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# Electrochemical properties of $CeMg_{11}Ni+ x\%$ Ni composites ($x= 0$, 50, 100 and 200) prepared by ball-milling①

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**Abstract:** The electrochemical properties of the as-cast $CeMg_{11}Ni$ and ball-milled $CeMg_{11}Ni+ x\%$ Ni($x= 0$, 50, 100 and 200, mass fraction) composites were investigated. The results show that homogeneous amorphous phase of $CeMg_{11}Ni+ x\%$ Ni composite can be obtained by ball-milling, and discharge capacity of the ball-milled $CeMg_{11}Ni+ x\%$ Ni composites differs greatly depending on the amount of Ni introduced during milling. The $CeMg_{11}Ni+ 200\%$ Ni composite after 90 h ball-milling was found to exhibit a large discharge capacity of about 1 012 mAh/g at 303 K, and it also shows better charge-discharge cycling stability than those with lower Ni content. This remarkable improvement in electrochemical properties of the ball-milled composites seems to be attributed to the formation of an amorphous composite as well as the improvement of the surface state of the ball-milled particles.

**Key words:** hydrogen storage alloy; $CeMg_{11}Ni$; amorphous phase; electrochemical properties

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## 1 INTRODUCTION

Magnesium and magnesium-based alloys are promising hydrogen storage materials because of their absorbability of hydrogen in large quantities, low specific gravity, rich mineral resources, low material cost and so on. Nevertheless, their hydrides are too stable to be used at room temperature[1]. It seems impossible for application of crystalline Mg-based alloys in nickel-hydrogen batteries.

It is well known that amorphous alloys have many advantageous properties over crystalline ones. However, amorphous Mg-based hydrogen storage alloys have not attracted much attentions till the end of 1980s because they cannot be prepared by the conventionally used rapid solidification method. In early 1990s, Lei et al[2, 3] reported that amorphous Mg-Ni alloys prepared by mechanical alloying of Mg and nickel powder. Since then many researchers have directed their work to Mg-Ni amorphous alloys[4, 5]. Kohno et al[6, 7] found that by mechanical grinding of $Mg_2Ni$ with Ni, a discharge capacity of about 750 mAh per gram of $Mg_2Ni$ (485 mAh per gram of $Mg_2Ni+ 100\%$ Ni) had been reached. Nohara et al[8, 9] reported the enhanced electrochemical characteristics of a nanocrystalline $Mg_2Ni$ and a homogeneous amorphous alloy prepared by ball-milling of $Mg_2Ni$ without or with Ni, and the latter exhibited a maximum discharge capacity of about 870 mAh per gram of $Mg_2Ni$ (512 mAh per gram of $Mg_2Ni+ 70\%$ Ni) at 303 K. Iwakura et al[10] reported an even higher discharge capacity of about 1 082 mAh per gram of $Mg_2Ni$ (636 mAh per gram of $Mg_2Ni+ 70\%$ Ni), which exceeded the theoretically calculated value of 999 mAh per gram of $Mg_2Ni$ on the basis of $Mg_2NiH_4$ for crystalline $Mg_2Ni$. These improvements in the characteristics of $Mg_2Ni$ alloy are mainly caused by the appearance of a nanocrystalline or amorphous structure.

The hydrogen storage capacity of Ln-Mg (Ln = La, Ce or mischmetal) series alloys such as $La_2Mg_{17}$ and $CeMg_{12}$ reaches 6.0%, much higher than that of $Mg_2Ni$ alloy[11, 12]. However, the electrochemical properties of amorphous $A_2B_{17}$ and $AB_{12}$ type Ln-Mg alloys are seldom reported. In our previous work[13], it was found that the amorphous $La_{1.8}Ca_{0.2}Mg_{14}Ni_3+ 100\%$ Ni composite after 50 h ball-milling exhibits a large discharge capacity of 1 004 mAh per gram of $La_{1.8}Ca_{0.2}Mg_{14}Ni_3$ at 298 K. In the present work, the electrochemical properties of $CeMg_{11}Ni+ x\%$ Ni ($x= 0$, 50, 100, 200) composites prepared by ball-milling method were studied in comparison with the as-cast $CeMg_{11}Ni$ alloy. The emphasis was placed on the

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influence of the amount of Ni on the microstructures and on the electrochemical capacities of the ball-milled composites.

