

Short communication

The effects of partial substitution of Cr for Ni on the electrochemical properties of $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{1-x}\text{Cr}_x$ ($0 \leq x \leq 0.3$) electrode alloys

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Abstract

In this paper, the substitution of different amounts of Cr for Ni in the hydrogen storage electrode alloy of $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$ has been carried out to form quaternary $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{1-x}\text{Cr}_x$ ($0 \leq x \leq 0.3$) alloys by means of solid diffusion method (DM). The XRD profiles exhibited that the quaternary alloys still kept the same main phase of Mg_3AlNi_2 (S.G. *Fd3m*) as that of ternary $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$ alloy. The electrochemical studies found that Cr substituted quaternary alloy reached its maximum discharge capacity (165 mAh g^{-1}) after 2 cycles, which was larger than that of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$ alloy (154 mAh g^{-1}). Among these quaternary alloys, the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.1}$ electrode alloy was found possessing the highest cycling capacity retention rate. Cyclic voltammetry (CV) results and anodic polarization curves demonstrated that appropriate content (x lower than 0.1) of Cr effectively improved the reaction activity of electrode and inhibited the cycling capacity degradation to some degree. Electrochemical impedance spectroscopy (EIS) analyses indicated that the increase of Cr content would raise the polarization resistance R_p on the particle surface of these quaternary alloys.

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Keywords: Mg–Al–Ni–Cr electrode alloys; Electrochemical properties; Solid diffusion method

1. Introduction

Mg-based alloys are very attractive hydrogen storage materials because of their high hydrogen storage capacity, low cost, abundant resources and light weight, etc. [1]. However, their rapid capacity degradation in alkaline solution prevented them from application in Ni–MH battery systems. Until now, the partial substitution of A side element (Mg) and/or B side element (Ni) in Mg–Ni based alloys has been widely adopted for improving their electrochemical performance in the 6 M alkaline solution [2,3]. It was reported that the substitution of Mg in Mg_2Ni -based alloys by Al was able to maintain a high discharge capacity [4,5]. The formation of $\text{Al}(\text{OH})_3$ on the particle surface of the alloys can effectively prevent the fresh surface from the corrosion of alkaline solution. However, the discharge capacity of ternary $\text{Mg}_{2-x}\text{Al}_x\text{Ni}$ alloys is still very low and the cycling stability also needs to be improved further.

Our previous work [6] found that the partial substitution of Co or Fe transitional metal for Ni in Mg–Al–Ni alloys did not change the original structure and played an important role in optimizing the cycle stability and other electrochemical properties. Since the substitution of Cr in Mg-based electrode alloys may cause positive influence on the cyclic discharge ability [2], it was chosen to substitute for Ni in the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$ to form the quaternary $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{1-x}\text{Cr}_x$ ($0 \leq x \leq 0.3$) alloys. The structural characteristics and electrochemical performances of these alloys were investigated in the present work.

2. Experimental

Pure Mg, Al, Ni and Cr powders were mixed according to the composition of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{1-x}\text{Cr}_x$ ($0 \leq x \leq 0.3$), and ground by ball mill at the speed of 300 rpm for 5 h under 0.5 MPa argon atmosphere. The ground mixture were pressed into pellets under pressure of 30 MPa and then heated for 5 h at 500 °C under argon atmosphere (0.5 MPa) for solid diffusion. After cooling down to room temperature with the furnace, the pellets were crushed into fine powders below 200 mesh.

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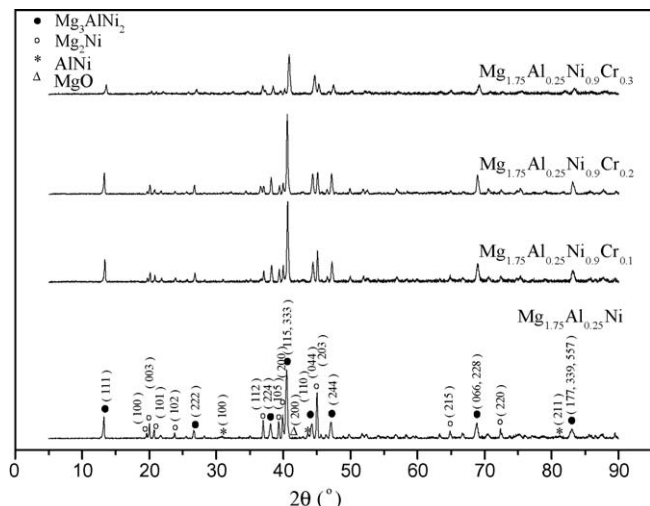


Fig. 1. XRD patterns of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{1-x}\text{Cr}_x$ ($0 \leq x \leq 0.3$) alloys.

