Structure and Electrochemical Hydrogen Storage Properties of as-Milled Mg–Ce–Ni–Al-Based Alloys

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Abstract

At room temperature, crystalline Mg-based alloys, including Mg₂Ni, MgNi, REMg₁₂ and La₂Mg₁₇, have been proved with weak electrochemical hydrogen storage performances. For improving their electrochemical property, the Mg is partially substituted by Ce in Mg–Ni-based alloys and the surface modification treatment is performed by mechanical coating Ni. Mechanical milling is utilized to synthesize the amorphous and nanocrystalline Mg_{1-x}Ce_xNi_{0.9}Al_{0.1} ($x=0, 0.02, 0.04, 0.06, 0.08$) + 50 wt%Ni hydrogen storage alloys. The effects made by Ce substitution and mechanical milling on the electrochemical hydrogen storage property and structure have been analyzed. It shows that the as-milled alloys electrochemically absorb and desorb hydrogen well at room temperature. The as-milled alloys, without any activation, can reach their maximal discharge capacities during first cycling. The maximal value of the 30-h-milled alloy depending on Ce content is 578.4 mAh/g, while that of the $x=0.08$ alloy always grows when prolonging milling duration. The maximal discharge capacity augments from 337.4 to 521.2 mAh/g when milling duration grows from 5 to 30 h. The cycle stability grows with increasing Ce content and milling duration. Concretely, the S_{100} value augments from 55 to 82% for the alloy milled for 30 h with Ce content rising from 0 to 0.08 and from 66 to 82% when milling the $x=0.08$ alloy mechanically from 5 to 30 h. The alloys' electrochemical dynamics parameters were measured as well which have maximum values depending on Ce content and keep growing up with milling duration extending.

Keywords Mg–Ni-based alloy · Ce substituting Mg · Surface modification · Mechanical milling · Electrochemical performance

1 Introduction

Human beings are facing two big challenges: the dwindled fossil fuel and accelerated greenhouse effect [1]. A project to limit fossil fuels wasting and reduce carbon dioxide emission is developing alternative energies, especially in vehicles as transport occupies 25% of worldwide entire energy consumption [2] and 23% CO₂ emission [3]. The government

of China has already declared “The regulation of access of new energy automobile production enterprises and products” which pressed the Ni-MH battery to become an auxiliary power and promoted the progress of Ni-MH batteries, whereas innovation must be carried out to ameliorate the performance of Ni-MH batteries and save their costs to gain more recognition from consumers for the electric vehicle (EV) and hybrid electric vehicle (HEV).

Extensive researches have been done to study hydrogen storage systems based upon various metal hydrides. Many metal hydrides with application potential were found [4–8]. Particularly, Mg-based hydrogen storage alloys, which are utilized in negative electrode material in Ni-MH batteries, are regarded as a selected candidate and attract high attention now for the reasons of high capacity and low price [9–14]. The international symposium on metal hydrogen system fundamental and applications (MH2016) still concentrated on the research as well as the application of Mg-based hydrogen storage alloys. Nevertheless, some attempts to apply the

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Mg-based alloys were frustrated because of their extremely terrible electrochemical cycle steadiness and exceedingly inadequate discharge capacity at room temperature when they are applied as negative electrode materials [15]. Apparently, drastically improving the electrochemical properties of Mg-based alloys is an enormous scientific challenge.

