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Letter

Study on the phase composition of $Mg_{2-x}M_xNi$ (M=Al, Ti) alloys

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Abstract

X-ray powder diffraction structure analysis showed that the hydrogen storage alloy $Mg_{2-x}M_xNi$ (M=Al, Ti) is a multiphase system composed of Mg_2Ni, Mg, $TiNi_3$, MgO, AlNi and Mg_3MNi_2 (M=Al, Ti) when the A component Mg in the A_2B type alloy Mg_2Ni is partially replaced by Al or Ti. Mg_3MNi_2 (M=Al, Ti) is a new type of compound with cubic structure, space group (S.G.), *Fd3m* (no. 227) and with 16 molecules per unit cell. The cell parameters are $a=1.15474(2)$nm for Mg_3AlNi_2 and $a=1.16178(2)$nm for Mg_3TiNi_2. The 48 Mg atoms are located on the 48(f) sites, the 16 M (Ti, Al) atoms on the 16(d) sites and the 32 Ni atoms on the 32(e) sites. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The raw materials needed for the A_2B type Mg_2Ni alloy are abundantly available at low cost. This alloy has a larger hydrogen storage capacity than AB_5 type LaM_5 and AB_2 type ZrM_2 [1]. Therefore it has attracted much attention. In order to weaken the Mg–Ni bond strength, lower the hydriding/dehydriding temperature and improve the cycling properties and life time, many researchers [2–4] substituted V, Cr, Fe, Co and Mn elements for part of the Ni and Al for part of the Mg in Mg_2Ni. The results show that such replacement can improve the hydriding/dehydriding properties of the alloy. According to Kohuo [5], partial replacement of Mg by Al or Mn will lower the absorption temperature of hydrogen. The formation of $Al(OH)_3$ on the surface of the alloy will increase the cycle life. But in all these reports, a proper account was not given of the phase compositions of the alloys and the relationship between the phase composition and the hydriding/dehydriding properties.

In our experimental, we found that such $Mg_{2-x}M_xNi$ alloys are multiphase systems and not a single A_2B type hexagonal phase when Mg is partially replaced by Ti or Al. Furthermore, the main phase appears to be a compound of a new structure type alloy, which determines its hydrogen storage properties. In this article, we use X-ray powder diffraction for a structure analysis in order to determine the crystal structure of this new type of hydrogen storage alloy and we discuss the structural effects on the hydriding/dehydriding properties that are more favorable than those of the Mg_2Ni alloy.

2. Experimental

The alloy was prepared from Mg, Al, Ni, Ti and Mn elements all having a purity above 99.95%. The metal powders were mixed with nominal compositions of $Mg_{1.7}Ti_{0.3}Ni_{0.8}Mn_{0.2}$ and $Mg_{1.5}Al_{0.5}Ni_{1.0}$, then pressed under 30 MPa to form pieces. The pieces were calcined at 540–550°C for 4 h under 0.5 MPa Ar atmosphere in a stainless vessel. After the furnace was cooled to room temperature, the pieces were removed and ground to 300 mesh powder for X-ray structure analysis.

XRD data for structure analysis were collected at 25°C on a horizontal Rigaku D/max-3B powder diffractomater, using CuKα radiation and a power of 40 kV×40 mA with a diffracting beam monochrometer over the 2θ range 20–150 degree with a 2θ step interval of 0.02 degree and a counting time of 10 s per step.

According to the XRD data, there is not only Mg, MgO, Mg_2Ni present in the sample, but also a new phase. In order to define the new phase, at first we used Rietveld

