Effect of Amorphous Transformation on Electrochemical Capacities of Rare Earth–Mg Based Alloys

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The effect of ball mill modification with Ni on the microstructure and electrochemical properties of La₂Mg₁₇ based and CeMg₁₂ based hydrogen storage alloys was characterized. The amount of the added Ni was one of the key factors controlling the earlier formation of homogenous amorphous phase for the ball-milled composites. The results of the study indicate that the electrochemical capacities of the composite samples were significantly associated with the amorphorization degree of the product and especially the diffuse peak position of their X-ray pattern in addition to the particle size and their microstructure.

1. Introduction

Recently, magnesium-based hydrogen storage alloys have received increasing attention because of their high hydrogen storage capacity, low material cost and abundance in resource. However, their hydrides are too stable and are not reversible within the required range of temperature and pressure.

According to the literatures [1–8], ball-milling is a preparation approach to amorphous alloys, that allows them to be readily charged and discharged at room temperature, displaying a very high discharge capacity. Nohara et al. [9] reported a very high discharge capacity of 870 mAh/g (Mg₂Ni) attained by ball-milling Mg₂Ni with Ni. And Iwakura et al. [10] reported an even higher discharge capacity of 1082 mAh/g (Mg₂Ni) by ball-milling, which

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is close to the theoretical capacity of the Mg$_2$Ni on the basis of Mg$_2$NiH$_4$. Rare earth (RE) metal–Mg based alloy such as La$_2$Mg$_{17}$ and CeMg$_{12}$ is another promising candidate for hydrogen storage electrode alloy, whose hydrides contain 4.0–6.0 wt.\% hydrogen that is much higher than typical metal hydrides Mg$_2$NiH$_4$ (3.6 wt.\%) and LaNi$_5$H$_6$ (1.4 wt.\%). Clearly, it is very worth studying the electrochemical behavior of this type of hydrogen storage alloy.

In this study, ball milling as-cast RE metal–Mg based alloy with Ni was employed to prepare composite samples. Ni was added to the composites as an amorphization-induced material. The effect of the amount of Ni on the microstructure and electrochemical properties of the prepared composites were investigated and discussed. Finally, the related mechanism was suggested.

2. Experimental

Ingots of La$_2$Mg$_{17}$, La$_{1.8}$Ca$_{0.2}$Mg$_{14}$Ni$_3$, CeMg$_{12}$ and CeMg$_{11}$Ni alloys were first prepared by induction melting and then mechanically pulverized to particles below 200 mesh. The La$_2$Mg$_{17}$, La$_{1.8}$Ca$_{0.2}$Mg$_{14}$Ni$_3$, CeMg$_{12}$ and CeMg$_{11}$Ni alloy powders thus prepared were mixed with Ni powder in the weight ratio of 1:0, 1:0.5, 1:1 and 1:2, with total mass of 5 g, respectively. Each mixture was introduced into a stainless steel vial together with stainless steel balls (diameter: 10 mm). The weight ratio of the mixed powders to the balls was 1:20. The vial was then evacuated, filled with high purity argon and tightly sealed. The sample was ball-milled at the rate of 225 rev./min. The ball-milling time was 50 h for La–Mg based composites, and 90 h for Ce–Mg based composites. The resulting powders led to La$_2$Mg$_{17}$+$x$ wt.\% Ni ($x = 0$, 50, 100), La$_{1.8}$Ca$_{0.2}$Mg$_{14}$Ni$_3$+$x$ wt.\% Ni ($x = 0$, 50, 100, 200), CeMg$_{12}$+$x$ wt.\% Ni ($x = 0$, 50, 100, 200), and CeMg$_{11}$Ni+$x$ wt.\% Ni ($x = 0$, 50, 100, 200) composites.

X-ray diffraction study of the milled alloy powders was carried out on a Philip X’Pert-MPD type X-ray diffractometer with Cu $K_a$ radiation. The surface morphology was examined by a scanning electron microscope (SEM).

