discussion

The characterisation of the structures by XRD and HRTEM reveals that the substitution of Y for Mg results in the formation of $\text{YMgNi}_4 + \text{YMg}_3$ phases and facilitates the glass forming of the Mg_2Ni alloy. Furthermore, the mechanical milling enables the polycrystalline structure of the as-cast alloys to transform into a nanocrystalline and amorphous structure. It is believed that the modified structures caused by Y substitution and mechanical milling lead to the change in the electrochemical performances of the alloys.

Lai *et al.* [24] considered that the discharge potential of an alloy electrode is closely related to the internal resistance of the battery, including the ohmic internal resistance and polarisation resistance, which mainly depend on the diffusion of hydrogen atoms in the alloy and decrease with an increase in the diffusion coefficient of hydrogen atoms. The discharge potential of the alloy electrode first increases and then decreases with increasing Y content and milling time, which is very similar to the variation trend of the diffusion coefficient of hydrogen atoms in the alloy, as observed in Fig. 8. This behaviour indicates that the

Fig. 10 EIS of the $\text{Mg}_{20-x}\text{Y}_x\text{Ni}_{10}$ ($x = 0-4$) alloys milled for 10 h **a** and as-cast and as-milled Y_2 alloy **b**

diffusion coefficient of hydrogen atoms is a predominate factor of the discharge potential of the alloy electrode.

The discharge capacity of an alloy electrode is determined by multiple factors, involving its crystal structure, phase composition and structure, grain size, composition homogeneity and surface state. The discharge capacities of the alloys have maximum values with variation in the Y content and milling time, indicating that Y substitution for Mg and mechanical milling cause beneficial and detrimental effects on the discharge capacity. The positive action caused by Y substitution is attributed to the decreased thermal stability of the Mg-based hydride [25, 26], enhancing the electrochemical discharge ability of the Mg-based alloy. The negative action is most likely attributed to the change in the major phase from Mg_2Ni to $\text{YMgNi}_4 + \text{YMg}_3$ when the Y content $x \geq 2$ because the amorphisation of the YMgNi_4 phase generated by mechanical milling markedly decreases its discharge capacity, which will be reported later. The positive contribution of mechanical milling on the discharge capacity of the alloy is attributed to the nanocrystalline structure created by mechanical milling. The formation of nanocrystalline grains dramatically increases the grain boundary fraction, which undoubtedly promotes the hydrogen storage properties because the hydrogen concentration in grain boundaries is much higher than that in the grain interior region and amorphous region [27, 28]. Furthermore, the internal strain increases with decreasing crystal size, which accelerates the hydrogen-absorbing/desorbing process [20, 29]. In other words, the amount of hydrogen absorption in the as-milled Mg_2Ni alloy increases with increasing internal strain. In addition, it has been reported that nanocrystalline Mg_2Ni alloys can electrochemically absorb and desorb a large amount of hydrogen at room temperature [30]. The negative contribution caused by mechanical milling to the

discharge capacity is considered to be associated with the formation of an amorphous structure. The substitution of Y for Mg facilitates the glass forming, and the amount of the amorphous structure increases with increasing milling time. Evidently, an amorphous structure is disadvantageous to capacity, as it is known that nanocrystalline microstructures can accommodate larger amounts of hydrogen than an amorphous structure.

Indeed, it is well known that the sharp degradation of the discharge capacity of an Mg_2Ni alloy during the charge–discharge cycling is caused by the formation and thickening of a $\text{Mg}(\text{OH})_2$ surface layer, which hinders the hydrogen atoms from diffusing in or out in alkaline solution [31]. However, the hydrogen storage material sustains an inevitable volume change during the charge/discharge process, resulting in alloy cracking and pulverising, which, in turn, makes the surface of the material apt to be oxidised. Moreover, the capacity degradation of the alloy is thought to be strongly related to the formation of lattice strain containing lattice defects during the milling [32]. The positive contribution of Y substitution for Mg on the cycle stability is attributed to the following phenomena. First, the partial substitution of Y for Mg can improve the resistance of the alloy against corrosion in alkaline solution, increasing the cycle life of the alloy [33], which is considered to be associated with the formation of a dense and protective yttrium oxide on the alloy surface that suppresses further oxidation of Mg and induces a Ni-enriched layer on the alloy surface [16]. Second, rare-earth elements (La, Nd, Sm and Y) can be dissolved in the Mg_2Ni alloy, which can easily enlarge the cell volume of the Mg_2Ni alloy [34], decrease the ratios of expansion/contraction in the process of hydrogen absorption/desorption and then enhance the anti-pulverisation