It is on the surface of alloys that $\text{Mg}(\text{OH})_2$ layers will form and grow during electrochemical reaction process. In charge transfer and hydrogen diffusion reactions, the $\text{Mg}(\text{OH})_2$ layer may consume active materials, serve as barriers and cause capacity degradation of Mg-based alloys [16, 17]. This detrimental phenomenon can be aggravated by the pulverization upon cycles which creates a new active surface and forms additional $\text{Mg}(\text{OH})_2$ when contacting with electrolyte [18]. In Mg-based alloys, an effective way to prohibit the capacity decay is to substitute Mg and/or Ni partially to adjust the composition. In this way, the alloy oxidation resistance can be improved in KOH electrolyte. Moreover, decreasing the expansion coefficient of the material following hydrogen absorption can enhance the anti-pulverization ability of electrodes. Adding rare earth (RE) or/and transition elements in Mg–Ni-based alloys is beneficial for enhancing electrode characteristics, especially the cycle stability which is attributed to the enhanced corrosion resistance [19–21]. Tian et al. [22] have researched the effects of Pd substituting Mg on the electrochemical performances of $\text{Mg}_{0.9-x}\text{Ti}_{0.1}\text{Pd}_x\text{Ni}$ ($x=0.04\text{--}0.1$) alloy. The results showed that the electrochemical cycle stability was greatly enhanced because of the newly formed passivation layer covering the alloys. By melt spinning, Zhang et al. [23] prepared $\text{La}_4\text{MgNi}_{17.5}\text{Mn}_{1.5}$ alloy which composed CeCu_5 -type, $\text{Pr}_5\text{Co}_{19}$ -type and CeNi_2 -type phases. They found that this alloy has better cycle stability and higher discharge capacity compared with the as-cast alloy. Yang et al. [24] improved the cycle stability and discharge kinetic performance of Mg–Al–Ni alloy by replacing partial Al by Ti.

Surface modification, especially mechanical coating, is a valid way to improve Mg-based alloys' electrochemical performances. The effect of mechanical coating Ni or Ni-5 at% Al on the Mg-50 wt%Ni alloy has been investigated by Santos et al. [25], which exhibits a significant enhancement in cycle stability and maximal discharge capacity. Du et al. [26] introduced graphite to Mg_2Ni by mechanical milling, which improved the alloy's cycle stability and increased the discharge capacity at 20th cycle from 116.9 to 178.5 mAh/g. Also, Sun et al. [27] ball-milled $\text{Mg}_{24}\text{Ni}_{10}\text{Cu}_2$ with Ni powder, which introduced a nanocrystalline and amorphous structure to the alloy, improved the electrochemical capacity to 899.2 mAh/g and promoted the alloy's high rate discharge capacity.

Young et al. [28] added Al in Mg–Ni-based alloys, which increased the cycle stability of alloys. A study made by us before showed that the discharge capacity, electrochemical

kinetics and cycle stability of Mg–Ni-based alloys can be improved by adding Ce [29]. Meanwhile, a Ni coating layer, in addition to corrosion inhibition, can behave as an electrocatalytic role in electrochemical processes, like hydrogen diffusion inside alloys and charge transfer on the alloy surface. As for the present work, for obtaining a synthetic improvement on Mg–Ni-based alloy's electrochemical performances, Mg and Ni were partly substituted by Ce and Al, respectively, and a Ni coating layer was made through ball milling. The influences on the electrochemical performances of $\text{Mg}_{1-x}\text{Ce}_x\text{Ni}_{0.9}\text{Al}_{0.1}$ ($x=0, 0.02, 0.04, 0.06, 0.08$) + 50 wt%Ni composites made by milling duration and Ce content were researched. The mechanism underlying the influences was discussed. For convenience, 50Ni is used to symbolize 50 wt%Ni in this study.

2 Experimental

The experimental alloys $\text{Mg}_{1-x}\text{Ce}_x\text{Ni}_{0.9}\text{Al}_{0.1}$ ($x=0\text{--}0.08$) were obtained through a vacuum induction furnace. The smelting environment was a 0.04 MPa helium atmosphere for the purpose of avoiding Mg from volatilization. The liquid alloy was poured into a mold which was made of copper and cooled by water; thus, the cast ingots were formed. The ingots were crushed into powders with about 50 μm in diameter. With a ratio of 2:1 in weight, the alloy and nickel powders were mixed. Then, a planetary-type miller was utilized to mill the mixed powders. The milling progress was under argon atmosphere for the propose of avoiding powders from being oxidized. The samples were handled in a glove box which was filled with argon to prevent oxidation. With the ratio of 35:1 in weight, grinding balls and the powders were put together in stainless steel ball mill tanks with a fixed milling speed of 135 rpm and different milling durations of 5, 10, 20 and 30 h, respectively. For describing conveniently, Ce content is utilized to denote the alloys, just as Ce_0 , $\text{Ce}_{0.02}$, $\text{Ce}_{0.04}$, $\text{Ce}_{0.06}$ and $\text{Ce}_{0.08}$.

