Int. J. Electrochem. Sci., 1(**2006**)47-54

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Structures and Hydrogen Storage Properties of $Mg_{45}M_5Co_{50}$ (M=Zr, Ni, Al) Ternary Alloys by Mechanical Alloying

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Received: 17 April 2006 / *Accepted:* 24 April 2006 / *Published:* 27 April 2006

Ternary alloys $Mg_{45}M_5Co_{50}$(M= Zr, Ni, Al)were synthesized by mechanical alloying technique to improve the hydrogen storage properties of $Mg_{50}Co_{50}$ binary body centered cubic (BCC) alloy. X-ray diffraction (XRD) revealed that the Bragg peaks of these alloys were broadened, which indicated that the crystalline size of these alloys was fully pulverized. Both BCC phase and amorphous phase in the ternary alloys were found after ball milling for more than 80 h by transmission electron micrograph (TEM). With the increase of ball milling time, however, the BCC phase disappears gradually and the amorphous phase dominated the alloys eventually. Pressure-Composition-Isotherms (P-C-T) measurements showed that these ternary alloys containing BCC phase can absorb hydrogen at 353 K within the hydrogen pressure range of 0 ~ 3 MPa. $Mg_{45}Al_5Co_{50}$ alloy had the maximum hydrogen absorption amount (2.0 wt. %) among these ternary alloys. Moreover, ternary $Mg_{45}Al_5Co_{50}$ alloy exhibited better hydrogenation kinetics than binary $Mg_{50}Co_{50}$ alloy. The former took about 30 h to reach the maximum capacity, which is faster than the latter of 40 h. The third elements Ni and Zr improve the hydrogen desorption properties of $Mg_{50}Co_{50}$ alloy which hardly desorbs any hydrogen. TG analysis showed that $Mg_{45}Ni_5Co_{50}$ and $Mg_{45}Zr_5Co_{50}$ can desorb hydrogen 0.5 wt. % at 350 K and 1.0 wt. % at 470 K, respectively.

Keywords: $Mg_{45}M_5Co_{50}$ ternary alloys, P-C-T curve, Mechanical alloying, Hydrogen storage property, Structure

1. INTRODUCTION

Mg and Mg-based alloys have been widely studied during the last decades because of the advantages such as lightweight, great abundance and large hydrogen absorption capacity [1-3].

However, the temperature of hydrogen absorption and desorption is too high and also the hydrogenation-dehydrogenation kinetics is not satisfied. Many amorphous or nano-crystalline Mg-based hydrogen storage alloys have been successfully prepared by mechanical alloying (MA) to improve their gaseous and electrochemical hydrogen storage properties [4-7]. Meanwhile, previous experimental studies showed that the BCC structure has more room for hydrogen accommodation in the lattice [8-11], because the BCC structure possesses lower density than the conventional hydrogen absorbing alloys that have usually closer packed structures.

In recent years, Mg-based hydrogen storage alloys with BCC phase have been prepared by MA technique. The metastable BCC structure for Mg-Tm-V (Tm= Ni, Co, Cu) immiscible system [12] was synthesized by MA and the maximum hydrogen storage capacity reached 2.3 wt.% at 298K and 3 MPa hydrogen pressure. Zhang Y. *et al.* [13-14] found that mechanical milling of Mg-Co and Mg-Co-X (X= Fe, Cu, Pd) led to formation of single BCC phase alloys in which the maximum hydrogen storage capacity was 2.7 wt.% at 373 K and 6 MPa hydrogen pressure. However, the Mg-Co alloys did not desorb hydrogen even under vacuum at 373 K.

Therefore, some third elements were introduced into Mg-Co binary alloy to partially substitute Mg in order to improve both the hydrogen desorption amount and the kinetics of hydrogen absorption-desorption. In this study, the ternary $Mg_{45}M_5Co_{50}$(M= Zr, Ni, Al) alloys with BCC phase were prepared by means of mechanical alloying. Their structures and hydrogen storage properties were investigated and will be discussed here.

2. EXPERIMENTAL PART

2.1. Preparation of $Mg_{45}M_5Co_5$ alloys

The ternary $Mg_{45}M_5Co_{50}$(M= Zr, Ni, Al)alloys was prepared by mechanical alloying (MA). The purity of all metal powders was higher than 99.5%. The powder mixtures as designed stoichiometry were ground by QM-1SP planetary ball mill. In each stainless milling pot, the ball-to-powder weight ratio was 20:1 under 0.2 ~ 0.3 MPa argon pressure. The rotation speed of the ball milling was fixed as 450 rpm. The study also prepared $Mg_{50}Co_{50}$ binary alloy for comparison.

