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Characteristics of $Mg_2Ni_{0.75}M_{0.25}$ (M=Ti, Cr, Mn, Fe, Co, Ni, Cu and Zn) alloys after surface treatment

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Abstract

The ternary $Mg_2Ni_{0.75}M_{0.25}$ (M=Ti, Cr, Mn, Fe, Co, Ni, Cu and Zn) alloys have been successfully synthesized by the ball milling diffusion method (BDM). XRD results show that they all have a hexagonal crystal structure. We show that the alloys after fluorination treatment show good performance: the hydrogen desorption capacity reaches the highest value after only two adsorption–desorption cycles. The ratio of H/M is about 1.18 (≈3.3 wt.%) on desorption at 250°C. The hydrides have monoclinic phases. The larger the unit volume, the more unstable is the hydride. The dissociation enthalpies and temperatures of the hydrides in an open system are decreased with increasing unit cell volume. Replacement of Ni in Mg_2Ni by Cr, Mn and Co has the same effect on Mg_2Ni: they lower the decomposition plateau pressure; Ti and Cu have the opposite effect and Fe and Zn have little effect. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ball milling diffusion method; Surface treatment; Ternary Mg–Ni–M alloys; Dehydriding properties; Crystal structure

1. Introduction

The interest in magnesium as a hydrogen storage material originates in the higher hydrogen weight percent of the metal hydride, and the lower price compared with other types of metal hydrogen systems [1]. However, it is inadequate for practical use for hydrogen storage applications because of its poor hydriding–dehydriding properties at ambient temperature: thermodynamically too stable and kinetically by far too slow.

In recent years, much effort has been made to improve the hydriding–dehydriding properties of the Mg–hydrogen system [2–12]. The hydriding–dehydriding properties of the Mg–hydrogen system have been substantially improved in several ways [7] including the formation of intermetallic compounds like Mg_2Ni. Among them, partial element replacement is a very effective method. This research was conducted in order to investigate the properties of the Mg_2Ni alloy after replacement of Ni by transition elements located in the fourth period.

It is known that the untreated Mg-based hydrogen storage alloy is very difficult to activate owing to the formation of MgO on the alloy surface [5–8]. Normally, the desorbed hydrogen capacity becomes constant after ten activation cycles [8]. In order to shorten the activation procedure, the surface treatment is necessary.

In our previous studies, a new fluorination treatment using a 0.06 mol/l NH_4F solution was developed and applied to treat Mg and Mg-based alloys in our laboratory [8]. The results showed that the fluorination treatment was very effective. An Mg-based alloy could be activated very well only after two cycles after treatment.

This research is an extension of our previous investigation [6–8] aimed at improving the hydriding–dehydriding properties of Mg-based alloys. In the present work, we have successfully synthesized the ternary $Mg_2Ni_{0.75}M_{0.25}$ alloys by BDM [7]. The fluorination treatment mentioned above is applied. Studies on the treated samples reveal improved behavior. The relationship between the crystal structure and the dehydriding properties is also discussed.

2. Experimental

The ternary $Mg_2Ni_{0.75}M_{0.25}$ (M=Ti, Cr, Mn, Fe, Co, Ni, Cu and Zn) samples are produced by BDM according to the previous studies [7]. The samples produced in this way are crushed and subjected to the component analysis methods (chemical analysis), which indicate that the samples are $Mg_2Ni_{0.75}M_{0.25}$. The X-ray diffraction (XRD)

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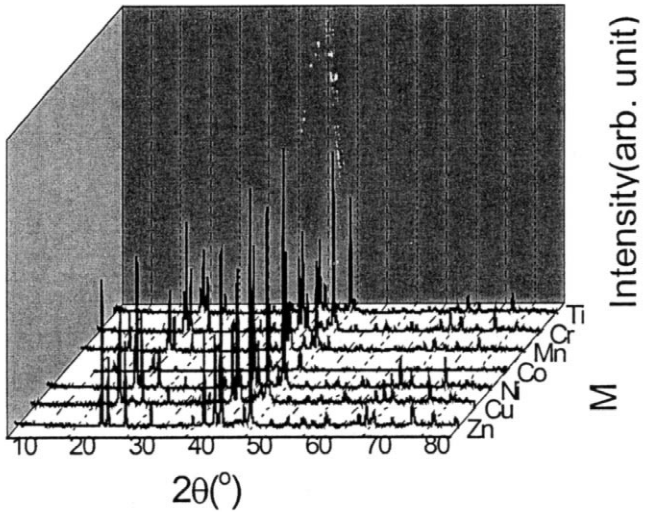

Fig. 1. XRD spectra of the ternary $Mg_2Ni_{0.75}M_{0.25}$ alloys (M=Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn).

spectra are recorded using a Rigaku D/max-2500 X-ray diffractometer with CuKα radiation. The ternary $Mg_2Ni_{0.75}M_{0.25}$ samples are treated by a fluorination solution according to the previous studies [8]. Then, the powder is rinsed with tap water and dried at 40°C in air. The specific surface area of each sample is obtained by the Brunaner–Emmett–Teller (BET) method using nitrogen adsorption at 77 K.