## 2 EXPERIMENTAL

CeMg$_{11}$Ni alloy was first prepared in an induction furnace and this alloy was mechanically pulverized to particles below 49 μm. The CeMg$_{11}$Ni alloy powder thus prepared was mixed with Ni powder in mass ratios of 1∶0, 1∶0.5, 1∶1 and 1∶2 (total mass of 1.5 g), respectively, followed by ball-milling under argon atmosphere for 90 h at a rate of 350 r/min. The resulting powder will be designated hereafter as CeMg$_{11}$Ni+ $x$% Ni ($x$= 0, 50, 100, 200) composites.

Each sample powder was mixed with Ni powder again in mass ratio of 1∶4, and 0.5 g mixture was pressed under a pressure of 12 MPa to form a pellet with diameter of 10 mm. Electrochemical measurements were performed in a three-electrode system and a 6 mol/L KOH aqueous solution was used as electrolyte. A nickel electrode ($Ni(OH)_2/NiOOH$) was used as the counter electrode and a mercury (Ⅱ) oxide electrode (Hg/HgO, 6 mol/L KOH) was used as the reference electrode. The discharge capacity and the cycle life of the test electrodes were determined by the galvanostatic method. The test electrodes were charged at 100 mA/g and discharged at 60 mA/g to the cut-off potential of − 0.55 V (vs Hg/HgO). After each charging, there was a 10 min break. The electrochemical tests were all carried out at 303 K. The discharge capacities of these sample alloys were calculated and expressed per gram of CeMg$_{11}$Ni.

The X-ray diffraction study was carried out on a Rikagu D/Max PC2500 X-ray diffractometer with Cu K$_\alpha$ radiation. The surface morphology of the ball-milled alloy powder was examined in a scanning electron microscope (SEM).

## 3 RESULTS AND DISCUSSION

### 3.1 Microstructures

The X-ray diffraction patterns of the as-cast CeMg$_{11}$Ni and ball-milled CeMg$_{11}$Ni+ $x$% Ni ($x$= 0, 50, 100, 200) composites are presented in Fig. 1. As can be seen from Fig. 1, initially the as-cast CeMg$_{11}$ Ni alloy mainly contains CeMg$_{12}$ phase, additionally, little amount of $Mg_2Ni$ and $CeO_2$ were also detected. The $CeO_2$ may be due to the oxidation of the alloy by the oxygen in the air. After ball-milling without Ni addition, the diffraction peaks of CeMg$_{12}$ apparently broaden and merge, which indicates that grain size is reduced and a nanocrystalline structure may be formed. For the ball-milled CeMg$_{11}$Ni+ $x$% Ni composites, in case of $x$ = 50, besides the broadened peaks of CeMg$_{12}$ phase, some characteristic diffraction peaks of metallic Ni (at positions 2θ= 44.5°, 51.8° and 76.5°) appear. However, as the value of $x$ increases, the peaks of crystalline CeMg$_{12}$ and Ni phases all weaken. In the case of the ball-milled CeMg$_{11}$Ni+ 100% Ni composite, a small broadened Ni peak is found coexisting with the broad hump, which reveals that some nanocrystalline Ni is embedded in the amorphous matrix. But when $x$ increases to 200, the crystalline diffraction peaks of CeMg$_{12}$ and Ni have disappeared completely and a single hump appears at 2θ angles of 40°−42°, indicating that a homogeneous amorphous phase has been formed for this ball-milled composite.

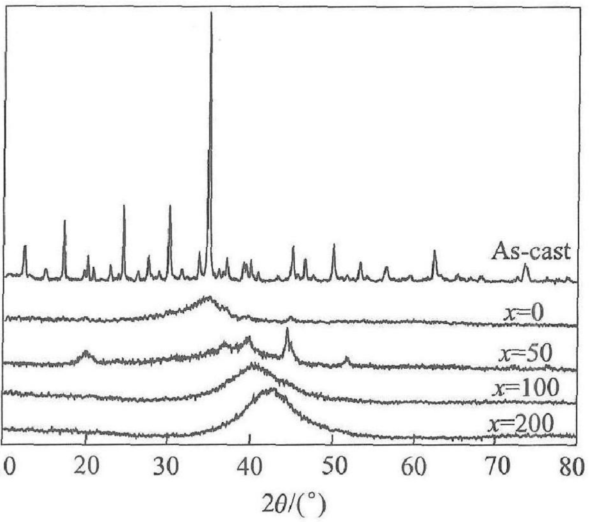

**Fig. 1** XRD patterns of as-cast CeMg$_{11}$Ni and ball-milled CeMg$_{11}$Ni+ $x$% Ni ($x$= 0, 50, 100, 200) composite

Based on the above analysis, it is clear that Ni addition is very effective in enhancing the amorphorization of the CeMg$_{11}$Ni alloy and the amount of Ni added is the key factor influencing the amorphorization in the present case.