2.2. Structure analysis

The structure of the ternary alloys was characterized by XRD (Rigaku D/max-2500, 50 kV, 200 mA) with Cu Kα radiation, and transmission electron microscopy (TEM, JEOL100CX).

2.3. Hydrogen absorption-desorption properties

The hydrogen absorption-desorption performances and the kinetics of hydrogen absorption of the $Mg_{45}M_5Co_{50}$(M= Zr, Ni, Al) alloys were determined by the conventional Sievert-type P-C-T apparatus as described in our previous study [15]. The P-C-T measurements without the activation were carried

out at 353 K and within the hydrogen pressure range of 0 ~ 3 MPa. The purity of the hydrogen was 99.9999%. The hydrogen desorption properties were also detected by thermo- gravimetry (TG, DT-20B) with a heating rate of 10 K/min under high-purity argon (purity>99.999%) atmosphere.

3. RESULTS AND DISCUSSION

3.1 The structure of $Mg_{45}M_5Co_{50}$ (M= Zr, Ni, Al) alloys

Fig. 1 shows XRD patterns of $Mg_{45}M_5Co_{50}$ (M= Zr, Ni, Al) alloys. For each alloy, a broadened Bragg peak is observed, which indicates the crystalline grain is pulverized to nano-scale or even nearly amorphous. The TEM observations (Fig. 2) of $Mg_{50}Co_{50}$ and $Mg_{45}Ni_5Co_{50}$ alloy confirm that the co-axial rings in the selected area electron diffraction (SAED) images are due to the formation of nano-scale BCC phase after around 80 h of milling time.

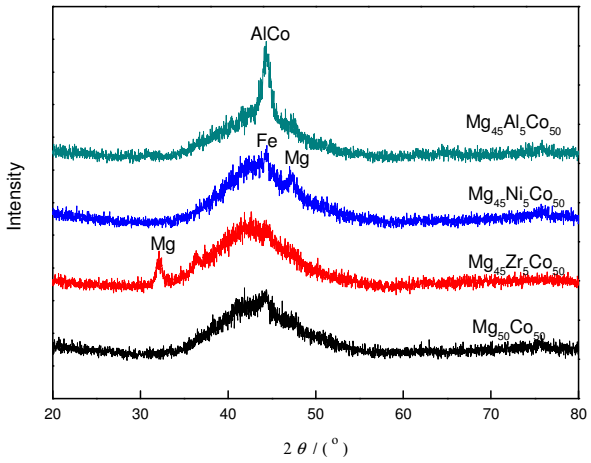

Figure 1. XRD patterns of Mg-M-Co ternary alloys

Meanwhile, the amorphous phases are also detected by SAED images as shown in Fig. 2. The XRD patterns of $Mg_{45}Ni_5Co_{50}$ and $Mg_{45}Zr_5Co_{50}$ alloys were similar to that of the $Mg_{50}Co_{50}$ alloy except for some diffraction peaks of impurities (metallic Mg and Fe). As for $Mg_{45}Al_5Co_{50}$ ternary alloy, the XRD pattern showed that AlCo phase was also formed after 100 h ball milling. The SAED images of $Mg_{45}M_5Co_{50}$ alloys exhibit the similar co-axial rings to that of $Mg_{50}Co_{50}$ from which the lattice parameters are evaluated as listed in Table 1. It can be concluded that the additional elements Ni and Zr introduced into Mg-Co binary alloy enlarge the lattice parameter and thus volumes of the parent $Mg_{50}Co_{50}$ BCC phase (also listed in Table 1). The sequence of the lattice parameters of the $Mg_{45}M_5Co_{50}$ ternary alloys is as follow:

$$Mg_{45}Al_5Co_{50} < Mg_{45}Ni_5Co_{50} < Mg_{45}Zr_5Co_{50}$$

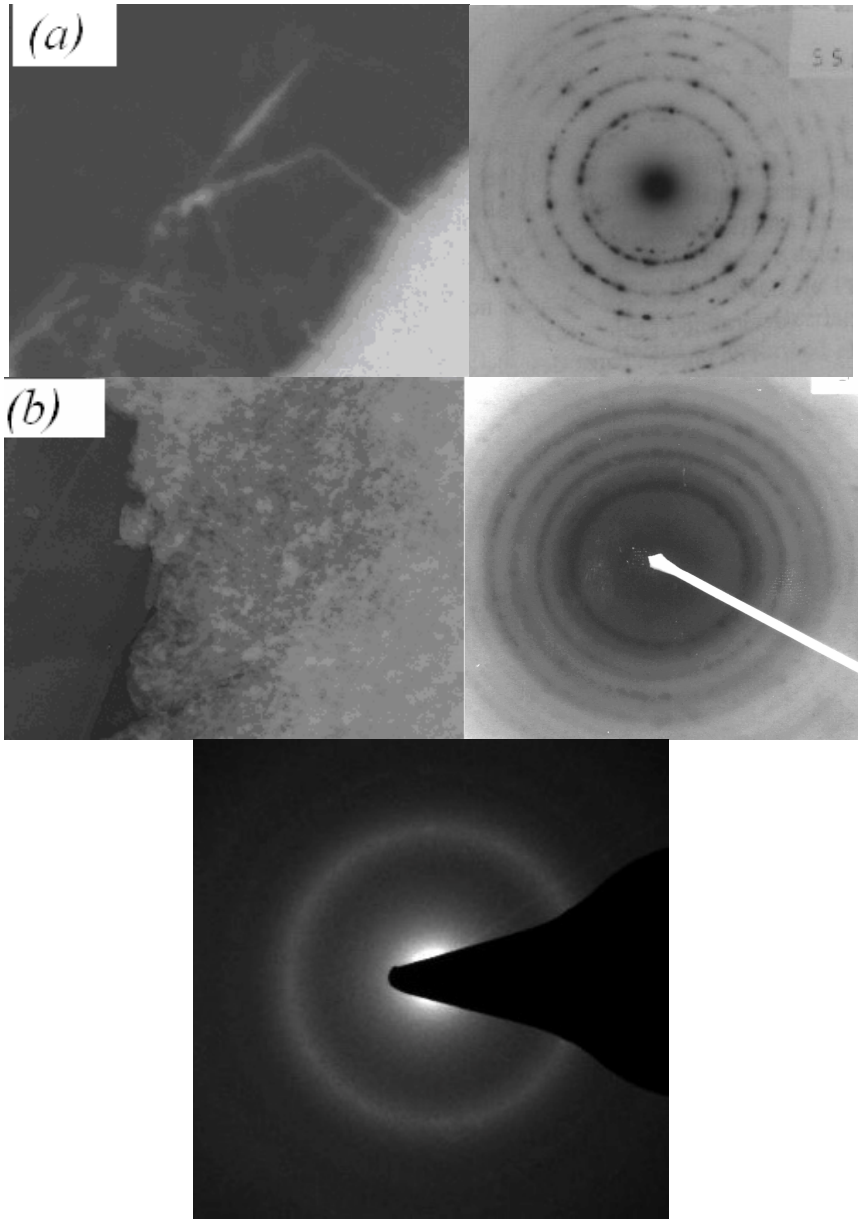

Figure 2. TEM images and SAED patterns of Mg-Co alloys after 80 h ball milling (*a*) $Mg_{50}Co_{50}$; (*b*) $Mg_{45}Ni_5Co_{50}$

Further TEM studies also find that, with the increase of ball milling time, the BCC phase in the ternary alloys disappears gradually, and the amorphous phase dominates the alloy eventually. For $Mg_{50}Co_{50}$ and $Mg_{45}M_5Co_{50}$ alloys, it usually takes more than 200 h to form fully amorphous phase. Since the fully amorphous Mg-Co-based alloy after 200 h milling time hardly absorbed and desorbed hydrogen by our studies, the time of ball milling would not be prolonged in the present work, which was set as 80 h or 100 h.