Fig. 11 SEM images and typical XRD pattern of the as-milled (30 h) Y_2 alloy before and after electrochemical cycling: **a** before cycling; **b** after cycling; **c** XRD pattern of the sample after cycling

capability. In addition, the change in the major phase of the alloy generated by Y substitution for Mg is another important reason resulting from the fact that the LaMgNi₄ phase possesses much higher cycle stability than the Mg₂Ni phase. The impaired cycle stability by mechanical milling is thought to be attributed to the formation of the nanocrystalline structure and production of the lattice strain resulting from milling because the intergranular corrosion is unavoidable [35]. Our experimental results also provide evidence that the major cause leading to the capacity degradation of the alloy is corrosion, as depicted in Fig. 11. The size of the alloy particles does not appear to change significantly after electrochemical cycling, indicating that the pulverisation of alloy particles scarcely occurs in the process of the electrochemical cycle. However, a rough and porous layer can clearly be observed on the surface of the alloy particles after electrochemical cycling, which was determined to be magnesium hydroxide by XRD detection, as shown in Fig. 11c. Hence, we believe that the formation of the rough and flocculent layer is an important factor in the capacity deterioration of the alloy.

The electrochemical hydriding/dehydriding reaction occurring at the hydrogen storage electrode in an alkaline solution during charging and discharging can be summarised as follows:

where M is the hydrogen storage alloy. Equation (3) indicates that when the alloy electrode is charged in a KOH solution, the hydrogen on the interface of the alloy and electrolyte diffuses into the bulk alloy and is then stored in the metallic lattice in the form of a hydride. In the process of discharging, the hydrogen stored in the bulk alloy diffuses towards the surface, where it is oxidised. Evidently, the electrochemical hydrogen kinetics of the alloy electrode is determined by the charge-transfer rate on the surface of the alloy electrode and the hydrogen diffusion capability in the bulk alloy [36]. Northwood *et al.* [37] considered that the diffusion coefficient of hydrogen atoms in metallic lattices is dominated by the strength of the metal–hydrogen interaction and the structure of the alloy. It is known that the hydriding properties of Mg-based alloys are significantly improved by the addition of rare-earth elements and transition metals, which act as catalysts to weaken the bond between Mg and H atoms, consequently yielding an increase in hydrogen diffusion. In addition, Cui *et al.* [38] reported that an increase in the lattice constants and cell volume facilitates a decrease in the diffusion activation energy of hydrogen atoms, which also enhances hydrogen diffusion.

The improved electrochemical kinetics of the alloys by milling is attributed to the refinement of the grains. A

crystalline alloy, when mechanically milled, becomes at least partially disordered, yielding ultrafine grain sizes. In addition, some defects such as dislocations, stacking faults and grain boundaries are introduced. By refining the microstructure, many new crystallites and grain boundaries are created, which can act as fast diffusion paths for hydrogen transport. Moreover, the introduction of defects, disordering and internal strain facilitates increasing hydriding/dehydriding rates. The enhanced charge-transfer rate by milling is primarily attributed to the increased surface area, formation of micro/nanostructures and creation of defects on the surface. Hydrogen attaches more strongly to the surface of a nanocrystalline alloy than to that of a polycrystalline one, accelerating the reaction of the dissociation of hydrogen and yielding an improvement in the electrocatalytic activity of the electrode [21]. Noticeably, a higher Y content ($x \geq 2$) and a longer milling time cause the electrochemical kinetics of the experimental alloys to decrease, for which the formation of an amorphous structure is primarily responsible because an amorphous phase impairs both the charge transfer and hydrogen atom diffusion simultaneously [39].

5 Conclusions

Nanocrystalline and amorphous Mg₂Ni-type Mg_{20-x}Y_xNi₁₀ ($x = 0-4$) alloys were fabricated by mechanical milling. The substitution of Y for Mg facilitates the glass forming in the as-milled alloy. For the Y content $x \geq 2$, Y substitution for Mg causes the major phase of the alloy to transform from Mg₂Ni to YMgNi₄ + YMg₃. The electrochemical measurements indicate that varying the Y content and milling time results in an obvious effect on the discharge potential of the alloy. The discharge capacity of the alloy first increases and then decreases with increasing Y content and milling time. The cycle stability of the alloy clearly increases with increasing Y content but decreases with increasing milling time. The electrochemical kinetics parameters, including HRD, diffusion coefficient (D), limiting current density (i_L) and charge-transfer rate, are first increased and then decreased with increasing Y content and milling time.

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