The phase structures of these alloys were characterized by XRD using nickel filtered $\text{Cu K}\alpha$ radiation on a Rigaku D/max- γ b.

The charge–discharge measurements were performed on an LAND automatic battery-testing system as reported in our previous work [6].

The CV, EIS and anodic polarization curves were measured by IM6/THALES electrochemical workstation. The scan rate of CV measurement was 1 mV s^{-1} and the scan range was between -1.2 and -0.1 V . In the tests of anodic polarization, the potential was executed from -1.0 to 1.0 V at the scan rate of 1 mV s^{-1} . The frequency range of EIS was from 100 kHz to 5 mHz with the scan rate of 10 mV s^{-1} .

3. Results and discussion

3.1. XRD patterns of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{1-x}\text{Cr}_x$ ($0 \leq x \leq 0.3$) alloys

Fig. 1 shows the X-ray diffraction patterns of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{1-x}\text{Cr}_x$ ($0 \leq x \leq 0.3$) alloys. The same as that of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$ alloy, the main phase in the quaternary alloys is still Mg_3AlNi_2 , which was reported possessing the cubic Ti_2Ni structure (S.G. $Fd\bar{3}m$, 16 molecules per unit cell) [7]. It was also found that some Mg_2Ni , MgO , Mg and AlNi phases were formed in the quaternary alloys according to the XRD analysis. It means that the partial substitution by Cr for Ni did not differ the main phase structure of the quaternary alloys from that of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$ ternary alloy. Table 1 shows that the lattice parameters of Mg_3AlNi_2 phase increased initially when Cr reached $x = 0.1$, and then decreased with the augmentation of Cr content from $x = 0.1$ – 0.3 . For Mg_2Ni phase, a increased while c decreased with the variation of Cr content.

3.2. Discharge performance

Fig. 2 exhibits the cyclic discharge ability of the electrode alloys at 25°C . The quaternary $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{1-x}\text{Cr}_x$

Table 1
The lattice parameters of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{1-x}\text{Cr}_x$ ($0 \leq x \leq 0.3$) alloys

Alloys	Phases	Lattice parameters		
		a (nm)	c (nm)	V (nm^3)
$\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$	Mg_3AlNi_2	1.1562		1.5456
	Mg_2Ni	0.5209	1.3279	0.3120
$\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.1}$	Mg_3AlNi_2	1.1579		1.5524
	Mg_2Ni	0.5206	1.3313	0.3125
$\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.2}$	Mg_3AlNi_2	1.1546		1.5392
	Mg_2Ni	0.5193	1.3328	0.3113
$\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.3}$	Mg_3AlNi_2	1.1501		1.5213
	Mg_2Ni	0.5174	1.3348	0.3094

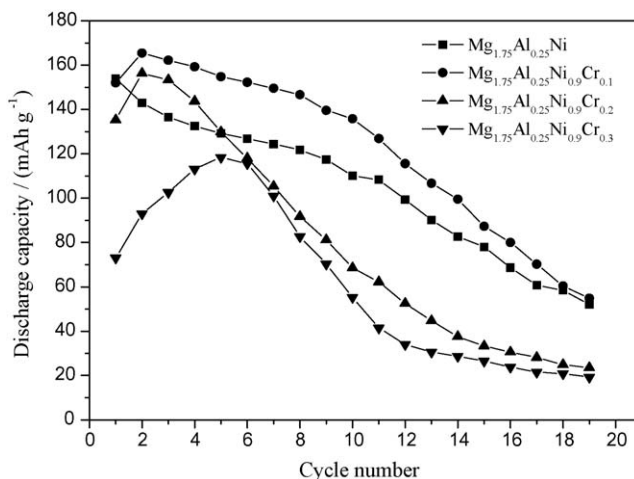


Fig. 2. Discharge capacity of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{1-x}\text{Cr}_x$ ($0 \leq x \leq 0.3$) electrode alloys at 25°C . Charge current density: 100 mA g^{-1} , 5 h; discharge current density: 25 mA g^{-1} .

