Highly improved hydrogen storage capacity and kinetics of the nanocrystalline and amorphous PrMg$_{12}$-type alloys by mechanical milling

Y H Zhang $^{1,2,3}$, H W Shang$^2$, Y Q Li$^2$, Z M Yuan$^2$, T Yang$^2$ and D L Zhao$^2$

1 Key Laboratory of Integrated Exploitation of Baiyun Obo Multi-Metal Resources, Inner Mongolia University of Science and Technology, Baotou 014010, China
2 Department of Functional Material Research, Central Iron and Steel Research Institute, Beijing 100081, China

E-mail: zhangyh59@sina.com

Abstract. Nanocrystalline and amorphous PrMg$_{11}$Ni + x wt.% Ni (x = 100, 200) alloys were synthesized by mechanical milling. Effects of Ni content and milling duration on the structures, hydrogen storage capacity and kinetics of the as-milled alloys were investigated systematically. The structures were characterized by XRD and HRTEM. The hydrogen desorption activation energy was calculated by using Kissinger method. The results show that increasing Ni content dramatically improves the electrochemical discharge capacity of the as-milled alloys. Furthermore, the variation of milling time has a significant impact on the kinetics of the alloys. As the milling time increased, the high-rate discharge ability (HRD), gaseous hydrogen absorption capacity and hydrogenation rate increased at first but decreased finally, while the dehydrogenation rate always increased.

1. Introduction

The threat of exhaustion of oil has always perplexed human. It is necessary to develop and use clean energy. Hydrogen is an ideal clean energy, however, it is limited in practical use due to lack of safe methods to store hydrogen [1]. REMg$_{12}$-type alloys are regarded to be the most promising alternative to satisfy the requirements for practical application because of their high hydrogen storage capacity [2]. However, some inherent drawbacks, such as sluggish kinetic and poor cyclic stability, have to be improved for the alloys.

Alloying and microstructure modification are effective approaches for improving the hydrogen storage properties of Mg-based alloys [3, 4], such as partially substituting Mg with rare earth elements [5-8] and adding transition metals [9, 10]. In our previous study, the Mg$_{10}$NiR (R = La, Nd and Sm) alloys possess excellent kinetics by adding rare earth element [11]. Furthermore, the kinetics of the Mg-based alloys is very sensitive to the structures [12]. In the present work, Mg in the PrMg$_{12}$-type alloy was partially substituted by Ni, and mechanical milling was used to fabricate the nanocrystalline and amorphous PrMg$_{11}$Ni + x wt.% Ni (x = 100, 200) alloys. The effects of Ni content and milling time on the hydrogen storage capacity and kinetics have been investigated in detail.

2. Experimental

The experimental alloys were prepared using a vacuum induction furnace. For avoiding the deviation from the stoichiometry, extra 10 percent of Mg was adding into the crucible to make up for Mg losses
During the smelting process, which have been proved quite effective and appropriate in our previous study. In addition, helium is used as a protective atmosphere to restrain Mg from volatilization. Besides that, the method of gradually increasing temperature was taken and the process parameters were repeated adjusted to short the melting time. The molten alloy was poured into a copper mould cooled and a cast ingot was obtained. The as-cast alloys were mechanically crushed into powder with a diameter of about 50 μm and mixed with carbonyl nickel powder with a weight ratio of 1:1 and 1:2 respectively. Then the mixed powder was mechanically milled in a planetary-type mill. The milling speed was 135 rpm and the duration time was 5, 10, 20, 40 and 60 h, respectively.

The phase structures were determined by X-ray diffraction (XRD) (D/max/2400). The diffraction, with the experimental parameters of 160 mA, 40 kV and 10°·min⁻¹ respectively, was performed with CuKα₁ radiation filtered by graphite. The powder samples of the as-milled alloys were observed by high resolution transmission electron microscope (HRTEM) (JEM-2100F, operated at 200 kV) and the crystalline states were ascertained by electron diffraction (ED).

The electrochemical properties of the alloys were measured at 303K using a tri-electrode open cell. The alloy electrodes were first charged, then rested for 15 min, and finally discharged to the cut-off voltage of -0.500 V with a constant current density of 60 mA·g⁻¹. The electrochemical impedance spectra (EIS) were measured at different temperature using an electrochemical workstation (PARSTAT 2273). The fresh electrodes were fully charged and then rested for 2 h for achieving to the stabilization of the open circuit potential. The EIS of the alloy electrodes were measured at a 50% depth of discharge (DOD), the frequency ranging from 10 kHz to 5 mHz, and the amplitude of signal potentiostatic or galvanostatic measurements being 5 mV. The potentiodynamic polarization 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⁻¹.