With the experimental parameters of 160 mA, 40 kV and $10^\circ/\text{min}$, X-ray diffraction (XRD) (D/max/2400) was utilized to determine the phase structures of sample alloys. The diffraction was performed with $\text{CuK}_{\alpha 1}$ radiation filtered by graphite. The morphologies of the as-cast $\text{Mg}_{1-x}\text{Ce}_x\text{Ni}_{0.9}\text{Al}_{0.1}$ ($x=0\text{--}0.08$) alloys were observed by using a Philips scanning electron microscope (SEM, QUANTA 400). The alloys' composition was analyzed with the help of the equipped energy-dispersive X-ray detector (EDX). The high-resolution transmission electron microscope (HRTEM, JEM-2100F) was also utilized in observation. The crystalline states were measured by electron diffraction (ED).

With the weight ratio of 1:4, the mixture of alloy and carbonyl nickel powders was cold-pressed under 35 MPa to

form a round electrode pellet whose diameter was 15 mm and weight was 1 g. The tri-electrode open cell, containing a working electrode, a sintered $\text{Ni}(\text{OH})_2/\text{NiOOH}$ counter electrode and a Hg/HgO reference electrode, was immersed in 6 mol/L KOH electrolyte at 303 K and used to measure the samples' electrochemical performances. The potential difference between the reference and negative electrodes is discharge voltage. In the process of testing the electrochemical property of an alloy electrode, the electrode was fully charged with a constant current density of 60 mA/g at first. Then, after a 15-min rest, the alloy electrode was discharged with different current densities till -500 mV for measuring different electrochemical properties. The discharge current remained 60 mA/g when measuring the activation capability and discharge potential curve. The discharge current density for testing alloys' capacity retaining rate was set at 300 mA/g. For getting alloys' high rate discharge ability, the electrode was discharging at different current densities of 300, 600, 900 and 1200 mA/g, respectively.

The measurements of electrochemical impedance spectra (EIS) and potentiodynamic polarization curves at 303 K of samples were taken with the electrochemical workstation of PARSTAT 2273. Before measurement, a series of electrochemically charge and discharge cycling were performed for the propose of activating experimental materials. When the fresh electrodes were charged fully, it needed to rest for

2 h for making the open circuit potential stable. The EIS of alloys were measured after discharging for 50% depth. The frequency range was from 10 kHz to 5 MHz, the alternating current amplitude was 5 mV, and the point number of each curve was 60. With the potential ranging from -1.2 to $+1.0$ V and scan rate being 5 mV/s, the potentiodynamic polarization curves were measured. As for potentiostatic discharge, the fully charged electrodes were discharging at 500 mV for 5000 s at the electrochemical workstation.

3 Results and Discussion

3.1 Microstructure Characterization

Figure 1 presents the XRD images of as-milled $\text{Mg}_{1-x}\text{Ce}_x\text{Ni}_{0.9}\text{Al}_{0.1}$ ($x=0-0.08$) + 50Ni composites. Just as what we can see from it, the diffraction peaks of as-milled (30 h) alloys are broad and flat, revealing there exists an amorphous and nanocrystalline structure. When extending milling duration from 5 to 30 h, the diffraction peaks are considerably broadened, indicating the appearance of amorphization or/and nanocrystallization. Generally, inhomogeneous strain and grain size change can be used to explain the broadening of diffraction peaks. With the prolongation of

Fig. 1 XRD profiles of sample alloys: **a** as-milled $\text{Mg}_{1-x}\text{Ce}_x\text{Ni}_{0.9}\text{Al}_{0.1}$ ($x=0-0.08$) + 50Ni alloys milled for 30 h, **b** $\text{Ce}_{0.08}$ alloy for different milled time

milling time, the diffraction peaks become broader, meaning the elevation of internal stress and defects inside materials.

SEM and the equipped EDX were used to measure the as-cast alloys. The SEM images and EDX curves are shown in Fig. 2. A dramatic refinement happens in the grains of as-cast alloys with Ce substitution for Mg. Similar results have been found in the investigations of A_2B_7 -type and AB_2 -type alloys [29, 30]. The grain refinement is in favor of enhancing the strength and toughness of alloys, consequently improving their anti-pulverization capability [31]. Synthetically analyzing the XRD curves above and the EDX curves as shown in Fig. 2e–g, the composition of different phases can be confirmed. Some similar results have been reported by other researchers [32–34].

