

Effects of Surface Coating on the Electrochemical Properties of Amorphous CeMg₁₂ Composite

Chen Rugan, Wang Xinhua, Ge Hongwei, Li Shouquan, Chen Lixin, Chen Changpin

Zhejiang University, Hangzhou 310027, China

Abstract: Amorphous CeMg₁₂ was prepared by ball milled CeMg₁₂ alloy with Ni powder. The effects of mechanical grinding and electroless deposition of nickel (EDN) on the electrochemical properties of CeMg₁₂ composites have been studied systematically. Amorphous CeMg₁₂ composites have a maximum discharge capacity of 1209.6 mAh/g, but their cycling stability is poor. The cycling retention rate of the electrode is 37.26% after 10 cycles. After EDN treatment, the cycling stability of CeMg₁₂ composite is improved markedly, and the cycling retention rate increases to 63.67% after 10 cycles. The improvement of cycling retention rate can be attributed to compact nickel coating that prevents the inner Mg from further corrosion by alkali. The nickel coating also enhances the high rate discharge (HRD) property of the composite owing to the good electrochemical catalytic properties of Ni. As oxidation and corrosion is unavoidable during EDN treatment, the maximum discharge capacity decreases slightly for CeMg₁₂ composite with EDN treatment.

Key words: hydrogen storage alloys; CeMg₁₂; surface treatment; mechanical grinding

Nickel-hydride batteries used hydrogen storage alloys as negative electrode materials have attracted great attention, because this kind of batteries is expected to have several advantages over the conventional lead-acid and nickel-cadmium batteries, such as high energy density, high-rate capability, tolerance to overcharge and overdischarge, lack of poisonous heavy metals and no electrolyte consumption during the charge-discharge cycles^[1]. But the sluggish hydriding kinetics at room temperature and easy oxidation of this system, restrict its application seriously.

Chen, Gao, and Wang et al.^[2-6] reported that amorphous La-Mg alloys exhibited greater hydrogen absorption capacity, and mechanical grinding of crystalline Mg-based alloys with Ni or Co could improve their electrochemical characteristics. Meanwhile, Wang et al.^[6] found that Ce-Mg alloys also have a large electrochemical discharge capacity. In this paper, the amorphous CeMg₁₂ was prepared by ball milled CeMg₁₂ alloy with Ni powder, and the maximum discharge capacity of the prepared amorphous CeMg₁₂ composite reached as high as 1209.6 mAh/g; however, its cycling stability was still poor. In

order to improve its cycling stability, electroless deposition of nickel was used.

1 Experimental

CeMg₁₂ alloy ingot was prepared by induction melting under the protection of argon gas. The ingot was mechanically pulverized to 74 μm mesh screen or less, and then CeMg₁₂ alloy powder was mixed with 200wt% Ni powder. Afterwards the mixture together with stainless balls with 10 mm in diameter was put into a stainless steel vessel. The vessel was evacuated and filled with argon gas. The ball milling was conducted for 50 h at the rate of 350 r/min. Thus the prepared composite powder was used for electroless deposition of nickel.

The metal hydride electrode with 10 mm in diameter was prepared by mixing the ball-milled CeMg₁₂ powder with electrolytic nickel powder in a weight ratio of 1:3. The microstructure analysis of the ball-milled composites was performed by X-ray diffraction (XRD, Rigaku D/Max PC2500), and scanning electron microscopy (SEM, SIRION-100). The

Received date: 2008-02-15

Foundation items: National "863" Program Foundation (2006AA05Z129, 2006AA05Z143) and National "973" Program Foundation (2007CB209706)

Biography: Chen Rugan, Candidate for Ph. D., Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China, Tel: 0086-571-87951152

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electrochemical tests were carried out in a tri-electrode system with nickel oxide ($\text{Ni}(\text{OH})_2/\text{NiOOH}$) as the counter electrode, mercury/mercury oxide (Hg/HgO , 6 mol/L KOH) was used as the reference electrode, and the metal hydride electrode (MH) as the working electrode. The counter electrode has a much larger excess capacity over the working electrode. The electrolyte was 6 mol/L KOH solution.