### 3.2 Electrochemical properties

The discharge curves of the as-cast CeMg$_{11}$Ni alloy and ball-milled CeMg$_{11}$Ni+ $x$% Ni ($x$ = 0, 50, 100, 200) composites at their respective discharge capacity are shown in Fig. 2.

From Fig. 2, we can see that the obtained discharge capacities of CeMg$_{11}$Ni ball-milled with Ni are greater than those of the as-cast alloy and the ball-milled composite without Ni addition. It is known that the electrochemical hydriding and dehydriding procedures of hydrogen storage alloy electrode in an alkaline solution include at least two steps[14]: electrochemical (charge-transfer) step and diffusion step. The electrode reaction can be expressed as

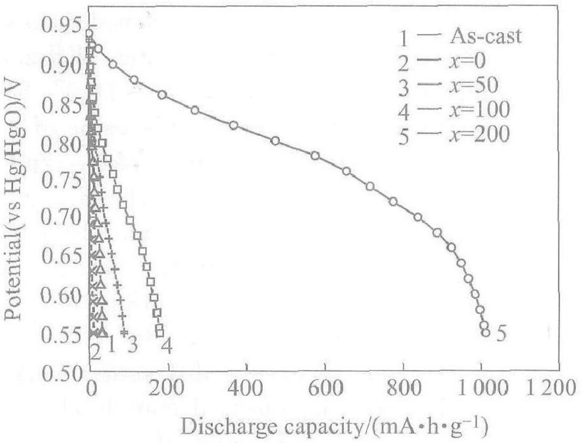

**Fig. 2** Discharge curves of as-cast $CeMg_{11}Ni$ alloy and ball-milled $CeMg_{11}Ni + x\%Ni$ ($x = 0, 50, 100, 200$) composites at their respective maximum discharge capacity at 303 K

$$M + H_2O + e \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} M - H_{ads} + OH^- \quad (1)$$

$$M - H_{ads} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} MH \quad (2)$$

It can be seen that the performance of electrochemical hydriding and dehydriding reactions in an alkaline solution is determined by both the charge-transfer reaction on the alloy/electrolyte interface (Eqn. (1)) and the rate of hydrogen diffusion within the bulk of the alloy (Eqn. (2)).

Nickel is well known to have a high electrocatalytic activity or a low overpotential for the hydrogen evolution reaction (HER) in alkaline solution. The nickel particles inserted in the $CeMg_{11}Ni$ alloy are, therefore, believed to act as the electrocatalytic active sites for the HER so that they may reduce the charge transfer resistance, resulting in a significant increase of the electrochemical capacity. Fig. 3 shows the SEM images of the ball-milled $CeMg_{11}Ni + x\%Ni$ ($x = 0, 50, 100, 200$) composites. As shown in Fig. 3, with the increase of Ni amount, the particle size decreases to different extent. The decrease of the particle size and the augmentation of the density of defects may improve the diffusion of hydrogen in the alloy, which is also believed to be beneficial for improving hydriding/dehydriding reactions. Thus the ball-milled primary $CeMg_{11}Ni$ alloy with nickel powder is not simply a mixture of two components, but a new composite system with high reactivity due to the inlaid electrocatalytic active sites, the large interface, the small interface, the small crystallite size and the presence of defects. And all the above factors lead to the higher discharge capacities of the composites ball-milled with Ni.