The dehydriding properties of the treated samples are evaluated by monitoring the desorption *P–C* isotherms by the conventional constant-volume method. The dehydriding procedure is described elsewhere [6,7].

3. Results and discussion

3.1. Crystal structure of the samples

The XRD spectra of the $Mg_2Ni_{0.75}M_{0.25}$ (M=Ti, Cr, Mn, Fe, Co, Ni, Cu and Zn) samples are shown in Fig. 1. The main phase of each sample is that of Mg_2Ni, which has a hexagonal crystal structure.

3.2. Fluorination treatment of the ternary alloys

In order to shorten the activation time, surface treatment is necessary. After fluorination, as part of the elements is removed from the alloy surface, more cavities with large holes, cracks and defects are formed [8]. Also, as the honeycomb MgF_2 layer is formed instead, a large amount of cavities with large holes at the surface are found. All these result in the enlarging of the specific surface area, which is known to accelerate the reaction kinetics [8]. The specific surface area obtained by the BET method is listed in Table 1.

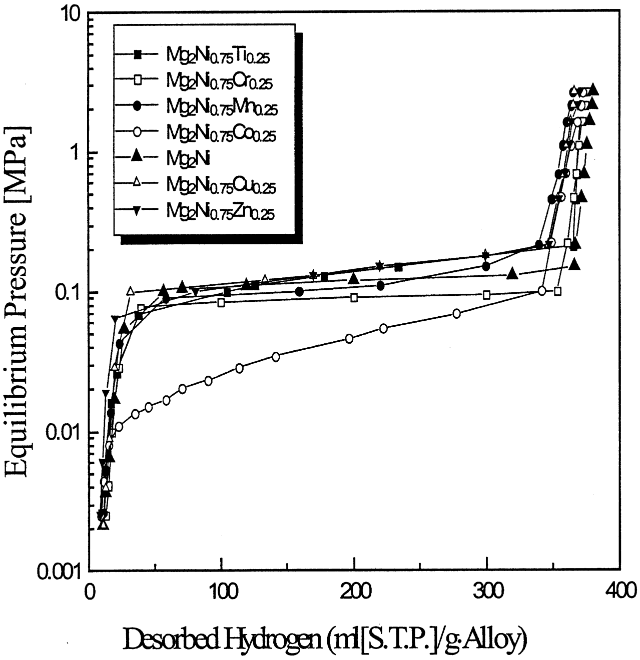

Fig. 2. *P–C* desorption isotherms of the ternary $Mg_2Ni_{0.75}M_{0.25}$ alloys at 250°C.

3.3. Dehydriding properties

The *P–C* hydrogen desorption isotherms of the ternary $Mg_2Ni_{0.75}M_{0.25}$ alloys at 250°C after fluorination are shown in Fig. 2. The desorption capacity given in Table 2 can reach the maximum values after only two adsorption–desorption cycles. They are only slightly lower than the theoretical value (H/M=1.3, ≈3.3wt.%), which is due to the loss of part of the Mg after fluorination. We consider the presence of the honeycomb MgF_2 layer and Ni-rich layer with high activity may be the main reason of the improvement of the hydriding–dehydriding properties after surface treatment [8].

After replacement of Ni in the Mg_2Ni alloy, there are three results shown in Fig. 2: Cr, Mn and Co have the same effects on the Mg_2Ni alloy as on $LaNi_5$, i.e. they lower the desorption plateau pressure; Ti and Cu have different effects on the Mg_2Ni alloy from $LaNi_5$, which

Table 1
Specific surface area of the $Mg_2Ni_{0.75}M_{0.25}$ alloys after treatment

Alloying elements	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn
Specific surface area (m^2/g)	4.1	4.3	3.9	4.5	3.9	3.8	4.1	5.1

Table 2
Hydrogen desorption capacity of the $Mg_2Ni_{0.75}M_{0.25}$ hydrides (250°C)

Alloying elements	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn
Desorbed hydrogen capacity (ml(S.T.P.)/g alloy)	372	381	370	375	372	381	372	375
H/M	1.17	1.18	1.18	1.17	1.18	1.18	1.18	1.18

increases the desorption plateau pressure; Fe and Zn have little effect.