In the charge-discharge cycle tests, the test electrodes were charged at 300 mA/g for 5 h, and after an interval of 10 min, discharged at 180 mA/g to the cut-off potential of -0.6 V (versus Hg/HgO). All the charge-discharge cycle tests were carried out at 303 K. Only the weight of CeMg_{12} hydrogen storage alloys was considered as active materials for the discharge capacity calculation. The test for high-rate dischargeability (HRD) was executed at the following current densities: 900, 1800 and 2700 mA/g.

2 Results and discussion

2.1 Microstructure analysis

The XRD patterns for as cast CeMg_{12} alloy, the amorphous CeMg_{12} composite (ball milled with 200wt%Ni powder for 50 h) and the amorphous CeMg_{12} composite after electroless deposition of nickel treatment (EDN treatment) are shown in Fig. 1, from which it can be seen that for the ball-milled composite with 200wt%Ni, all peaks corresponding to CeMg_{12} disappear and a broad diffusion peak at $40\text{--}45^\circ$ appears; it is suggested that a phase transformation of CeMg_{12} from polycrystalline structure to amorphous/nanocrystalline structure has been finished. As for the amorphous CeMg_{12} composite with EDN treatment, the peaks corresponding to Ni are distinct. Meanwhile, the broad diffusion peak still exists, which indicates that the electroless deposition of nickel does not alter the crystal structure of the composites. Fig. 2 shows EDS pattern of the amorphous CeMg_{12} composite after electroless deposition of nickel. Strong peak intensity of Ni indicates that compact Ni out-layers have been formed, which is obviously displayed in Fig. 3. Chakk et al.^[7] put forward a model for amorphization by mechanical grinding (MG) or mechanical alloying (MA). In the present case, during the mechanical grinding

of polycrystalline CeMg_{12} with 200wt% Ni, the Ni atoms penetrate into the CeMg_{12} lattice, which may occupy either a substitutional or interstitial site in the CeMg_{12} lattice. A prolonged mechanical grinding may make particles agglomerate each other, and the optimized mechanical grinding duration is 50 hours here.

The SEM images of the amorphous CeMg_{12} composite with and without EDN treatment are shown in Fig. 3. Both of them

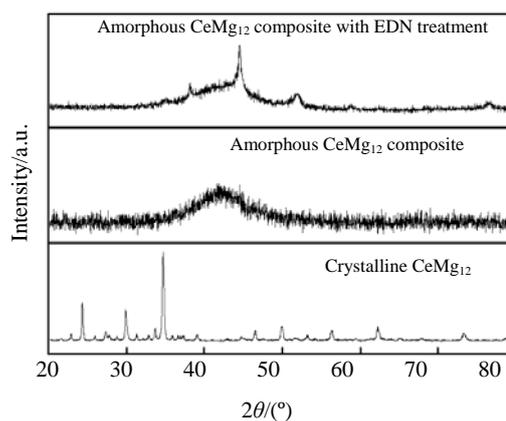


Fig.1 The XRD patterns of as-cast CeMg_{12} , amorphous ($\text{CeMg}_{12}+200\text{wt}\%\text{Ni}$) composite and amorphous CeMg_{12} composite after EDN treatment