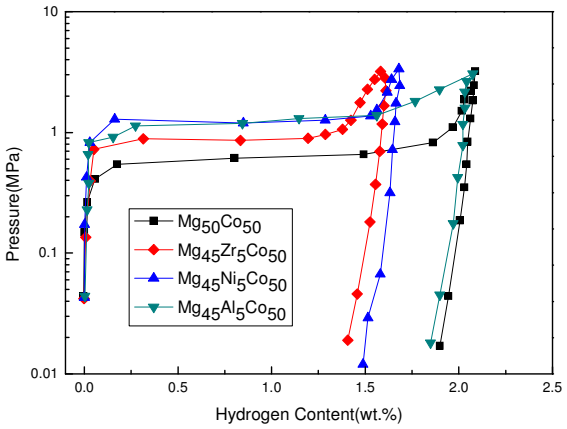

Figure 3. P-C-T diagrams of $Mg_{45}M_5Co_{50}$ alloys for the first cycle at 353 K within H_2 pressure range of 0 ~ 3 MPa

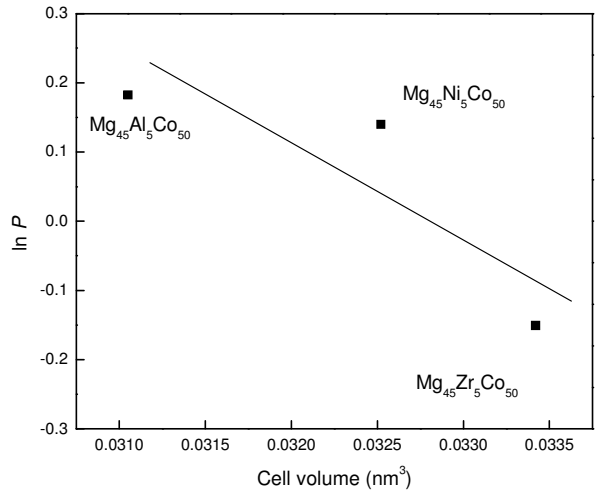

Figure 4. Plot of ln *P* against cell volume for $Mg_{45}M_5Co_{50}$ alloys

3.2 The hydrogen absorption-desorption performances of $Mg_{45}M_5Co_{50}$ alloys

Fig. 3 shows P-C-T diagrams of $Mg_{45}M_5Co_{50}$ alloys at 353 K for the first cycle. All P-C-T curves have significant plateaus (see Table 1). The hydrogen absorption amount was 2.0 wt. %, 1.7 wt. % and 1.6 wt. % for $Mg_{45}Al_5Co_{50}$, $Mg_{45}Ni_5Co_{50}$ and $Mg_{45}Zr_5Co_{50}$, respectively. Table 1 indicates that the lattice volumes of ternary alloys are inversely proportional to the logarithm values of their plateau pressures. Their relationship described by Fig. 4 was similar to that of $LaNi_{5-x}Al_x$ alloys [16]. The

atomic radii of Ni and Zr were larger than that of Mg, which led the lattice parameters much higher than suitable parameter of those BCC solid solution alloys (a = 0.302□0.304 nm) [11]. Therefore, it was difficult to occupy stably in the crystal lattice for the hydrogen atoms, which resulted in the decrease of hydrogen storage amount. As for metallic Al, its doping hardly changed the lattice parameter of the ternary alloy and did not affect the hydrogen storage amount compared to $Mg_{50}Co_{50}$ alloy.

Table 1 The lattice parameters and hydrogen storage properties of Mg-Co-based alloys

Alloys	Lattice parameters (nm)[a]	Lattice volumes (nm^3)	Amount of hydrogen absorbed (wt.%)	Plateau of hydrogen absorption (MPa)	Amount of hydrogen desorbed (wt.%)[b]
$Mg_{50}Co_{50}$	0.3143	0.03105	2.1	0.65	0
$Mg_{45}Al_5Co_{50}$	0.3143	0.03105	2.0	1.20	0
$Mg_{45}Ni_5Co_{50}$	0.3192	0.03252	1.7	1.15	1.0
$Mg_{45}Zr_5Co_{50}$	0.3221	0.03342	1.6	0.86	0.5