As seen in Fig. 3, HRTEM was used to analyze the morphological characteristic and crystal state of the as-milled $Mg_{1-x}Ce_xNi_{0.9}Al_{0.1}$ ($x=0-0.08$) + 50 wt% Ni composites. Through observing Debye–Scherrer rings, an amorphous and nanocrystalline structure can be confirmed. The proportion of amorphous phase increases with Ce content and milling time grow. Obviously, with milling duration extending from 10 to 30 h, the disordered degree elevates and the grain sizes conspicuously shrink. Mechanical milling leads to an amorphous structure and ultrafine grains because it causes non-stabilization of the lattice and stores large quantity of

internal energy. Furthermore, in the as-milled alloys, lots of different crystal defects appear, like dislocations, crystal boundaries and stacking faults. As crystal defects provide low activation energy sites, hydrogen diffusion will be accelerated when many lattice defects exist [35].

3.2 Electrochemical Performances

In Fig. 4, the effects of cycling number on the discharge capacity of as-milled specimens at 60 mA/g are delineated. Clearly, at the first discharging process, the as-milled alloy can reach its maximum discharge capacity with no activation, meaning the experimental alloys possess a remarkable activation property. The Ce substitution for Mg does not weaken the activation capability of alloys. It is necessary for the materials in Ni–MH batteries to be activated easily. Apparently, the experimental alloys show better activation capability than the alloys that need several charging and discharging cycles before attaining maximum discharge capacity, such as AB_5 -type alloys. The outstanding activation performances are considered to be related to the coating Ni which results in the formation of an active surface. Besides, it is a crucial part to elevate the activation capability that ball milling is able to produce a lot of interfaces by creating ultrafine grains and nanocrystalline. Ma et al. [36] reported

Fig. 2 SEM images and EDX curves of the as-cast $Mg_{1-x}Ce_xNi_{0.9}Al_{0.1}$ ($x=0-0.08$) alloys: **a–d** SEM of Ce_0 , $Ce_{0.04}$, $Ce_{0.06}$ and $Ce_{0.08}$ alloys, **e–g** EDX of Mg_2Ni , Ni and Ce_2Ni_7

Fig. 3 HRTEM micrographs and ED patterns of the as-milled $\text{Mg}_{1-x}\text{Ce}_x\text{Ni}_{0.9}\text{Al}_{0.1}$ ($x=0-0.08$) + 50Ni alloys milled for different durations: **a–c** Ce_0 , $\text{Ce}_{0.04}$ and $\text{Ce}_{0.06}$ alloys milled for 10 h; **d–f** $\text{Ce}_{0.08}$ alloy milled for 10 h, 20 h and 30 h

that compared with polycrystalline nickel, nanocrystalline nickel can stick hydrogen on the electrode surface much stronger. Thus, it can elevate the activation property of the electrodes and accelerate the dissociation reaction of hydrogen. Chen et al. [37] ball-milled Mg_2NiH_4 with nano-nickel, which is beneficial for promoting the charge transfer reaction on alloy surface and the hydrogen diffusion inside hydride bulk, thus, leading to an enhancement of the activation performance of the sample electrode. Li et al. [38] drew a similar conclusion as well.

Capacity retaining rate (S_n) can be utilized to characterize the ability of restraining capacity degradation of an alloy electrode which is known as cycle stability and calculated by $S_n = C_n/C_{\max} \times 100\%$. The maximal discharge capacity is represented by $C_{\max}$ and the discharge capacity of the n th dis-

charging cycle is symbolized by C_n in the previous equation. In this experiment, the discharge current density was set at 300 mA/g for testing alloys' capacity retaining rate. For the 30-h-milled alloys, the $C_{\max}$ values are 412.6, 463.8, 519.4, 469.8 and 450.8 mAh/g, respectively, with Ce content increases from $x=0$ to $x=0.08$. As for the $\text{Ce}_{0.08}$ alloy, when milling time increases from 5 to 30 h, the $C_{\max}$ values are 197.4, 321.8, 422.5 and 450.8 mAh/g, respectively. Figure 5 shows the evolution of S_n value of sample alloys when the cycle number is an independent variable, which clearly reflects the decay process of discharge capacity. When Ce content and milling duration increase, the degradation rate of discharge capacity diminishes drastically. For directly showing the effect of Ce content and milling duration on cycle stability, we take the capacity retaining rate of the 100th

