Hydrogenation Character and Crystal Structures of Hydrides in RMgNi₄ (R = Nd, Gd, Er)

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Whether the pseudo-binary RNi₂ compounds consistent with the criterion $r_A/r_B = 1.37$ for HIA. The hydrogenation performances and crystal structures of the pseudo-binary RMgNi₄ (R = Nd, Gd, Er) were investigated at fixed R/Mg ratio equal to 1. The pseudo-binary RMgNi₄ (R = Nd, Gd, Er) compounds can repetively absorb and desorb hydrogen without the occurrence of HIA and decomposition during hydrogen absorption and desorption cycles at 298 K, 6 MPa. The HIA criterion r_A/r_B of pseudo-binary RMgNi₄ alloys should be higher than 1.37 at fixed R/Mg equal to 1. [doi:10.2320/matertrans.MT-M2019224]

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1. Introduction

RMgNi₄ (R = rare earth metals) compounds with MgCu₄Sn structure crystallizing in space group F-43m have been widely explored for their capability to maintain hydrogen in storage in solid state.¹⁻⁵⁾ In the RMgNi₄ structure, R and Mg atoms are within 4a and 4c sites, respectively, which provide two different [R₂MgNi₂] bipyramids and [RNi₃] tetrahedral for hydrogen occupation.^{1,6-9)} RMgNi₄ compounds grow out of RNi₂ binary compounds assorted as C15 space group Fd-3m.¹⁰⁾ With different rare earth elements, R_xMg_{1-x}Ni₄ phases have different hydrogen absorption/desorption performances.

The occurrence of HIA is assumed to be related to an atomic radius ratio $r_A/r_B > 1.37$ in the RNi₂ binary compounds. When the atomic radius is larger than r_A/r_B , and $(r_{(R,Mg)}/r_{Ni})$ is greater than 1.37, the R_{2-x}Mg_xNi₄ compound will undergo partial amorphization or partial decomposition during hydrogen absorption. On the contrary, when the atomic radius is ≤ 1.37 , no partial amorphization nor partial decomposition will occur on the R_{2-x}Mg_xNi₄ compound during hydrogen absorption, thus, the alloy remains steadfast during hydrogen absorption/desorption circulation.^{10,15)} In the binary compounds HIA is bound up with the value of r_A/r_B , that is, $r_A/r_B > 1.37$ is a necessary condition for the appearance of HIA.¹¹⁾ Notably, PrMgNi₄ was affirmed to repeatedly absorb and desorb hydrogen with a cubic MgCu₄Sn structure.¹²⁻¹⁵⁾ Sakaki *et al.* reported that SmMgNi₄ can repeatedly absorb and desorb hydrogen with a high r_A/r_B value of 1.37.¹⁶⁾ However, whether partial amorphization occurs during hydrogen absorption/desorption cycles for RMgNi₄ alloys remains unclear. To some extent, the ternary RMgNi₄ compounds could be considered as pseudo-binary RNi₂ compounds because rare earth atoms are partially substituted by Mg. This leads to the question whether the pseudo-binary RNi₂ obey the r_A/r_B critical value 1.37 for HIA. Furthermore, the ratio of R/Mg is fixed at 1 to avoid interference from other factors. Nd, Gd, and Er possess an atomic radius of 1.82, 1.80, and 1.76 Å, respectively. On the other hand, the atomic radius of Mg and Ni measures 1.60

and 1.24 Å, respectively. Furthermore, the r_A/r_B ($r_{(R,Mg)}/r_{Ni}$) of Nd, Gd, and Er reaches 1.38, 1.37, and 1.35, respectively, which are greater than, equal to, and less than 1.37. Thus, a critical value of hydrogen-induced amorphization or hydrogen-induced decomposition (1.37) is produced when R/Mg = 1 in RMgNi₄. Ternary RMgNi₄ compounds can be considered pseudo-binary Laves with C15-type structure. Hence, the cycling capability and structural change in RMgNi₄ upon repeated hydrogen absorption and desorption cycles were studied in this paper.