From Fig. 2 it can also be clearly seen that the discharge capacity of the ball-milled $CeMg_{11}Ni$ with Ni differs greatly depending on the amount of Ni introduced during milling. The discharge capacities of the ball-milled $CeMg_{11}Ni + 50\%$ Ni and $CeMg_{11}Ni + 100\%$ Ni composites are only 90 and 180 mAh/g, respectively. But in the case of the ball-milled $CeMg_{11}Ni + 200\%$ Ni composite with a homogeneous amorphous structure, a plateau of the potential based on the oxidation of desorbed hydro-

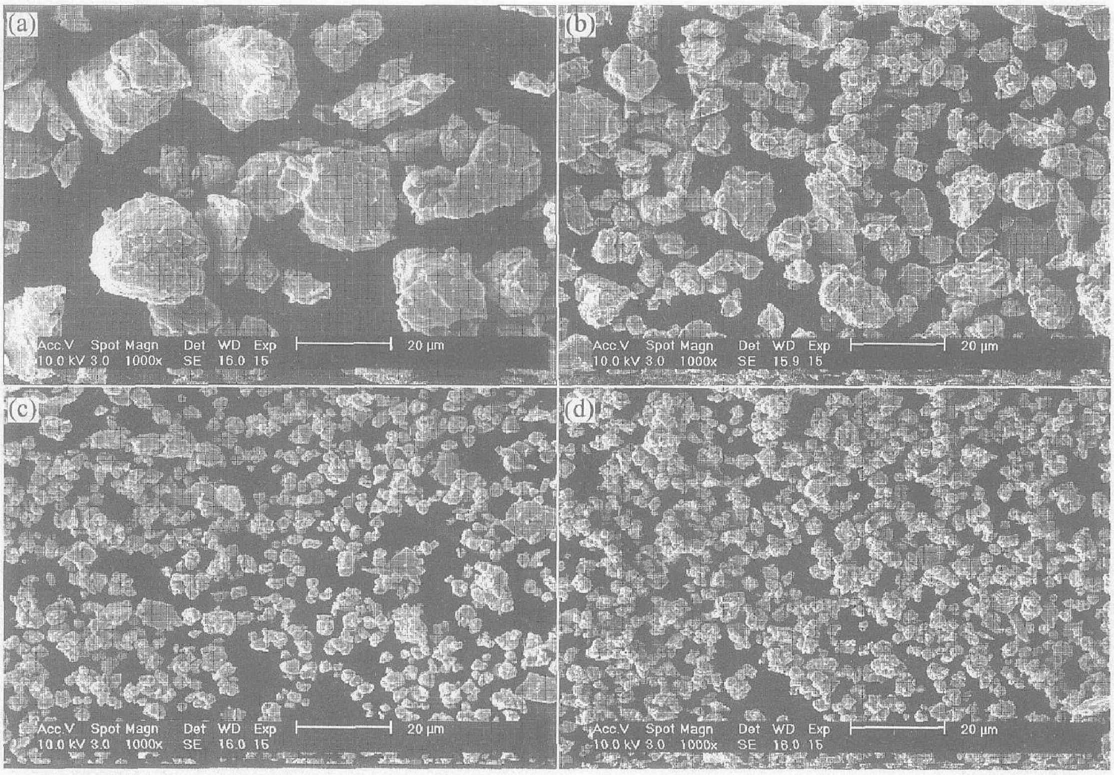

**Fig. 3** SEM images of ball-milled $CeMg_{11}Ni + x\%Ni$ ($x = 0, 50, 100, 200$) composites
(a) —$x = 0$; (b) —$x = 50$; (c) —$x = 100$; (d) —$x = 200$

gen was observed at more negative potential than that for other composites, and an extremely high discharge capacity was exhibited, about 1 012 mAh per gram of $CeMg_{11}Ni$ (337 mAh per gram of $CeMg_{11}Ni+200\%$ Ni). The marked improvement in discharge characteristics of the $CeMg_{11}Ni$ alloy ball-milled with 200% Ni seems to be partly ascribed to the formation of homogeneous amorphous region which can have a higher equilibrium hydrogen pressure and make the desorption of hydrogen much easier. In other words, the discharge capacity depends to a great degree on the amorphorization degree of the composite alloy. From Fig. 1 we can see that the amorphorization degree of the composite alloy increases with the increasing amount of Ni, and thus leads to the result that the discharge capacity increases with the increasing Ni amount during ball-milling. On the other hand, from Fig. 4 we can see that the particle size of the ball-milled $CeMg_{11}Ni+x\%$ Ni ($x=50$, 100, 200) composites decreases with the increasing Ni amount, especially in the case of the ball-milled $CeMg_{11}Ni+200\%$ Ni composite, the particle size decreases a lot. As the particle size decreases, the discharge capacity increases due to the increase in effective surface area for hydrogen electrode reaction and shortened hydrogen diffusion length. So the discharge capacity of the ball-milled $CeMg_{11}Ni+200\%$ Ni composite exhibits a larger increase compared with the others. These results clarify that mechanical grinding with proper amount of Ni powder is an effective way to improve the charge-discharge capability of the negative electrode containing Mg-based alloy.