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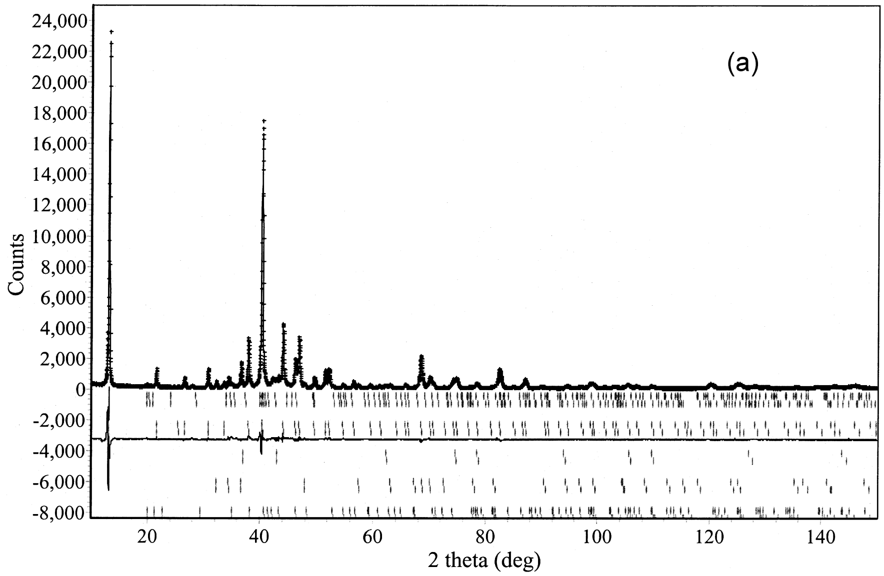
structure analysis to distinguish the diffraction lines of the known phases. Subsequently we indexed the remaining lines by means of the DICVOL91 program [6] and determined the cell parameters and the space group. The constituent Bragg reflections of the new phase were decomposed by the Lebal extraction method [7]. Through Fourier analysis, the electron cloud density pattern was obtained. According to the shape of the electron cloud pattern and the values of the electron density, using the atomic numbers of Mg, Ti, Al and Ni, we obtained the primitive structure model of the new phase. This structure model was tested and refined by multiphase Rietveld analysis. Finally, the Rietveld analysis pattern was checked carefully in order to determine if there were any small abundance phases. Rietveld refinements were performed on a 586 personal computer using Rietica software [8].

3. Results and discussions

Fig. 1 shows XRD Rietveld analysis patterns of two samples whose nominal composition are $Mg_{1.7}Ti_{0.3}Ni_{0.8}Mn_{0.2}$ and $Mg_{1.5}Al_{0.5}Ni_{1.0}$ respectively. Besides the phases Mg_2Ni, MgO and Mg, there also existed Mg_3TiNi_2, TiNi and Mg_3AlNi, AlNi in the samples. The indexes of fitting are the following: Rwp=11.57,



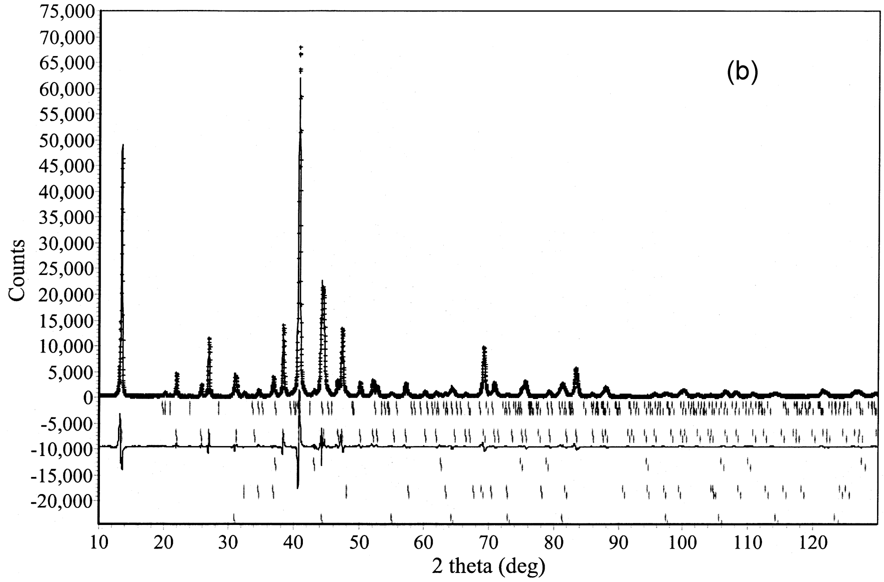


Fig. 1. Rietveld analysis profile of Mg_3MNi_2 alloys. The broken line in (a) and (b) is due to Mg_3TiNi_2 and Mg_3AlNi_2, respectively. The crosses represent the observed pattern, the continuous line the calculated pattern. Lower curves give the differences between the observed and the calculated pattern. The rows of vertical bars from top to bottom are the positions of all possible Bragg reflections of Mg_2Ni, Mg_3MNi_2(M=Ti, Al), MgO, Mg and $TiNi_3$(AlNi) respectively.