Fig. 4 Evolution of the discharge capacity of sample alloys: (a) as-milled $\text{Mg}_{1-x}\text{Ce}_x\text{Ni}_{0.9}\text{Al}_{0.1}$ ($x=0-0.08$) + 50Ni alloys milled for 30 h, (b) $\text{Ce}_{0.08}$ alloy for different milled times

Fig. 5 Evolution of the capacity retaining rates (S_n) of sample alloys: **a** as-milled $\text{Mg}_{1-x}\text{Ce}_x\text{Ni}_{0.9}\text{Al}_{0.1}$ ($x=0-0.08$) + 50Ni alloys milled for 30 h, **b** $\text{Ce}_{0.08}$ alloy for different milled time

cycle (S_{100}) as a criterion. Hence, the S_{100} value dependence of Ce content and milling duration can be obtained and is provided in Fig. 6. The S_{100} value markedly grows when Ce content and milling duration increase. To be specific, the S_{100} value of 30-h-milled alloys rises from 55 to 82% with Ce content increasing from 0 to 0.08 and it augments from 66 to 82% for $\text{Ce}_{0.08}$ alloy when milling duration extending from 5 to 30 h.

For investigating how ball milling and Ce substitution affect the cycle stability of alloys positively, the SEM images of alloys before and after electrochemical cycles and the XRD curve of $\text{Ce}_{0.08}$ after cycling were measured, as shown in Fig. 7. After several electrochemical cycles, some cracks appear on the alloy particle surface. Comparing Fig. 7b and c, we find that the cracks decrease with milling time

prolonging, which means the increase in alloy's cycle stability. This cycle stability enhancement is thought to be in connection with the formation of a dense Ni coating layer. During mechanical milling progress, through the repeated collision between balls and powders, nickel will be deformed mechanically and form a coating layer covering alloy particles because of the ductility of Ni. Apparently, the compactness of Ni coating layer increases when prolonging milling duration, which enhances the alloy's corrosion resistance and cycle stability. The XRD curve of 30-h-milled $\text{Ce}_{0.08}$ alloy reveals that Ce in Mg-based alloys will transform into CeO_2 after charging/discharging cycles in 6 mol/L KOH electrolyte. CeO_2 is insoluble and compact in alkaline aqueous solution. When the CeO_2 grains intersperse in the porous $\text{Mg}(\text{OH})_2$ layer, a corrosion-resistant passive film

Fig. 6 Evolution of the capacity retaining rates (S_n) of sample alloys: **a** as-milled $\text{Mg}_{1-x}\text{Ce}_x\text{Ni}_{0.9}\text{Al}_{0.1}$ ($x=0-0.08$) + 50Ni alloys milled for 30 h, **b** $\text{Ce}_{0.08}$ alloy for different milled times

Fig. 7 SEM images before and after electrochemical cycles and XRD curve after cycling of $\text{Ce}_{0.08}$ alloy: **a** 5-h-milled $\text{Ce}_{0.08}$ before cycling, **b** 5-h-milled $\text{Ce}_{0.08}$ after cycling, **c** 30-h-milled $\text{Ce}_{0.08}$ after cycling, **d** 30-h-milled $\text{Ce}_{0.08}$ after cycling

will form. The passive film makes the OH^- ion penetration difficult and prevents the inner alloy from oxidation, which results in the improvement corrosion resistance and cycle stability of alloys. The advantage of core-shell structure

has been reported by many researchers as well. Sun et al. [39] coated $\text{Ti}_{1.4}\text{V}$ alloy with a Cu layer. The coating layer can enhance not only the electrochemical hydrogen storage capacity, but also the corrosion resistance. Lu et al. [40]

covered the metal-nitride supercapacitor electrodes with a thin carbon shell. The carbon shell can improve the cycle stability of electrodes by suppressing their electrochemical oxidation reactions. Transition metals and rare earth elements were also used to prepare core-shell structured Mg-based composites [41–43]. The transition metal or rare earth oxide shells showed good catalysis, especially in dehydrogenation progress.