[a] Calculated from the SAED images
[b] Determined by TG analysis

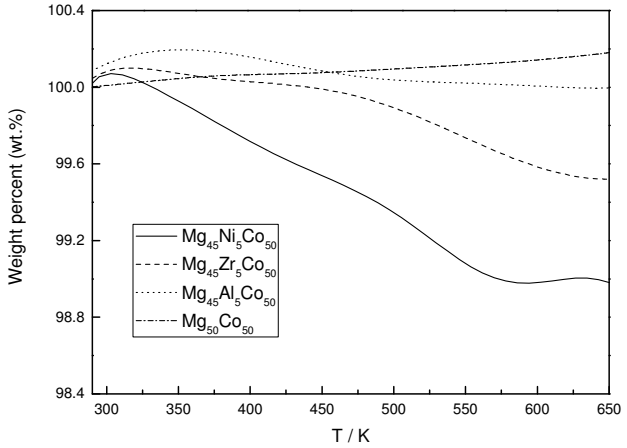

Figure 5. The TG curves of hydrogenated $Mg_{45}M_5Co_{50}$ alloys

Fig. 5 is the TG curves for the hydrides of $Mg_{45}M_5Co_{50}$ alloys. The weight loss was found at about 350 K and 470 K and the desorption amount was 1.0 wt. % and 0.5 wt. % for $Mg_{45}Ni_5Co_{50}$ and $Mg_{45}Zr_5Co_{50}$ after hydrogenation, respectively. The weight loss was only ascribed to the hydrogen

desorption, which could not be detected by P-C-T apparatus because of low desorption hydrogen pressure and apparatus precision. No mass loss of $Mg_{50}Co_{50}$ and $Mg_{45}Al_5Co_{50}$ alloys was detected in this work. It is still unclear for the reason why they cannot desorb any hydrogen. However, the thermal stability, hydrogen desorption, kinetics and cycling properties of these alloys are being investigated.

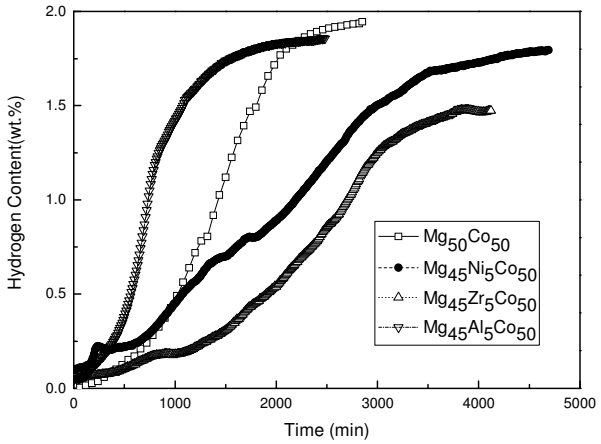

Figure 6. The kinetic curves of H_2 absorption for $Mg_{45}M_5Co_{50}$ at 353 K at initial hydrogen pressure of about 3.5 MPa

3.3 The kinetics of hydrogen absorption of $Mg_{45}M_5Co_{50}$ alloys

In general, the kinetics of absorption-desorption of Mg-based hydrogen storage alloys is very poor. In the present work the hydrogen uptake kinetics had been improved from binary $Mg_{50}Co_{50}$ alloy when Mg was partially substituted by Al. Fig. 6 shows the hydrogen absorption curves of the binary $Mg_{50}Co_{50}$ alloy and ternary $Mg_{45}M_5Co_{50}$ alloys at 353 K under initial hydrogen pressure of about 3.5 MPa and the ending pressure of 3.0 MPa without any activation process. From the Fig. 6, we can find that the hydrogen absorption rate of ternary $Mg_{45}Al_5Co_{50}$ alloys is superior to that of $Mg_{50}Co_{50}$ binary alloy. The former took about 30 h to reach its maximum hydrogen capacity which is more quickly than the latter of 40 h. The improvement on kinetics may be ascribed to the additional Al. Since metallic Al with catalytic activity could facilitate diffusion of hydrogen atom in the bulk of the alloy, which provided favourable paths for diffusion of hydrogen atom in grain boundaries [17].

4. CONCLUSIONS

The structures and hydrogen storage characteristics of ternary $Mg_{45}M_5Co_{50}$ (M= Zr, Ni, Al) alloys prepared by mechanical alloying were systematically investigated. TEM observation confirmed

that the ternary alloys consist of the BCC phase that played an important role in hydrogen absorption-desorption and amorphous phase. $Mg_{45}Al_5Co_{50}$ alloy showed the most hydrogen-absorbing amount (2.0 wt.%) among the studied ternary alloys at 353 K. $Mg_{45}Zr_5Co_{50}$ and $Mg_{45}Ni_5Co_{50}$ ternary desorbed 0.5 wt.% and 1.0 wt.% hydrogen determined by TG analysis, respectively. Additional Al was beneficial to improve the kinetics of hydrogen absorption. Further studies are in progress to improve the thermal stability, the properties of hydrogen desorption kinetics and the cycling stability.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the National Nature Science Foundation of China for financial support to this work under Grant No. 20473091 and 20573112.

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