Table 1
The phase abundance and R_{Bragg} values for $Mg_{2-x}M_xNi$ (M=Al, Ni) multiphase system

$Mg_{1.7}Ti_{0.3}Ni_{0.8}Mn_{0.2}$			$Mg_{1.5}Al_{0.5}Ni_{1.0}$		
Phase	w_i (%)	R_{Bragg}	Phase	w_i (%)	R_{Bragg}
Mg_2Ni	4.07(9)	2.05	Mg_2Ni	1.54(8)	5.06
Mg_3TiNi_2	71.88(6)	2.46	Mg_3AlNi_2	72.88(7)	4.01
MgO	11.43(4)	2.99	MgO	0.59(3)	5.06
Mg	7.09(3)	4.33	Mg	5.66(3)	4.53
$TiNi_3$	5.53(7)	2.41	AlNi	19.33(4)	1.79

Rp=8.11, S=2.39 for $Mg_{1.7}Ti_{0.3}Ni_{1.0}$ and Rwp=12.64, Rp=9.12, S=2.55 for $Mg_{1.5}Al_{0.5}Ni_{1.0}$ respectively. The calculated pattern matches the experimental pattern very well in the entire range.

Table 1 gives the phase abundance and the Bragg *R* values obtained by multiphase Rietveld analysis. Mg_3MNi_2 (M=Al, Ti) is the main phase and the percentage present is higher than 70%. From a multiphase Rietveld analysis, the sample compositions were determined to be $Mg_{1.6}Ti_{0.34}Ni_{0.76}$ and $Mg_{1.38}Al_{0.62}Ni_{1.0}$. The results indi-

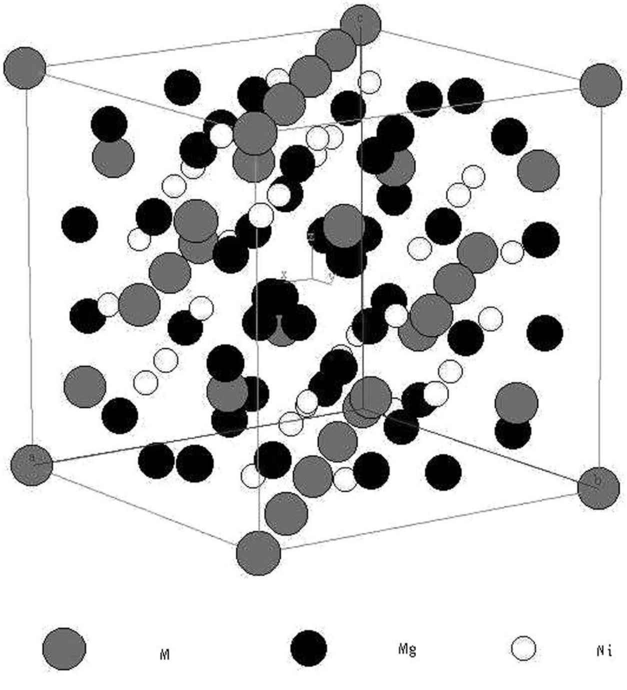


Fig. 2. Crystal structure of the Mg_3MNi_2 (M=Al, Ti) compound.

Table 2
Crystallographic data for Mg_3TiNi_2 and Mg_3AlNi_2

	Mg_3AlNi_2	Mg_3TiNi_2
Space group	*Fd3m* (no. 227)	*Fd3m* (no. 227)
Origin choice	1 (origin at 1/8,1/8,1/8 from center 4−3 m)	
Cell parameter(nm)	1.15474(2)	1.16178(2)
Density	3.748	4.035

Table 3
Atomic fractional coordinates, isotropic thermal displacements and occupation numbers for Mg_3TiNi_2, (Mg_3AlNi_2)

Atom	Site	*x*	*y*	*z*	*B* (Å)	*n*
Mg	48*f*	0.4305(2)	0.1250	0.1250	0.54(5)	1.0
(Mg	48*f*	0.4298(1)	0.1250	0.1250	0.54(4)	1.0)
Al	16*c*	0.0	0.0	0.0	0.16(7)	1.0
(Ti	16*c*	0.0	0.0	0.0	0.21(4)	1.0)
Ni	32*e*	0.2067(1)	0.2067(1)	0.2067(1)	0.51(4)	1.0
(Ni	32*e*	0.2058(1)	0.2058(1)	0.2058(1)	0.56(3)	1.0)