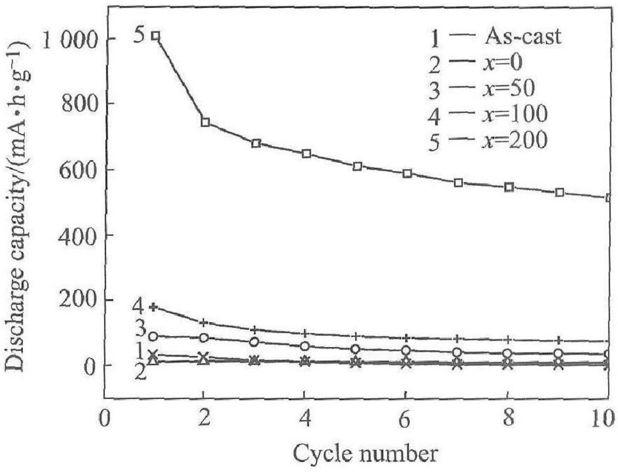

**Fig. 4** Discharge capacities as function of cycle number for as-cast $CeMg_{11}Ni$ alloy and ball-milled $CeMg_{11}Ni+x\%$ Ni ($x=0$, 50, 100, 200) composites at 303 K

Fig. 4 shows the specific discharge capacities as function of cycle number for the ball-milled $CeMg_{11}Ni+x\%$ Ni ($x=0$, 50, 100, 200) composites at 303 K. And Table 1 lists the maximum discharge capacity and cycling retention rate of the composites after 10 cycles.

**Table 1** Maximum discharge capacity(mAh/g) and cycling retention rate(%) of ball-milled $CeMg_{11}Ni+x\%$ Ni($x=0$, 50, 100, 200) composites after 10 cycles

| $x$ | $C_m$/ (mAh·g$^{-1}$) | $C_{m+10}$/ (mAh·g$^{-1}$) | Retention rate/ % |
|---|---|---|---|
| 0 | 12.4 | 9.3 | 75.0 |
| 50 | 89.8 | 35.5 | 39.5 |
| 100 | 180.5 | 75.7 | 41.9 |
| 200 | 1 012.1 | 515.2 | 50.9 |

For the ball-milled $CeMg_{11}Ni+100\%$ Ni composite the discharge capacity decreases to 41.9% of its original one after 10 cycles. While the composite with $x=200$ can maintain 515.2 mAh/g and 50.9% of its initial discharge capacity. This means that compared with the ball-milled $CeMg_{11}Ni+100\%$ Ni composite, the ball-milled $CeMg_{11}Ni+200\%$ Ni composite not only has a higher discharge capacity, but also its cycling stability is improved. This may be attributed to the fact that the higher Ni content reduces the contact between Mg and the KOH solution, and thus can enhance the stability of the composite. It is ever reported[15] that nanocrystalline $Mg_2Ni$ alloy lost 80% of its maximum discharge capacity within 10 cycles. Compared with the rapid capacity degradation of Mg-Ni type alloys, the cycle life of the samples is improved. The slower deterioration of the cycle stability may be explained by the existence of Ce, which forms a passive oxide layer on the particle surface reducing the contact of Mg with alkaline solution, thus prolonging the cycle lifetime of the Ce-Mg system alloys.

## 4 CONCLUSIONS

Mechanical grinding with nickel powder is an effective method of improving the electrode properties of Mg-based alloys because of the changed amorphous structure. The amount of Ni added has an important influence on the amorphorization degree in certain duration ball-milling. After 90 h of ball-milling, a homogenous amorphous $CeMg_{11}Ni+200\%$ Ni composite is formed, and its discharge capacity reaches 1 012 mA·h per gram of $CeMg_{11}Ni$). Complete amorphorization of the composites, which in turn is influenced by the amount of Ni added, turns out to be the main factor controlling the electrochemical capacity. The Ni addition also changes the surface state, and enhances the charge transfer reaction and hydrogen diffusion at the surface, thus accelerating the electrochemical reaction. More Ni addition improves the charge-discharge cycling stability of the ball-milled composite due to the reduced contact between Mg and the KOH solution.

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