2. Experimental

2.1 Sample preparation

RMgNi₄ alloys were first prepared by induction melting of different rare earth elements (Nd, Gd, Er) with Mg and Ni strips. To ensure homogeneity of the composition, we performed three remelting, with the alloy being reversed each time. To compensate for evaporation of rare earth and Mg during melting, we added extra 5% rare earth element and 25% Mg. The as-cast alloys were ground into powders and pressed into pellets in glove boxes. Under Ar atmosphere, the pellets were wrapped in tantalum foil and annealed in quartz tube furnace at 1173, 1223, and 1273 for 6 h. The pellets were then re-ground into powders with particle size not greater than 45 μm in the glove box.

2.2 Hydrogen absorption/desorption cycles

Each powder was packed in a stainless steel reactor in a glove box, which was connected to a sievert reactor and activated at 358 K for 2 h. The cycle performance test was then started at 298 K. Hydrogen was filled in, and 6 MPa pressure was maintained until it reached a stable state. Vacuum was then maintained at 0.001 MPa for 1 h. The amount of hydrogen absorption and desorption was recorded, and this method was performed for 50 cycles.

2.3 Structural characterization

Phase structures of annealed and cycled samples were tested by X-ray diffraction (XRD) measurements (Bruke D8 Advance) with Cu Kα radiation at 40 KV and 40 mA. The diffraction patterns were refined by RIETAN-2000. During

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refinement, a pseudo-Voigt function containing Gaussian and Lorentzian parts was selected to fit the XRD peak profile by using a method described previously.

3. Results and Discussion

3.1 Structure characteristics of RMgNi₄

Figure 1 shows the XRD patterns of sintered RMgNi₄ samples. XRD data for RMgNi₄ were refined by RIETAN-2000 with a cubic structural model of MgCu₄Sn, where Mg atoms substitute the rare earth site.^{17,18} R and Mg atoms exclusively occupy the 4a and 4c sites in RMgNi₄, respectively.^{1,6,7} As shown in Fig. 1, all alloys were in single phase, including a cubic MgCu₄Sn structure and (No. 216) space group F-43m.¹⁰ This result is consistent with that of a previous report.^{19,20} Lattice constants of NdMgNi₄, GdMgNi₄, and ErMgNi₄, which were refined from Rietveld analyses of XRD patterns, totaled 7.075(0), 7.037(5) and 6.963(4) Å, respectively. Lattice constants decreased with decreasing radius of rare earth atoms because they all have the same structural characteristics and occupancy of atoms and the atomic radii of the rare earth elements decrease with increasing atomic number. According to RIETAN-fitted results, orderly atomic occupations were observed in RdMgNi₄, that is, rare earth elements and Mg atoms occupied the 4a and 4c positions, respectively. The RMgNi₄ crystal structure and the tetrahedron interstices are shown in the Fig. 2. Table 1 shows the refined results of atomic coordinates, isotropic thermal parameters and occupation for RMgNi₄.

Fig. 2 The RMgNi₄ crystal structure and the tetrahedron interstices.

3.2 Durable reversibility of RMgNi₄

Figure 3 presents the absorption capacity of RMgNi₄ (R = Nd, Gd, Er) at room temperature under 6 MPa. A single plateau behavior was noted in absorption/desorption isotherms. The hydrogen absorption plateaus of NdMgNi₄ and GdMgNi₄ showed minimal difference. P-C isotherms revealed a plateau pressure of approximately 0.9 MPa, whereas that of ErMgNi₄ was higher at 1.5 MPa. The measured absorption capacities reached 0.96%, 0.94%, and 0.72%. When the gaseous hydrogen molecule contacts with the alloy, it dissociates into hydrogen atoms on the surface of the alloy, and then diffuses into the alloy, gradually occupying the lattice space to form solid solution. RMgNi₄ alloys usually have C15 Laves phase structure, which is a typical topological close-packed phase. The lattice space in

Fig. 1 Rietveld refinements of XRD patterns for (a) NdMgNi₄, (b) GdMgNi₄, and (c) ErMgNi₄ samples.