For electrochemical investigation, each powder sample was mixed with Ni powder again in the weight ratio of 1:4 and 0.5 g, and the mixture was pressed under a pressure of 20 MPa to form a circular pellet of 10 mm in diameter. Electrochemical measurements were performed in a three-electrode system and a 6 M KOH aqueous solution was used as electrolyte. Ni(OH)/NiOOH and Hg/HgO were used as the counter electrode and the reference electrode, respectively. The charge/discharge measurements were performed by an automatic galvanostatic system (DC-5) and each negative electrode was charged at 50 mA/g (M) ($M = \text{La}_2\text{Mg}_{17}$, La$_{1.8}$Ca$_{0.2}$Mg$_{14}$Ni$_3$, CeMg$_{12}$ and CeMg$_{11}$Ni) and discharged at 50 mA/g (M) with a cut-off voltage set at $-0.55$ V (vs. Hg/HgO). The electrochemical tests were all examined at 298 K.
Fig. 1. X-ray diffraction patterns of the composites after ball milling modification for times up to 90 h and their corresponding as-cast alloys. (a) La$_2$Mg$_{17}$ + $x$ wt.% Ni, (b) La$_{1.8}$Ca$_{0.2}$Mg$_{14}$Ni$_3$ + $x$ wt.% Ni, (c) CeMg$_{12}$ + $x$ wt.% Ni, and (d) CeMg$_{11}$Ni + $x$ wt.% Ni.

The charge/discharge capacities of these alloy samples were calculated and reported on the basis of per unit gram of M.

3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of La$_2$Mg$_{17}$ + $x$ wt.% Ni ($x = 50, 100$) and La$_{1.8}$Ca$_{0.2}$Mg$_{14}$Ni$_3$ + $x$ wt.% Ni ($x = 0, 50, 100, 200$) composites after 50 h of ball milling and CeMg$_{12}$ + $x$ wt.% Ni ($x = 0, 50, 100, 200$) and CeMg$_{11}$Ni + $x$ wt.% Ni ($x = 0, 50, 100, 200$) composites after 90 h of ball milling modification. For comparison, the X-ray diffraction patterns of their corresponding as-cast alloys are also shown in Fig. 1. Before hydriding, the as-cast La$_2$Mg$_{17}$ and CeMg$_{12}$ alloys do not present any impurity phase or phase disproportionation. Partly substituting Mg by Ni in these two as-cast alloys results in the formation of the minor Mg$_2$Ni phase in addition to their main phases. A broadening of diffraction peaks is clearly observed for all
ball-milled samples, indicating that the ball-milling treatment causes a phase transition from a well crystalline structure to a disorder structure. And with the increase of Ni content in the ball-milled composites, the diffraction peaks tend to be broad. When \( x \) increases to 100, the crystalline diffraction peaks of \( \text{La}_2\text{Mg}_{17} + x \text{wt.}\%\text{Ni} \) and \( \text{La}_{1.4}\text{Ca}_{0.2}\text{Mg}_{14}\text{Ni}_3 + x \text{wt.}\%\text{Ni} \) composites disappear and a single hump appears at \( 2\theta = \sim 42^\circ \). This means that for both composites a homogeneous amorphous phase has been formed within 50 h ball milling. However, further addition of Ni does not obviously influence the X-ray diffraction pattern except for a slight left migration (1°–2°) of the hump position in the case of the \( \text{La}_{1.4}\text{Ca}_{0.2}\text{Mg}_{14}\text{Ni}_3 + 200 \text{wt.}\%\text{Ni} \) composite.

The as-cast CeMg\(_{12}\) and the CeMg\(_{11}\)Ni alloys also present a hump at approximately \( 2\theta = 35^\circ \) after 90 h ball milling. For the CeMg\(_{12}\) + \( x \text{wt.}\%\text{Ni} \) and the CeMg\(_{11}\)Ni + \( x \text{wt.}\%\text{Ni} \) composites, the corresponding diffuse peaks of the broad humps migrated towards higher diffraction angles with the increase of \( x \). Comparing the diffraction patterns of the ball-milled as-cast alloys to those of the ball-milled alloys with 50 wt.\% Ni addition, as presented in Fig. 1(c) and 1(d), we can find that, the milled alloys with 50 wt.\% of Ni addition still exhibited some crystal diffraction peak characteristic of the Ni element. This result refers to that kind of composites whose amount of Ni addition is below a certain value, presenting more difficulty for amorphorization even than the ball-milled as-cast alloys within 90 h in the present case. On the other hand, for the CeMg\(_{11}\)Ni \( + 100 \text{wt.}\%\text{Ni} \) composite, a homogeneous amorphous phase had been formed within 90 h ball milling, as evidenced by its X-ray diffraction pattern. However, we noticed that the diffuse peaks corresponding to this composite appear at \( 2\theta = 40^\circ \). With \( x \) increased to 200, the CeMg\(_{12}\) + \( x \text{wt.}\%\text{Ni} \) and the CeMg\(_{11}\)Ni + \( x \text{wt.}\%\text{Ni} \) composites were both in the amorphous structure with the diffuse peaks located at \( 42^\circ–43^\circ \).