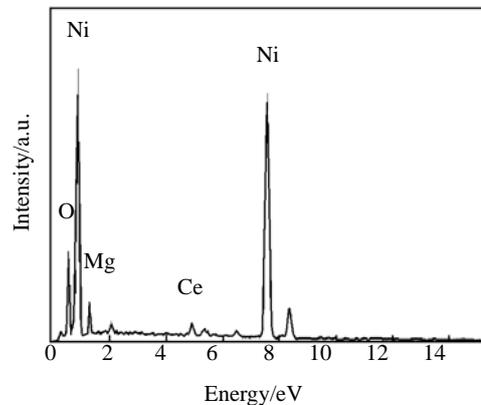


Fig.2 The EDS pattern of the composites after EDN treatment

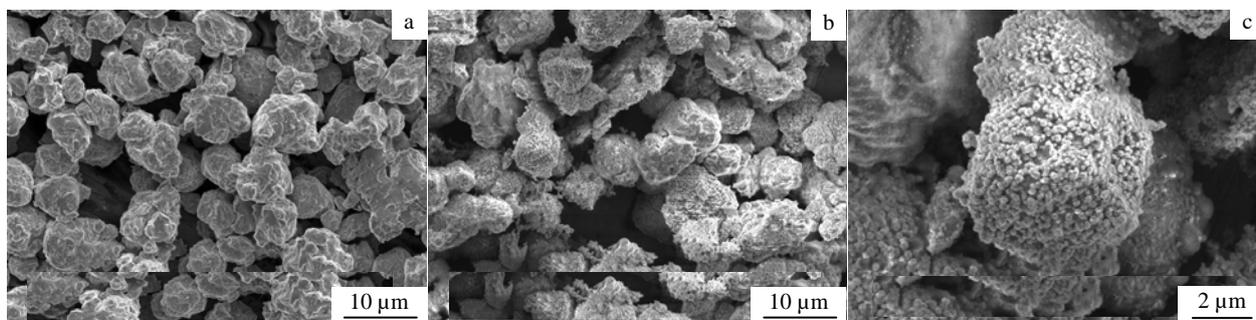


Fig.3 The SEM micrographs of composites before and after EDN treatment: (a) original particles of the CeMg_{12} powder; (b) particles of the composite after EDN treatment; and (c) high resolution image of Ni cover outside the composite

have smooth morphology, and EDN treatment does not alter the particle sizes of the composite. High resolution SEM image (Fig. 3c) shows that thousands of micro Ni grains with average diameter of about 0.2 μm cover the composite particles. The nickel coating is suggested to prevent the alloy from being eroded by electrolyte efficiently. The high oxygen content in nickel-coating as shown in Table 1 is due to the oxidation during the surface coating process.

Nickel added to mechanical grinding process can enhance the amorphous content of CeMg₁₂ alloy. Meanwhile, nickel particles with high electrocatalytic activity are in favor of enriching in outer layer, which are believed to act as the electrocatalytic active sites for hydrogen evolution reaction^[8]. Therefore, they may reduce the charge transfer resistance, and thus result in a significant increase of electrochemical capacity. The optimized amount of nickel addition is 200 wt% for CeMg₁₂.

2.2 Electrochemical properties

The discharge curves of amorphous CeMg₁₂ composites with and without EDN treatment are shown in Fig. 4. It can be seen from it that the maximum discharge capacity of the amorphous CeMg₁₂ composite reaches as high as 1209.6 mAh/g. For the amorphous CeMg₁₂ composite with EDN treatment, a maximum discharge capacity of 887.76 mAh/g is achieved. There are two possibilities for the reduction of the maximum discharge capacity during the EDN treatment. One would be that the oxidation/corrosion of hydrogen absorption element Mg took place. The other would be that nickel coating

Table 1 The atomic percentage of amorphous CeMg₁₂ composites after EDN treatment

Element	O	Mg	Ce	Ni	Cu
Surface scan/at%	21.38	15.71	2.18	59.52	1.22
Little gain/at%	37.98	13.54	1.18	47.3	-

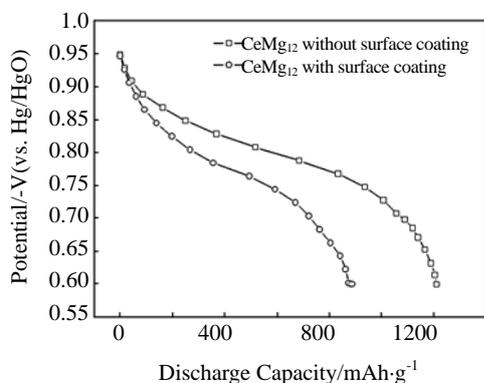


Fig.4 The first cycle discharging curves of amorphous CeMg₁₂ composites without and with EDN treatment

prevented H from diffusing into the inner of the alloy despite of its electrocatalytic property for hydrogen evolution reaction.