Figure 8 shows the discharge potential curves of specimens. The potential plateau in discharge curves can characterize a battery of its discharge potential characteristics and the stability of output power. The output power will be more stable when the discharge plateau turns more horizontal and longer. Notably, just like the experimental alloys shown in Fig. 8, slope potential plateaus exist in all discharge potential curves of Mg-based alloys as a common feature, which has been reported by many kinds of references [44–46]. Increasing Ce content and milling duration will conspicuously increase the discharge potential and prolong the discharge plateau, thus improving the discharge potential characteristics of electrodes. The potential characteristics of batteries are compactly related to their internal resistance which includes ohmic internal resistance and polarization resistance. The internal resistance will decrease with the hydrogen diffusing coefficient increasing [47]. Lots of efficient diffusion paths for hydrogen atoms are provided by grain boundaries. Increasing Ce content and milling duration will improve the refinement of alloy grains, which will provide more grain boundaries, thus improving the potential characteristics [48]. In Fig. 8, the discharge capacities as a function of Ce content and milling duration are depicted. The discharge capacity initially ascends and subsequently descends for the 30-h-milled alloys when increasing Ce content, while it always grows with milling duration prolonging

for the $\text{Ce}_{0.08}$ alloy. Concretely, the discharge capacity augments firstly from 482 mAh/g (Ce_0) to 578.4 mAh/g ($\text{Ce}_{0.04}$), soon after decreases to 521.2 mAh/g ($\text{Ce}_{0.08}$) for the 30-h-milled alloys, but that of $\text{Ce}_{0.08}$ alloy grows from 337.4 to 521.2 mAh/g with the prolongation of milling time from 5 to 30 h. Many researchers have reported the advantageous effects caused by Ce substituting Mg on the discharge capacity of Mg-based alloys. Spassov et al. [49] reported that adding rare earth element into Mg–Ni-based alloys can improve their glass formation and hydrogen absorption. Ma et al. [50] introduced Ce in a Mg–Li–Al–Ce alloy, which increased its anti-corrosion ability and electrochemical activity. Yartys et al. [51] obtained the best electrochemical property of RE–Mg–Ni-based alloys by adjusting the proportion of rare earth element. As for the positive side of prolonging milling duration acting on discharge capacity is related to the refined grains since the maximal hydrogen concentration distributes at grain boundaries [52]. Besides, in the charge/discharge process, the electrodes performances will be enhanced by the homogeneously dispersed Ni inclusions which can provide electrocatalytic sites and impair the charge transfer resistance.

3.3 Electrochemical Kinetics

It is a common method to analyze the electrochemical kinetics of alloy electrodes through high rate discharge ability (HRD). The HRD value can be gotten through the formula of $\text{HRD} = C_i/C_{60} \times 100\%$. In this formula, the maximal discharge capacity of an electrode during charging/discharging processes at i mA/g is represented by C_i and the maximal discharge capacity at 60 mA/g is represented by C_{60} . Figure 9 presents the variety of the HRDs with discharge current density. The HRD distinctly declines when current

Fig. 8 Discharge potential curves of sample alloys: **a** as-milled $\text{Mg}_{1-x}\text{Ce}_x\text{Ni}_{0.9}\text{Al}_{0.1}$ ($x=0-0.08$) + 50Ni alloys milled for 30 h, **b** $\text{Ce}_{0.08}$ alloy for different milled times

Fig. 9 Evolution of the HRD of sample alloys: **a** as-milled $Mg_{1-x}Ce_xNi_{0.9}Al_{0.1}$ ($x=0-0.08$) + 50Ni alloys milled for 30 h, **b** $Ce_{0.08}$ alloy for different milled times

density rises. For directly showing the effect of Ce content and milling duration on HRD values, the current density of 300 mA/g was set as a criterion. The insets in Fig. 9 represent the HRD dependence on Ce content and milling duration. In this experiment, the HRD value initially mounts up then subsequently cuts down when Ce content rises, while it always grows up with milling duration prolonging. Concretely, the HRD ($HRD = C_{300}/C_{60}$) firstly increases from 85.6% (Ce_0) to 94.4% ($Ce_{0.02}$), soon after goes down to 86.5% ($Ce_{0.08}$) for 30-h-milled alloys, but it augments from 58.5 to 86.5% for the $Ce_{0.08}$ alloy while prolonging milling time from 5 to 30 h.