($0 \leq x \leq 0.3$) alloys reached their maximum discharge capacity after 2–5 cycles. When the atomic ratio of Cr reached $x = 0.1$, the discharge capacity of the alloy was 165 mAh g^{-1} , which was higher than that of the ternary $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$ (154 mAh g^{-1}). It means that the additional Cr helped to improve the discharge capacity of Mg–Al–Ni based alloys. By comparing the discharge capacity retention rates C_{10}/C_{max} of different alloys listed in Table 2, one can see that the cyclic discharge ability of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.1}$ alloy was higher than that of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$ after 10 cycles. However, excessive Cr (x higher than 0.1) reduced the cycle stabilities of quaternary alloys. It was suggested that appropriate content (x lower than 0.1) Cr substitution for Ni was beneficial to inhibiting the rapid corrosion from

Table 2
The cyclic stability of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{1-x}\text{Cr}_x$ ($0 \leq x \leq 0.3$) electrode alloys

Alloys	C_{max} (mAh g^{-1})	C_{10} (mAh g^{-1})	C_{10}/C_{max} (%)
$\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$	154	110	71.59
$\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.1}$	166	136	82.05
$\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.2}$	156	69	43.83
$\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.3}$	118	55	46.71

C_{10} stands for the discharge capacities of the alloys at the 10th cycle and C_{max} stands for the maximal discharge capacities of the alloys.

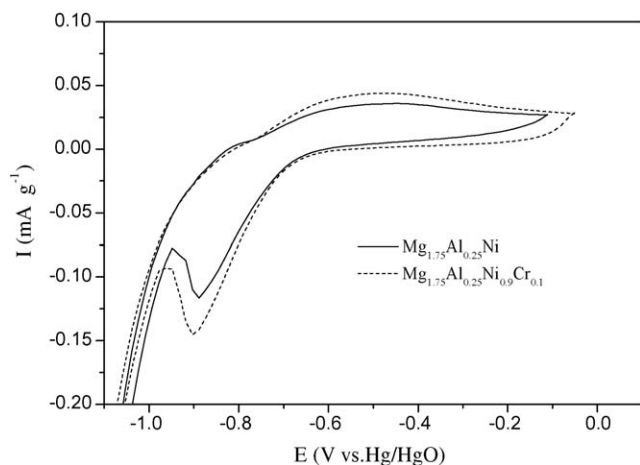


Fig. 3. Cyclic voltammograms curves of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$ and $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.1}$ electrode alloys.

high-density alkaline solution, and therefore improving the discharge capacity retention rate.

Fig. 3 exhibits the cyclic voltammogram curves of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$ and $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.1}$ electrode alloys in 6 M KOH solution at room temperature. The anodic peak around -500 mV versus Hg/HgO could be ascribed to the oxidation of hydrogen absorbed in the alloys, while the cathodic peak around -895 mV versus Hg/HgO is ascribed to the reduction of H_2O and adsorption of hydrogen on the alloys surface (or the overall surface).

It can be seen from Fig. 3 that the hydrogen absorption/adsorption peak of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.1}$ alloy in this potential range is more significant than that of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$ alloy. It demonstrated that additional Cr promoted the reduction of H_2O and also the absorption of hydrogen on the electrode surface. In the anodic branch of voltammogram curves, one observed that Cr substituted alloy possessed a higher current density and area of the anodic peak. These results revealed that additional Cr elements could improve the oxidation activity of alloy electrode, which subsequently helped to improve the hydrogen discharge capacity of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.1}$ alloy. The hydrogen desorption peaks of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.1}$ alloy is observed at a more negative potential than that of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$ alloy. It is obvious that the discharge of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.1}$ electrode alloy proceeded more rapidly than that of $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$ alloy.

3.3. Corrosion of the alloys

Fig. 4 shows the anodic polarization curves of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$ and $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.1}$ electrode alloys after 5 cycles. The anodic dissolving potentials of the alloy containing Cr was -0.925 V, which shifted a little toward positive direction compared with the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$ alloy (-0.967 V).

The corrosion current values can be obtained according to the formulas deduced by Barnartt [8]. The I_{corr} values were calculated and listed in Table 3. It can be seen that the I_{corr} of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.1}$ is lower than that of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$. It means that the substituting element Cr decreased the corro-

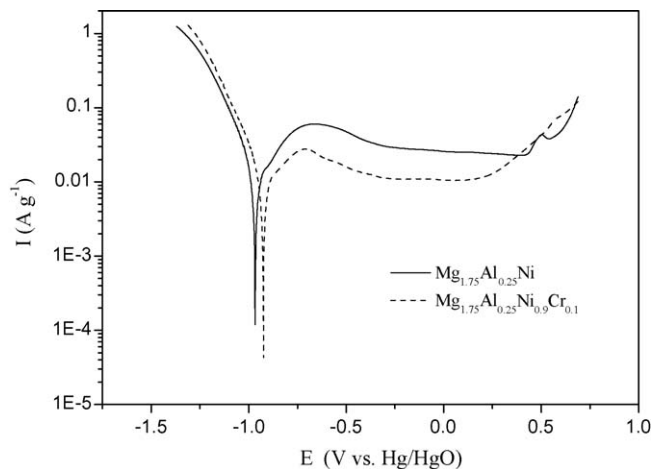


Fig. 4. Corrosion potential curves of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$ and $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.1}$ electrode alloys after 5 cycles.