3.4. Relationship between the hydride stability and crystal structure

The unit cell parameters derived from Fig. 1 are shown in Fig. 3. It is found that the parameters *a*, *c* and *V* are varied with the alloying elements substituted for Ni atoms. The atomic radii of the eight substitutional elements vary as follows: Ti>Mn>Zn>Cu>Co>Cr>Ni>Fe, as shown in Fig. 4. After substitution, the unit cell parameters of the ternary $Mg_2Ni_{0.75}M_{0.25}$ alloys vary considerably with M in approximately the same way as that of the alloying elements (M) except Ti. That probably means most of the alloying elements occupy the same sites. It is estimated to be the Ni atoms.

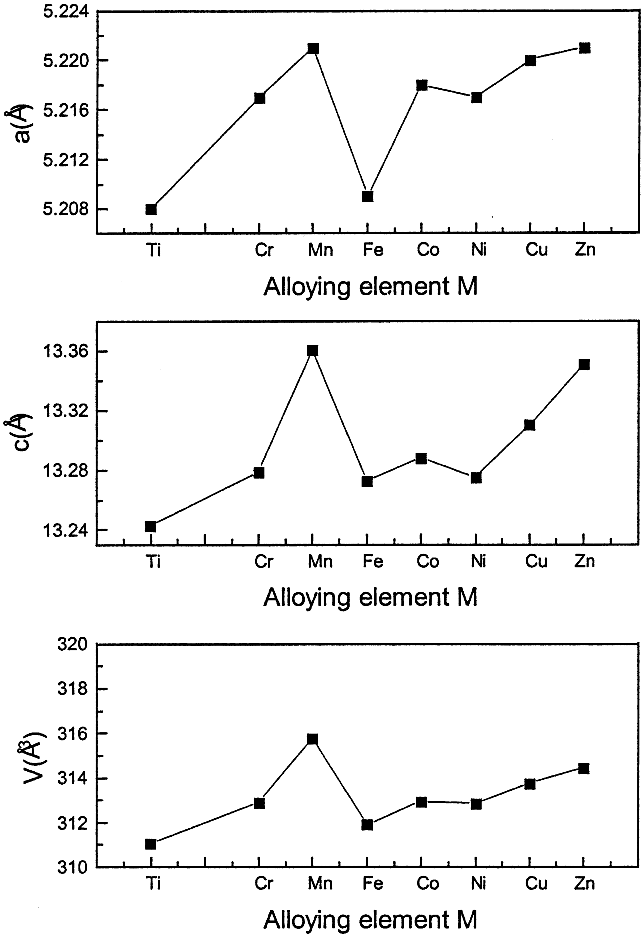

Fig. 3. Relationship between the unit cell parameters and alloying elements.

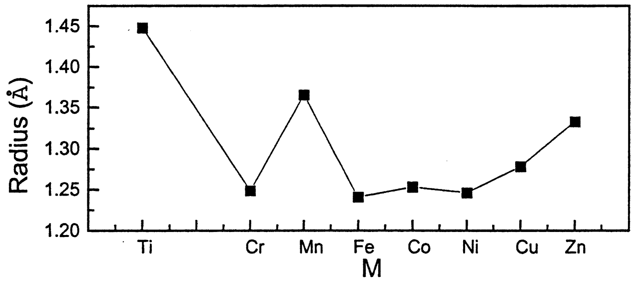

Fig. 4. Atomic radii of the alloying elements.

The typical cluster model used has been shown elsewhere [13,14]. It is a cluster constructed on the crystal structure of the HT phase of Mg_2NiH_4 [15]. For Cu substitution, it is found that the unit cell volume is increased. As we know, the larger the unit cell volume, the more stable the hydride. However, there are some exceptions to this rule. For example, there is an opposite correlation in a $Mg_2Ni_{1-x}Be_x$ system [1]. Then, in order to test this correlation in the present system, the relationship between the stability and the unit cell volume for each hydride is discussed in the following.

Fig. 5 and Table 3 show that the dissociation enthalpies and temperatures vary in opposite ways with increasing atomic number. This has been discussed elsewhere [13]. When comparing Fig. 5 with the figure in Ref. [16], there is a clear difference. The rule mentioned above is generally satisfied for the AB_5 compounds. However, for the $Mg_2Ni_{0.75}M_{0.25}$ alloys, data are scattered, but still there is a tendency for the compounds to become unstable with increasing unit cell volume (compared with Table 3). Thus,

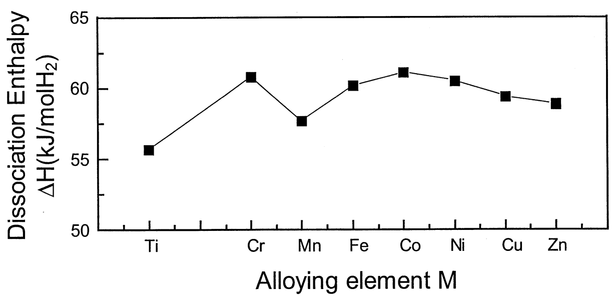

Fig. 5. Relationship between the dissociation enthalpies of the ternary $Mg_2Ni_{0.75}M_{0.25}$ hydrides and the atomic number of the substitution element M.