Generally speaking, electrochemical hydrogen storage kinetics principally depends on two things, viz. charge

transferring on electrode surface and hydrogen diffusing inside electrode [53]. For the purpose of deeply understanding the kinetic mechanism, studying how Ce content and milling duration work on the hydrogen diffusing and charge transferring is very necessary. It is suggested by Volodin et al. [54] that the hydrogen diffusion coefficient (D) can be analyzed through potential-step method. Figure 10 shows the semilogarithmic curves of discharging current density versus discharging time of the fully charged samples. It is observed that the $\lg i$ value drops sharply at the beginning, which is related to the electro-oxidation as it reduces the hydrogen concentration absorbed on the electrode surface. Soon afterward, the main decisive factor transfers from the electro-oxidation to hydrogen diffusion, so these curves

Fig. 10 Semilogarithmic curves of anodic current vs. time responses of sample alloys: **a** as-milled $Mg_{1-x}Ce_xNi_{0.9}Al_{0.1}$ ($x=0-0.08$) + 50Ni alloys milled for 30 h, **b** $Ce_{0.08}$ alloy for different milled times

become linear. The D value of electrodes can be estimated by the following equation with the fitting lines of the linear part of the curves demonstrated in Fig. 10 [55]:

$$\lg i = \lg [\pm 6FD(C_0 - C_s)/(da^2)] - \pi^2 Dt/(2.303a^2), \quad (1)$$

$$D = -2.303a^2 [d(\lg i)/d(\lg t)]/\pi^2. \quad (2)$$

In these equations, the diffusion current density is represented by i (A/g), hydrogen diffusion coefficient is represented by D (cm²/s), the initial hydrogen concentration inside alloy and hydrogen concentration on the alloy surface are symbolized by C_0 and C_s (mol/cm³), respectively, a means the alloy particle radius (cm), d stands for the alloy density (g/cm³), and t represents discharging time (s). The dependences of D value on Ce content and milling time are insets in Fig. 10. Evidently, D has a maximal value with Ce content varying, while it keeps growing up when prolonging milling time.

Limit current density (I_L) is another crucial kinetic parameter connected with hydrogen diffusing rate. Potentiodynamic polarization curves were measured to get the I_L value, as presented in Fig. 11. The I_L value is the value of the current density at the inflection point in each potentiodynamic polarization curve. Usually, the I_L is treated as the critical current density for passivation as oxidizing reactions take place at I_L and result in an oxidation layer covering the electrodes which will prevent hydrogen atoms from further penetrating [56]. With the data of Fig. 11, the influences of Ce content and milling duration on I_L value can be built, as the insets in Fig. 11 show. Evidently, I_L grows up firstly then decreases when rising Ce content, while it always increases when prolonging milling duration.

Fig. 11 Potentiodynamic polarization curves of sample alloys: **a** as-milled Mg_{1-x}Ce_xNi_{0.9}Al_{0.1} ($x=0-0.08$)+50Ni alloys milled for 30 h, **b** Ce_{0.08} alloy for different milled times

Electrochemical impedance spectrum (EIS) was measured for assessing the charge transfer rate on the electrode surface based on Kuriyama's model [57]. The EIS curves of the as-milled Ce_{0.08} alloy, as a typical representative, are demonstrated in Fig. 12. The EIS curves show two circular arcs in the high and middle-frequency regions and show a line in the low-frequency region. The smaller semicircle in the high-frequency region symbolizes the contact resistance between alloy powders and conductive material. The charge transfer resistance (R_{ct}) on alloy surface is reflected by the larger semicircle in the middle-frequency region. The linear part corresponding to the low-frequency region represents Warburg impedance. Relying on the equivalent circuit as shown in Fig. 12, we can use the fitting program Z-View to get the fitting line and the R_{ct} value easily. R_{ct} is mainly

Fig. 12 Electrochemical impedance spectra (EIS) of the Ce_{0.08} alloy milled for different times and the equivalent circuit

related to the electrochemical reactivity of the alloy surface as Kuriyama et al. [57] considered. The electrochemical reactivity of alloy surface basically depends on the apparent activation enthalpy change ($\Delta_r H^*$) which is available by using the equation followed [58]:

$$\ln \left[(T/R_{ct}) / (K/\Omega) \right] = C_0 - \Delta_r H^* / (RT). \quad (3)$$