Table 3

The corrosion current density of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$ and $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.1}$ electrode alloys after 5 cycles

Alloys	I_{corr} after 5 cycles (mA g^{-1})
$\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$	2.40
$\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.1}$	1.58

sion rate of Mg–Al–Ni electrode alloys. These results suggested that the appropriate content ($x=0.1$) of Cr improved the anti-corrosion behavior to a certain degree. The cyclic stability of charge–discharge experiment also supported the conclusion.

3.4. Electrochemical impedance analysis

Fig. 5 shows the impedance spectra of the Mg–Al–Ni–Cr electrode alloys with different Cr content at 50% DOD of the fifth cycle. By means of non-linear least squares (NLLS) fitting program EQUIVCT to the diagrams, the equivalent circuit is

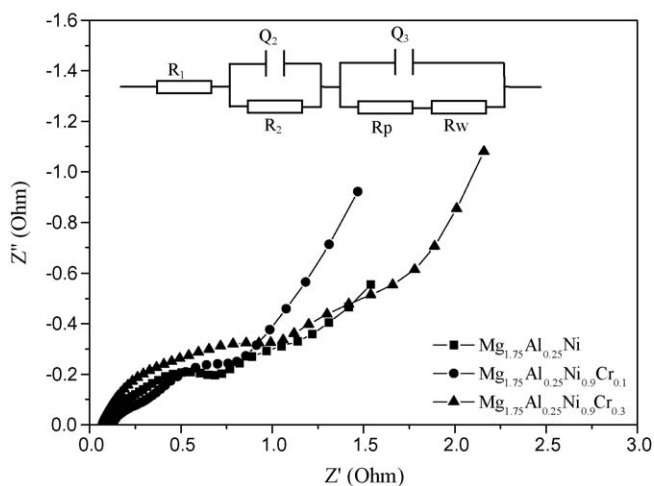


Fig. 5. The EIS Nyquist diagrams and their equivalent circuit of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{1-x}\text{Cr}_x$ ($0 \leq x \leq 0.3$) electrode alloys at 50% DOD of the fifth cycle.

Table 4

R , Q and I_0 values of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{1-x}\text{Cr}_x$ ($0 \leq x \leq 0.3$) electrode alloy at 50% DOD of the fifth cycle

Alloys	R_p (Ω)	I_0 (mA g^{-1})
$\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$	0.756	16.96
$\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.1}$	0.625	20.52
$\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.8}\text{Cr}_{0.3}$	1.123	11.42

plotted. Table 4 gave their values of polarization resistance (R_p) and surface exchange current density (I_0) calculated by the below equation [9]:

$$I_0 = \left(\frac{RT}{nF} \right) \left(\frac{1}{R_p} \right) \quad (1)$$

The variation of R_p shows that appropriate content ($x=0.1$) of Cr addition in the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$ alloy could reduce the reaction resistance and raise the exchange current density considerably. However, excessive Cr (x more than 0.1) would increase the polarization resistance R_p on the particle surface for these quaternary alloys.

4. Conclusions

The effects of partial elements substitution for Ni in the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$ alloy by Cr on the structural characteristics and electrochemical performances of the quaternary alloys were investigated. It was found that the quaternary alloys still kept the main phase of Mg_3AlNi_2 (S.G. $Fd\bar{3}m$) as the ternary $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}$ alloy. The $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{1-x}\text{Cr}_x$ ($0 \leq x \leq 0.3$) electrode alloys need 2–5 cycles to reach their maximum discharge capacity. The discharge capacity increased from 154

to 165 mAh g^{-1} with the x increasing from zero to 0.1. The $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{0.9}\text{Cr}_{0.1}$ electrode alloy possessed the highest cycling discharge capacity retention rate among the alloys. Cyclic voltammetry (CV) results and anodic polarization curves demonstrated that additional Cr could improve the electrocatalytic oxidation activity and the anti-corrosion behavior to some degree. EIS results of the $\text{Mg}_{1.75}\text{Al}_{0.25}\text{Ni}_{1-x}\text{Cr}_x$ ($0 \leq x \leq 0.3$) revealed that with the augmentation of Cr content, the reaction resistance increased considerably.

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