Table 4
Inter-atomic distances for Mg_3TiNi_2 and Mg_3AlNi_2

Mg_3TiNi_2 (nm)		Mg_3AlNi_2 (nm)	
Mg–Al	0.2918(1)	Mg–Ti	0.2929(1)
Mg–Ni	0.2909(1)	Mg–Ni	0.2921(1)
Mg–Ni	0.2766(1)	Mg–Ni	0.2797(1)
Al–Ni	0.2489(1)	Ti–Ni	0.2499(1)
Ni–Ni	0.2666(1)	Ni–Ni	0.2654(1)

Table 5
X-ray powder diffraction data of Mg_3TiNi_2 and Mg_3AlNi_2

h k l	Mg_3TiNi_2		Mg_3AlNi_2	
	d (nm)	I/I_0	*d* (nm/10)	I/I_0
1 1 1	6.71	100	6.67	58
0 2 2	4.107	5	4.083	5
1 1 3	3.503	<1	3.482	3
2 2 2	3.354	3	3.333	13
0 0 4	2.904	6	2.887	2
1 3 3	2.665	1	2.649	<1
2 2 4	2.384	18	2.357	19
1 1 5, 3 3 3	2.236	87	2.222	100
0 4 4	2.0538	25	2.0413	20
1 3 5	1.9638	9	1.9519	6
2 4 4	1.9363	21	1.9246	25
0 2 6	1.8369	5	1.8258	5
3 3 5	1.7717	8	1.7610	6
2 2 6	1.7514	8	1.7408	3
4 4 4	1.6769	2	1.6667	<1
1 1 7, 1 5 5	1.6268	3	1.6169	5
2 4 6	1.5525	2	1.5431	2
1 3 7, 3 5 5	1.5125	1	1.5033	2
0 0 8	1.4522	<1	1.4434	<1
3 3 7	1.4193	2	1.4107	1
4 4 6	1.4089	<1	1.4003	<1
0 6 6, 2 2 8	1.3692	20	1.3609	23
1 5 7, 5 5 5	1.3415	6	1.3333	6
2 6 6	1.3326	2	1.3246	1
0 4 8	1.2989	<1	1.2910	<1
1 1 9, 3 5 7	1.2752	5	1.2675	4
2 4 8	1.2676	6	1.2599	7
4 6 6	1.2384	<1	1.2310	<1
1 3 9	1.2179	4	1.2105	3
4 4 8	1.1857	<1	1.1785	<1
1 7 7, 3 3 9, 5 5 7	1.1676	16	1.1606	16
0 2 $\underline{10}$, 2 6 8	1.1392	2	1.1323	2
1 5 9, 3 7 7	1.1231	1	1.1163	1
2 2 $\underline{10}$, 6 6 6	1.1179	7	1.1111	6
3 5 9	1.0834	<1	1.0768	<1

cate that the element ratios Mg/Ti and Mg/Al are very close to that of the starting mixture. But, there are some differences between the nominal and experimental element ratios in $Mg_{1.7}Ti_{0.3}Ni_{0.8}Mn_{0.2}$. It was assumed that Mn did not alloy with the other elements in $Mg_{1.7}Ti_{0.3}Ni_{0.8}Mn_{0.2}$. Probably, Mn was oxidized. The two weak peaks ($d=2.56$, 3.21) in the difference pattern used for the Rietveld analysis may be the diffraction peaks of MnO_2 (JCPDS 5-0600).

Fig. 2 displays the crystal structure of the new compound Mg_3MNi_2 (M=Al, Ni). Tables 2–5 list the crystallography data, structure data, inter-atomic distances and X-ray powder diffraction data, respectively.

According to Table 2, the bond lengths of Mg–Ni in Mg_3MNi_2 are 0.2766(1)nm and 0.2921(1)nm, slightly longer than 0.2642 nm and 0.2682 nm respectively, in hexagonal Mg_2Ni. But the density of Mg_3MNi_2 (3.748) is higher than that of Mg_2Ni (2.981). This is due to the fact that the coordination number of Ni in the cubic Mg_3MNi_2 structure is 12, whereas it is 10 in Mg_2Ni. Therefore, the stability of the cubic Mg_3MNi_2 structure may be higher than that of Mg_2Ni while the bond length of Mg–Ni is longer than in Mg_2Ni.

4. Conclusions

1. Mg_3MNi_2 (M=Al, Ni) is a new type of hydrogen storage alloy with cubic structure and S.G. *Fd3m*.
2. The bond lengths of Mg–Ni in Mg_3MNi_2 are longer and the density is bigger than that of Mg_2Ni.

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