Table 3
Dissociation enthalpies ΔH, entropies ΔS and the temperatures of the $Mg_2Ni_{0.75}M_{0.25}$ hydrides

Alloying element (M)	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ni[a]
ΔH (kJ/mol H_2)	56	61	58	60	61	61	59	59	64
ΔS (J/K mol H_2)	103	106	102	107	105	108	109	107	122
T (°C)[b]	266	302	291	288	310	285	271	280	253

[a] Ref. [15].

[b] Dissociation temperature is defined as in Ref. [7].

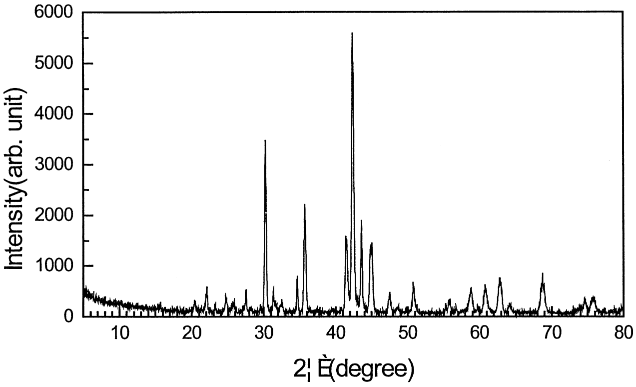

Fig. 6. XRD spectrum of $Mg_2Ni_{0.75}Co_{0.25}H_{1.18}$.

this empirical rule is no longer valid in the $Mg_2Ni_{0.75}M_{0.25}$ systems.

Fig. 6 is the XRD spectrum of the $Mg_2Ni_{0.75}Co_{0.25}H_{1.18}$. The hydride has a monoclinic crystal structure, which is completely different from that of Mg_2Ni. As a result, the hydrogen atoms easily occupy a portion of the corner sites in the small octahedron existing around every Ni atom, as shown in Ref. [13]. This occupancy of hydrogen atoms will not accompany any significant lattice expansion because of the large atomic volume in it, and the occupied portions of the octahedron sites will simply increase as the hydrogenation proceeds. Therefore, the hydride phase will not be stabilized by the increase of the unit cell volume even if it is induced by alloying into Mg_2Ni, but rather it is destabilized because the lattice expansion weakens the Ni–Mg interaction which is primarily responsible for the formation of the solid metal-framework of the hydride [13].

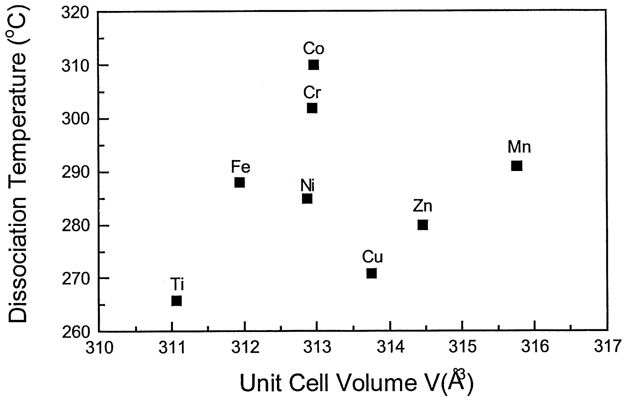

Fig. 7. Relationship between the dissociation temperature in an open system and the unit cell volume.

Fig. 7 shows the relationship between the dissociation temperature in an open system and the unit cell volume. From the above discussion, it is known that for the $Mg_2Ni_{0.75}M_{0.25}$ alloys, the larger the unit cell volume, the more unstable the hydride. We also know that the dissociation temperature has a good correlation with the enthalpy. Therefore, the larger the unit cell volume, the lower the dissociation temperature generally, as shown in Fig. 7.

4. Conclusions

The ternary alloys after treatment have the best performance: the hydrogen desorption capacity reaches the highest value (H/M=1.18) after only two adsorption–desorption cycles. It is found that the hydrides have monoclinic phases. The larger the unit volume, the more unstable is the hydride. After replacement of Ni in Mg_2Ni, Ti and Cu are found to have the most promising effects on Mg_2Ni. In addition, due to the enlargement of the specific surface (3.8–5.1 m^2/g) after fluorination treatment, the activation procedure is considerably reduced.

Acknowledgements

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