Fig. 5 shows the specific discharge capacities as a function of number of cycles for the composites with and without EDN treatment. The maximum discharge capacity (C_m) and the discharge capacity after 10, 20, 30 (C_{10} , C_{20} , C_{30}) cycles are summarized in Table 2. The cycling capacity retention rate for n th cycle expressed as C_n/C_m is also calculated and tabulated. The discharge capacity of the amorphous CeMg₁₂ composite without EDN treatment decreases rapidly as charge/discharge cycles continue. In contrast, the amorphous CeMg₁₂ composite after EDN treatment exhibits a much better cycling stability at the expenses of slight reduction of maximum discharge capacity. The cycling retention rates of 10 cycles for the composites increase from 37.26% without EDN treatment to 69.67% after EDN treatment.

It is demonstrated that the oxidation/corrosion of hydrogen absorptive element Mg is the main reason causing the rapid discharge capacity decay during charge/discharge cycling^[9,10]. As the corrosion product, Mg(OH)₂ is insoluble in water. The Mg(OH)₂ mulch over the composite particles is porous and could not prevent the inner alloy from being eroded by alkali. Contrarily, the surface activity of the composites is depressed evidently. After EDN treatment, the compact nickel coating restrains the corrosion of Mg/Ni as well as the formation of porous Mg(OH)₂ mulch and acts as the electrochemical catalyst^[11]. Therefore, the overall properties of the composite are improved.

Fig. 6 illustrates the high-rate discharge (HRD) ability of amorphous CeMg₁₂ composite before and after EDN treatment. The value of HRD is calculated according to the following equation:

$$HRD = \frac{C_d}{C_d + C_{60}} \times 100\% \quad (1)$$

Where C_d is the discharge capacity at the current density (I_d) to a cut-off potential of -0.6 V vs. Hg/HgO reference elec-

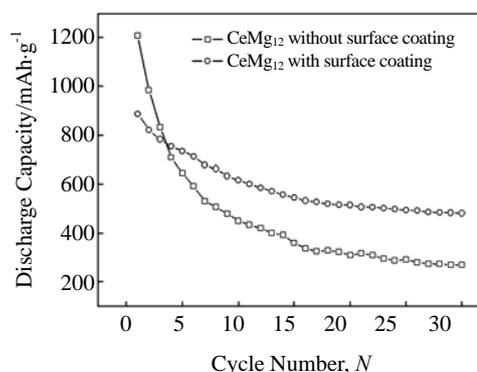
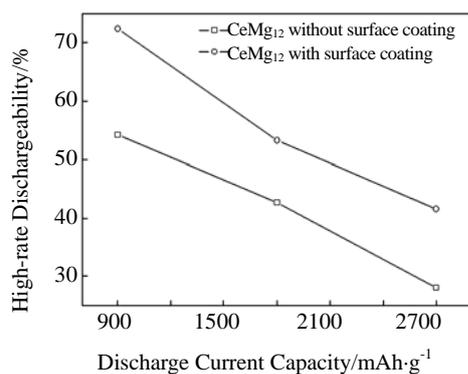