In this equation, the charge transfer resistance is represented by R_{ct} , the temperature of samples is represented by T , K and Ω are the units of temperature and resistance, respectively, R is the gas constant, and C_0 stands for a constant in which the surface area is considered. The EIS curves

of $\text{Mg}_{1-x}\text{Ce}_x\text{Ni}_{0.9}\text{Al}_{0.1}$ ($x=0-0.08$) + 50Ni alloys at 303, 318 and 333 K were measured for getting the $\Delta_r H^*$ value through Eq. (3). As representatives, the EIS curves of $\text{Ce}_{0.02}$ and $\text{Ce}_{0.06}$ alloys milled for 30 h are illustrated in Fig. 13. Based on Eq. (3) and the data in EIS curves, the Kuriyama graphs of $\ln(T/R_{ct})$ versus $1/T$ are established and inset in Fig. 13. The $\Delta_r H^*$ value is able to be gotten expediently from the slopes of the fitting lines of Kuriyama plots. Figure 14 shows the changes of $\Delta_r H^*$ value with Ce content and milling duration. Evidently, the $\Delta_r H^*$ value descends at first and soon after ascends when increasing Ce content, and it drops with the prolongation of milling duration.

Comparing Figs. 9, 10 and 14, we found that the variation tendency of HRD value is similar with D and contrary

Fig. 13 Electrochemical impedance spectra (EIS) of as-milled (30 h) $\text{Ce}_{0.02}$ and $\text{Ce}_{0.06}$ alloys at various temperatures: **a** $\text{Ce}_{0.02}$ alloy, **b** $\text{Ce}_{0.06}$ alloy

Fig. 14 Evolutions of the activation enthalpy $\Delta_r H^*$ values of sample alloys: **a** as-milled $\text{Mg}_{1-x}\text{Ce}_x\text{Ni}_{0.9}\text{Al}_{0.1}$ ($x=0-0.08$) + 50Ni alloys milled for 30 h, **b** $\text{Ce}_{0.08}$ alloy for different milled times

to $\Delta_r H^*$, which means the hydrogen diffusing coefficient and apparent activation enthalpy change have important implications on the high rate discharge ability of electrode. Based on the results in Figs. 10, 11 and 14, the substitution of Ce for Mg exerts both advantageous and pernicious effects on hydrogen diffusing coefficient and charge transferring rate, while ball milling exerts a positive impact. The positive contribution caused by substituting Mg with Ce is that adding Ce improves the alloy's corrosion resistance, which is beneficial for suppressing Mg from further oxidation and inducing a Ni-enriched layer covering the alloy [18], thus improving the electrocatalytic activity of the electrode surface. The further increase in Ce content will consequentially result in the incrustation of CeO_2 passivation layer, which forbids the hydrogen diffusing and charge transferring on the alloy surface. When prolonging milling duration, both the charge transferring rate and hydrogen diffusing rate improve, which mainly because the Ni coating layer possesses a high electrocatalytic activity. Moreover, the improved properties through mechanical milling are also related to the nano-/amorphous structure which accelerates both charge transferring and hydrogen diffusing and brings about a high electrochemical capacity [59]. The amount of interface and grain boundary increases with milling duration extending, which will produce many easy pathways for hydrogen atoms and elevate the absorption of hydrogen.

4 Conclusions

The microstructure characteristics and electrochemical performances of the as-milled $\text{Mg}_{1-x}\text{Ce}_x\text{Ni}_{0.9}\text{Al}_{0.1}$ ($x=0-0.08$) + 50 wt%Ni alloys were investigated comprehensively in this study. The main conclusions can be summarized as follows.

1. A nanocrystalline and amorphous structure will appear in the experimental alloys after ball milling. The grain size of the as-cast alloys considerably shrinks with increasing Ce content.
2. The as-milled alloys display well electrochemical hydrogenation/dehydrogenation characteristics. The cycle stability and discharge capacity visibly improve with increasing milling time, while the discharge capacity shows a maximal value with increasing Ce content.
3. With Ce content growing, the electrochemical kinetics of alloys rises initially and cuts down subsequently, while it keeps growing with milling duration prolonging. The high rate discharge ability is mainly controlled by the hydrogen diffusing coefficient and apparent activation enthalpy change.

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