Surface morphologies of the ball-milled CeMg\(_{11}\)Ni + \( x \text{wt.}\%\text{Ni} \) (\( x = 0, 50, 100 \) and 200) composites are shown in Fig. 2. It can be seen that the amount of Ni addition plays a significant role on the structure and morphology of the ball-milled products. After 90 h ball milling modification, most product particles without Ni addition are in the size range of 10 to 30 \( \mu \)m. On the other hand, in the same modification condition, the increase of Ni content in the composites results in the decrease of the size of the product particles. Especially, when \( x \) was increased to 100, the product particles became much finer. Most of them are in the size range below 5 \( \mu \)m. However, further increase of the Ni content to \( x = 200 \) can not reduce the particle size anymore, except that more even particles are attained.

Figure 3 shows the discharge curves of the as-cast La–Mg based alloys and their corresponding ball-milled composites with different Ni addition at 298 K. Both the as-cast La\(_2\)Mg\(_{17}\) and La\(_{1.4}\text{Ca}_{0.2}\text{Mg}_{14}\text{Ni}_3\) alloys exhibited low discharge capacities of only 137 mAh/g and 246 mAh/g, respectively. On the other hand, the discharge capacity of the ball-milled La–Mg based alloys with Ni differs greatly depending on the amount of Ni intro-
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Reduced during milling. The discharge capacity of ball-milled La$_{1.8}$Ca$_{0.2}$Mg$_{14}$Ni$_3$ without Ni is only 27 mAh/g higher than that of its crystalline counterpart. However, ball-milled La–Mg alloys with 100 wt.% Ni composite reach fairly high discharge capacities, which are 1060 mAh/g (La$_2$Mg$_{17}$) [530 mAh/g (La$_2$Mg$_{17}$ + Ni)] for the La$_2$Mg$_{17}$ + 100 wt.% Ni composite and 1004 mAh/g (La$_{1.8}$Ca$_{0.2}$Mg$_{14}$Ni$_3$) [502 mAh/g (La$_{1.8}$Ca$_{0.2}$Mg$_{14}$Ni$_3$ + Ni)] for the La$_{1.8}$Ca$_{0.2}$Mg$_{14}$Ni$_3$ + 100 wt.% Ni composite. When associated with XRD analysis result, it could be found that complete amorphorization of the composites and reduction of the particle size are the main factors controlling the electrochemical capacity. Our former work [8] revealed that as-cast La$_{1.8}$Ca$_{0.2}$Mg$_{14}$Ni$_3$ alloy and ball milled La$_{1.8}$Ca$_{0.2}$Mg$_{14}$Ni$_3$ + x wt.% Ni ($x = 0, 50$) composites, that are not completely transformed to the amorphous structure, exhibited a poor charge acceptance capability during the second charge cycle, and such a result was because the hydrides formed in the first charge cycle remained quite stable and could only release a small part of the hydrogen absorbed in the first discharging cycle. On the contrary, ball milled La$_{1.8}$Ca$_{0.2}$Mg$_{14}$Ni$_3$ + x wt.% Ni ($x = 100, 200$) composites were completely amorphorized, and as a result they showed a relatively good electro-

Fig. 2. SEM surface morphology of ball-milled CeMg$_{11}$Ni + x wt.% Ni composites. (a) $x = 0$, (b) $x = 50$, (c) $x = 100$, and (d) $x = 200$. 

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Fig. 3. Discharge curves of the as-cast La–Mg based alloys and their corresponding ball-milled composites with different Ni addition. (a) as-cast La<sub>2</sub>Mg<sub>17</sub> alloys and the ball-milled La<sub>2</sub>Mg<sub>17</sub> + x wt.% Ni composites (x = 50, 100), and (b) as-cast La<sub>1</sub>Ca<sub>0.8</sub>Mg<sub>14</sub>Ni<sub>3</sub> alloys and the ball-milled La<sub>1</sub>Ca<sub>0.8</sub>Mg<sub>14</sub>Ni<sub>3</sub> + x wt.% Ni composites (x = 0, 50, 100, 200).