The gaseous hydrogen absorption capacity and kinetics of the alloys were measured by an automatically controlled Sieverts apparatus. The hydrogen absorption was conducted at 3 MPa of hydrogen pressure and 573 K of temperature. The hydrogen desorption was conducted under the pressure of 1×10⁻⁴ MPa and the same temperature. Hydrogen desorption properties were also measured by using DSC (NETZSCH STA 449F3) at heating rates of 5, 10, 15 and 20 K·min⁻¹.

3. Results and discussion

3.1. Microstructure characteristics

The phase components and structure of the as-cast and milled PrMg₁₁Ni + x wt.% Ni (x =0, 100, 200) alloys are identified by XRD analysis, as shown in figure 1. The as-cast PrMg₁₁Ni alloy contains a major phase PrMg₁₂ and a secondary phase Mg₂Ni. Mechanical milling makes the diffraction peaks of the PrMg₁₂ and Mg₂Ni phases almost disappear, indicating that the crystalline structure has transformed to the nanocrystalline or amorphous structure. The diffraction peaks become broaden is because of a large amount of internal energy were generated in the alloys. In addition, increasing Ni content makes the intensity of diffraction peaks evidently lower and the width clearly increase. It means that increasing Ni content facilitates the glass forming of the alloys. As reported by Abdellaoui et al. [13], increasing Ni content in REMg₁₂ alloys can lower the activation energy that crystalline turns to amorphous. Moreover, it can be seen from figure 1 (b) that PrH₃, MgH₂ and Mg₂NiH₄ are formed in the hydrogen absorption reaction, originating from the following reactions [14, 15]:

\[ \text{Pr}_{12}\text{Mg}_{17} + \text{H}_2 \rightarrow \text{MgH}_2 + \text{PrH}_3 \]  
\[ \text{Mg}_2\text{Ni} + \text{H}_2 \rightarrow \text{Mg}_2\text{NiH}_4 \]

Also, hydrogenation results in the diffraction peaks become broaden, which is ascribed to the lattice internal stress and cell volume expansion generated by hydrogen atoms entering the lattice interstitials. The saturated hydrogen absorption alloys still maintain a nanocrystalline and amorphous structure, meaning that they have good structural stability.

Figure 2 shows HRTEM micrographs and ED patterns of the as-milled PrMg₁₁Ni + x wt.% Ni (x =
Figure 1. XRD profiles of the as-cast and milled PrMg$_{11}$Ni + x% Ni (x = 0, 100, 200) alloys before and after hydriding: (a) before hydriding, (b) after hydriding. It can be seen that the as-milled alloys exhibit a nanocrystalline and amorphous structure, and the amount of the amorphous phase in the as-milled alloys visibly increases with milling time and Ni content increasing, which is supported by the analysis of Debye-Scherrer rings. Also, it is noted that prolonging milling time from 5 h to 20 h gives rise to the grain sizes of the alloys visibly decrease and the disordered degree of the microstructure increase dramatically. It is ascribed to the generation of a large amount of internal energy during mechanical milling, which causes non-stabilization of the lattice, ultimately generating the fine ultrafine grain or amorphous structure.

3.2. Electrochemical discharge capacity and kinetics

Figure 3 presents the relationship between the discharge capacity of the alloys and the milling time. The as-milled alloys exhibit excellent activation capability, reaching to the maximum discharge capacities at the first cycle. The discharge capacities of the alloys markedly increase with milling time increasing, but it is noteworthy that long time milling (more than 40 h) brings on a slight decrease in the discharge capacity for the x = 200 alloy. As desired, increasing Ni content has a great contribution on the discharge capacity of the alloys. To be specific, increasing Ni content from 100 to 200 wt.% makes the discharge capacity of the as-milled (40 h) alloys grow from 141.8 to 1059.4 mAh·g$^{-1}$ at a discharge current density of 60 mAh·g$^{-1}$. Mechanical milling significantly ameliorates the discharge capacity which is most likely ascribed to the formation of the nanocrystalline structure due to hydrogen concentrations in the grain boundary are much higher than that of the grain interior and amorphous region. In addition, it is believed that hydrogen atoms adhere more strongly to the surface of the nanocrystalline nickel than the polycrystalline nickel, and facilitating the dissociation of hydrogen. As for the positive effect caused by increasing Ni content on the discharge capacity, it is unquestionably ascribed to its high electrocatalytic activity. Mechanical milling can cause the cold welding of nickel particles and alloy particles, forming the highly dispersed metallic Ni nanocrystals through alloy matrix which reduces the stability of the hydride and improves the discharge capacity of
The electrochemical kinetics of an alloy electrode is characterized by high rate discharge ability (HRD), which is defined as: 