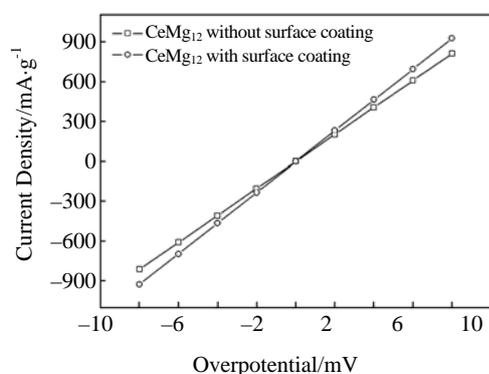
Fig.5 The cycling stabilities of amorphous CeMg₁₂ composites without and with EDN treatment

Table 2 The effect of EDN treatment on the maximum discharge capacity and cycling stability of CeMg₁₂ composites

Cycle retention rate	CeMg ₁₂ without EDN	CeMg ₁₂ with EDN
Max discharge capacity/mAh·g ⁻¹	1209.6	887.76
Cycle retention rate of 10 cycles/%	37.26	69.67
Cycle retention rate of 20 cycles/%	25.63	58.16
Cycle retention rate of 30 cycles/%	22.34	54.4

Fig.6 The high-rate dischargeability (*HRD*) of the amorphous CeMg₁₂ composites before and after EDN treatment

trode, and C_{60} is the residual discharge capacity at a discharge current density of 60 mA/g to a cut-off potential of -0.6 V vs. Hg/HgO reference electrode after the alloy electrode is fully discharged at I_d . It can be seen that the *HRD* of each alloy electrode decreases significantly with increasing of discharge current density, and EDN treatment enhances the high rate discharge ability of the amorphous composite evidently. After EDN treatment, HRD_{900} increases from 54.2% to 72.4%. The improvement of high rate discharge ability is attributed to the Ni coating with high electrochemical catalytic capability. The results of *HRD* are consistent to the linear polarization analysis which is shown in Fig.7.

Fig.7 The linear polarization curves of the amorphous CeMg₁₂ composites before and after EDN treatment

3 Conclusions

1) Amorphous CeMg₁₂ composites prepared by mechanical grinding of crystalline CeMg₁₂ and 200wt% nickel powder have high electrochemical hydrogen storage capacity, but their cycling stability is quite poor.

2) EDN treatment will form a compact nickel coating over the amorphous CeMg₁₂ composite particles which restrains the corrosion of Mg and Ni by alkali, and thus, the cycling stability is improved.

3) The cycling capacity retention rate after 10 cycles increases from 37.26% to 69.67% after EDN treatment.

4) Oxidation and corrosion is unavoidable during EDN treatment, which leads to the decrease of maximum discharge capacity.

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表面包覆对非晶态 CeMg_{12} 合金电化学性能的影响

陈如柑, 王新华, 葛红卫, 李寿权, 陈立新, 陈长聘
(浙江大学, 浙江 杭州 310027)

摘要: 采用在 CeMg_{12} 中添加镍粉球磨制备非晶态合金, 并研究化学镀表面包覆 Ni 对其电化学性能的影响。结果表明, 非晶态 CeMg_{12} 具有很高的电化学放电容量, $\text{CeMg}_{12}+200\%\text{Ni}$ (质量分数)球磨 50 h 后复合电极材料电化学容量达到 1209.6 mAh/g, 但是电化学循环稳定性较差, 10 次循环保持率为 37.26%。通过化学镀镍进行表面包覆能明显提高合金的综合电化学性能。化学镀表面包覆 Ni 后, 合金 10 个循环的保持率上升到 69.67%; 同时由于添加的 Ni 和包覆 Ni 的共同催化作用, 合金高倍率性能也得到了相应的提高, HRD_{900} 由原来的 54.2% 提升到 72.4%; 但是由于化学镀过程中部分合金被氧化, 使复合合金的最大放电容量略有下降。

关键词: 贮氢合金; CeMg_{12} ; 表面包覆; 机械合金化

作者简介: 陈如柑, 男, 1983 年生, 博士生, 浙江大学材料系, 浙江 杭州 310027, 电话: 0571-87951152