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Fig. 4. Discharge curves of the as-cast Ce–Mg based alloys and their corresponding ball-milled composites with different Ni addition. (a) as-cast CeMg$_{12}$ alloys and the ball-milled CeMg$_{12} + x$ wt.% Ni composites ($x = 0, 50, 100, 200$), and (b) as-cast CeMg$_{11}$Ni alloys and the ball-milled CeMg$_{11}$Ni + $x$ wt.% Ni composites ($x = 0, 50, 100, 200$).

Ball-milled products still show relatively low discharge capacities, that are merely 139 mAh/g (CeMg$_{12}$) for CeMg$_{12} + 100$ wt.% Ni composite and 180 mAh/g (CeMg$_{11}$Ni) for CeMg$_{11}$Ni + 100 wt.% Ni composite. Only when $x$ was increased to 200, such Ce–Mg based alloys start to attain their maximum discharge capacities in the present case, which are 1170 mAh/g (CeMg$_{12}$) for CeMg$_{12} + 200$ wt.% Ni composite and 1012 mAh/g (CeMg$_{11}$Ni) for CeMg$_{11}$Ni + 200 wt.% Ni composite.

For the La–Mg based composites, we use the formation of amorphous structure and the reduction of the particle size as two main factors to explain the effect of the microstructure on the electrochemical properties [8]. Obviously,
such two points can not be applied to explain the electrochemical behavior of Ce–Mg based composites in the present case. The CeMg$_{11}$Ni $+ x$ wt.% Ni ($x = 100, 200$) composites as examples are both in amorphous structure (Fig. 1) and in the similar particle size and morphologies (Fig. 2). However, they show distinct difference concerning their discharge capacities. Also, it can not be just simply explained that by increasing the Ni content results higher efficient for improving the electrochemically properties for hydrogen absorbing/desorbing, since the Ni contents of $100$ wt.% and $200$ wt.% are in the same magnitude of degree. By analyzing the X-ray diffraction patterns of these four series of La–Mg based and Ce–Mg based alloys as shown in Fig. 1, we can find that the test alloy with the maximum discharge capacity in its related alloy series is always associated with the appearance of its X-ray diffuse peak (broad amorphous peak) position at approximately $2\theta = 42^\circ$. For example, the La$_{13}$Ca$_{0.2}$Mg$_{14}$Ni$_3 + 100$ wt.% Ni composite attains a maximum discharge capacity at the diffuse peak at $2\theta = \sim 42^\circ$. When $x$ was increased from $100$ to $200$, the corresponding diffuse peak of amorphous composite migrated slightly to $2\theta = 40^\circ$, resulting in the decrease of discharge capacity of the composite. On the other hand, for the CeMg$_{11}$Ni $+ x$ wt.% Ni composites, the diffuse peak positions migrated from $2\theta = 40^\circ$ to $2\theta = 42.5^\circ$–$43^\circ$ when $x$ increase from $100$ to $200$, resulting in a maximum discharge capacity for the CeMg$_{11}$Ni $+ 200$ wt.% Ni composite. All these results imply that hydrogen absorption/desorption may take place readily in the test amorphous alloys when a certain structure is formed. The open literatures indicated that in some intermetallic compound-hydrogen systems the electronic structure and crystal structure are relatively important in hydrogen absorption [11, 12]. The maximum hydrogen absorption capacity is determined by the electronic structure which, to a first approximation, is quite similar in the metallic glass and the corresponding intermetallic compound. However, in certain metallic glasses, a wide distribution of local environments and fluctuation in local symmetry may increase the number of sites available for hydrogen occupation (with respect to the crystalline state) by lowering the energy and thus allowing a higher hydrogen absorption capacity [13]. In the present case, we propose that for La–Mg based and Ce–Mg based composites an amorphous phase formed with a diffuse peak located at $2\theta = 41^\circ$–$43^\circ$ is associated with a certain short-range order and thus such structured glass alloy can accommodate a high hydrogen absorption capacity. Our test metallic glass will be characterized in a further analysis to obtain the structural information associated with hydrogen absorption capacity.

4. Conclusion

For La–Mg based and Ce–Mg based composites the amorphous phase formed with a diffuse peak located at $2\theta = 41^\circ$–$43^\circ$ is associated with a certain short-
range order and thus such structured glass alloy can accommodate a high hydrogen absorption capacity.

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References