$$\text{HRD} = \frac{C_{600}}{C_{60}} \times 100\%,$$

where $C_{600}$ and $C_{60}$ are the maximum discharge capacities of the alloy electrode at the current densities of 600 and 60 mA·g$^{-1}$, respectively. The milling time dependence of the HRD of as-milled PrMg$_{11}$Ni + $x$ wt.% Ni ($x = 100, 200$) alloys is depicted in figure 4. Evidently, the HRDs of the alloys first increase and then decrease with milling time prolonging, and the maximum HRDs of the alloys are 68.53% and 71.98%, respectively. In addition, the $x = 200$ alloy exhibits a higher HRD than that of the $x = 100$ alloy for the same milling duration, indicating that increasing Ni content facilitates the improvement of the electrochemical kinetics of alloys. When the ball mill time doesn't exceed 20 h, the HRDs only have a little difference. However, when the ball mill time is more than 20 h, the difference of the HRDs has a sharp increase, suggesting that the catalytic action of Ni on the electrochemical kinetics of alloy electrodes is closely related to the size and the surface state of Ni particles.

The HRDs of an alloy electrode basically depends on the hydrogen diffusion capability in the alloy bulk and the charge-transfer rate on the surface of the alloy electrode. To reveal the mechanism of the electrochemical kinetics of alloys, the effects of Ni content and milling time on the diffusion ability of hydrogen atoms and the charge-transfer rate are studied. Here, we use the limiting current density ($I_L$) to evaluate the effect of the Ni content and milling duration on the hydrogen diffusion rate of the alloy electrodes. The $I_L$ value can be obtained by measuring the potentiodynamic polarization curve of an alloy electrode, as depicted in figure 5. An inflection can be clearly seen in each anodic polarization curve, which is termed as limiting current density ($I_L$). It is deemed an oxidation reaction occurring on the surface of the alloy electrode, and the oxidation layer hindering hydrogen atoms from further penetrating. Thereby, the limiting current density ($I_L$) can be viewed as a critical current density for passivating. Based on the data in figure 5, the relationships between the $I_L$ values of the alloys and milling time can be established, as inserted in figure 5 (a) and (b), respectively. Obviously, the $I_L$
values of the alloys first increase and then decrease with milling time prolonging. A close inspection shows that the milling times corresponding to the maximum $I_L$ values are different with HRDs, which implies that there is other factor affecting electrochemical kinetics of the alloys in addition to the diffusion ability of hydrogen atoms. Apparently, it is charge transfer rate which can be characterized by the electrochemical impedance spectrum (EIS).

The EIS curves of the as-milled (5h) PrMg_{11}Ni + x wt.% Ni ($x = 100, 200$) alloys were measured at different temperatures (303 K, 313 K and 323 K), as shown in figure 6. There are two distorted capacitive loops at the high and the middle frequency region as well as a line at the low frequency region in each EIS. The smaller semicircle in the high frequency region represents the contact resistance between the alloy powder and the conductive material, and the larger one represents the charge-transfer resistance ($R_{ct}$) on the alloy surface while the straight line in the low frequency region represents Warburg impedance. Kuriyama considered that the $R_{ct}$ depends on both the reactivity of the alloy surface and reaction area. And the electrochemical reactivity of the alloy surface can be determined with apparent activation enthalpy $\Delta_r H^*$, which can be obtained by the following equation:

$$\ln\left(\frac{T}{R_{ct}}\right) = C_0 - \frac{\Delta_r H^*}{RT}$$

where $R_{ct}$ is the charge-transfer resistance for the metal hydride electrodes, $R$ is the gas constant, $T$ is
Figure 6. Plots of $\ln(T/R_c)$ vs. $1/T$ of the as-milled PrMg$_{11}$Ni + $x$ wt.% Ni ($x = 100, 200$) alloys and the EIS of the as-milled (5 h) alloys: (a) $x = 100$, (b) $x = 200$. The Kuriyama plots of $\ln(T/R_c)$ vs. $1/T$ of the as-milled alloys are nearly linear, as inserted in figure 6. From the slopes of the Kuriyama plots, the $\Delta rH^*$ can be calculated. The $\Delta rH^*$ first decreases and then increases with milling time increasing, which is opposite with the change trend of HRDs, implying that the electrochemical kinetics is basically dominated by the charge-transfer ability on the surface of the alloy electrode. Therefore, it can be inferred that the improvement of HRDs of the as-milled alloys are principally ascribed to the decrease of the activation enthalpy by increasing milling time.

3.3. Gaseous hydrogen absorption/desorption capacity and kinetics

Figure 7 shows the variations of the hydrogen absorption capacities of the as-milled PrMg$_{11}$Ni + $x$ wt.% Ni ($x = 100, 200$) alloys with the hydrogen adsorption time at 3 MPa H$_2$ and 573 K. The alloys exhibit a very fast hydrogen absorption rate in the initial stage and the hydrogen content is almost saturated in 100 s. Meanwhile, the variation of milling time has an obvious effect on the hydrogen absorption capacity of the alloys. The relationship between the hydrogen absorption capacity $C_1^{a}$ (approximately represents the maximum hydrogen absorption capacity) and the milling time are inserted in figure 7. The decisive factor of the hydrogen desorption reaction can be determined by calculating activation energy. Here, Kissinger method is used to estimate the hydrogen desorption activation energy of the

Figure 7. Hydrogen absorption capacity and kinetic curves of the as-milled PrMg$_{11}$Ni + $x$ wt.% Ni ($x = 100, 200$) alloys at 573 K: (a) $x = 100$, (b) $x = 200$. 
alloys to reveal the mechanism of the action of adding Ni and prolonging milling time on the hydrogen desorption kinetics of the alloys. The dehydrogenation activation energy ($E_{de}^{ac}$) can be calculated using the Kissinger equation [19]:

$$\frac{d[\ln(\beta / T_p^2)]}{d(1/T_p)} = \frac{-E_{de}^{ac}}{R}$$ (4)

where $E_{de}^{ac}$ is the activation energy, $\beta$ is the heating rate, $T_p$ is the absolute temperature corresponding to the maximum desorption rate in the DSC curves, and $R$ is the ideal gas constant. As a representative, the hydrogen desorption DSC curves of the as-milled (5 h) alloys are presented in figure 8. It is noted that there is a clear endothermic peak corresponding to the hydrogen desorption. Simultaneously, the endothermic peak of the $x = 200$ alloy has a drift to low temperature at the same heating rate, suggesting that the hydrogen desorption reaction rate is improved by increasing Ni content. The Kissinger graphs of $\ln(\beta / T_p^2)$ vs. $1/T_p$ of the as-milled alloys can be plotted by using logarithmic transform of the equation (2), as inserted in figure 8, which is nearly linear. Thus, the activation energy of the alloys can be easily calculated from the slopes of the plots. The relationship between the activation energy and milling time can be established, as illustrated in figure 9. Apparently, increasing milling time leads to a visible reduction in the $E_{de}^{ac}$ value of the alloys. Moreover, increasing Ni content results in a notable decrease in the hydrogen desorption activation energy. Hence, the real driving force for the improvement of the kinetics is the hydrogen desorption activation energy decreased by increasing Ni content and milling time.
4. Conclusions
The hydrogen storage capacity and kinetics of the as-milled PrMg11Ni + x wt.% Ni (x = 100, 200) alloys has been investigated. The major conclusions are summarized as follows:

(1) Increasing Ni content dramatically enhances electrochemical capacity of the as-milled alloys. Ni content increased from 100 to 200 wt.% gives rise to the discharge capacity of the as-milled (40 h) alloys grows from 141.8 to 1059.4 mAh·g⁻¹.

(2) The gaseous hydrogen absorption capacity of the alloys first augments and then declines with milling time prolonging. The maximum value is 5.75 wt.% and 6.03 wt.% for the x=100 and 200 alloys, respectively.

(3) Kissinger method was used to evaluate hydrogen desorption activation energy of the as-milled alloy. ΔH* obviously decreases with Ni content and milling time increased, which is convinced to be the real driving force of the improvement of the hydrogen desorption kinetics of the as-milled alloys.

(4) The electrochemical kinetics of the alloys first increases and then decreases with milling time increasing, and the maximum HRD values of the as-milled alloys correspond with the minimum ΔH* values, suggesting the charge transfer ability of the alloy electrode surface is a major governing factor of the electrochemical kinetics of the alloys.

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