Table 1 Atomic Coordinates, isotropic thermal parameters (*B*), and occupation for RMgNi₄ refined by RIETAN.

phase	a=b=c(Å)	Atom	Site	g	x	y	z	B(Å ²)
NdMgNi ₄	7.075 (0)	Nd	4a	0.96	0	0	0	1.10
		Mg	4c	0.86	1/4	1/4	1/4	1.23
		Ni	16e	1	5/8	5/8	5/8	0.96
GdMgNi ₄	7.037(5)	Gd	4a	0.99	0	0	0	0.02
		Mg	4c	0.90	1/4	1/4	1/4	1.58
		Ni	16e	1.0	5/8	5/8	5/8	0.78
ErMgNi ₄	6.963 (4)	Er	4a	0.98	0	0	0	0.74
		Mg	4c	0.95	1/4	1/4	1/4	0.85
		Ni	16e	1	5/8	5/8	5/8	0.57

Fig. 3 P-C isotherms of RMgNi_4 under 6 MPa at 298 K.

C15 Laves phase are all tetrahedral interstices. Magee *et al.* reported that there are 17 tetrahedral interstices per unit of AB_2 structure, including one B_4 -type, four AB_3 -type and twelve A_2B_2 -type, respectively. From the above analysis, it can be seen that the gap in RMgNi_4 is mainly AB_3 and A_2B_2 -types. With the decrease of rare earth radius, the interstices also decreases, so the hydrogen absorption capacity also decreases.

A total of 50 cycles were carried out at 298 K to test whether HIA occurs in RMgNi_4 ($\text{R} = \text{Nd, Gd, Er}$) alloys during hydrogen absorption and desorption. Figure 4 displays variations in hydrogen absorption capacity of RMgNi_4

Fig. 4 Variation curve of hydrogen storage capacity with cycle number at 298 K.

alloys with a cycle number at 298 K. Hydrogen content decreased from 0.96% to 0.86%, from 0.94% to 0.83%, and from 0.72% to 0.63% after 50 cycles. Hydrogen absorption and desorption capacities of NdMgNi_4 and GdMgNi_4 remained the same and decreased slowly during the first 30 cycles but decreased rapidly during the first 12 cycles for the ErMgNi_4 . In subsequent cycles, hydrogen uptake showed no remarkable decrease with prolonged cycle time. Thus, reductions were not due to slow kinetics but reduced hydrogen absorption and desorption capacity.²¹⁾ XRD was carried out after 50 cycles of hydrogen absorption and desorption.

Figure 5 shows the XRD profiles, no new phases were found after cycling but the Bragg peak showed a slight broadening. The lattice parameter for NdMgNi_4 , GdMgNi_4 and ErMgNi_4 only increases to 7.080(1), 7.042(7) and 6.969(9) Å from 7.075(0), 7.037(5) and 6.963(4) Å, respectively. It can be seen that the hydrogen absorption and desorption capacity decreases with the radius of rare earth elements decrease. The gap in RMgNi_4 decreases with the radius of rare earth atoms decrease, so that hydrogen atoms are not easy to release, which leads to the increase of lattice strain. As reported previously, there are three factors contributing to material recycling failure. a). The increase of lattice strain, the hydrogen absorption and desorption cycle induces the “reproduction” of defects such as vacancies and dislocations, but these defects will induce lattice strain. Typically, the direct cause of LaNi_5 cycle decline is lattice strain.²⁵⁾ b). Hydrogen trapped in the lattice gap of alloys, which often leads to lattice expansion after hydrogen absorption and desorption cycles. The results of hydrogenation of $\text{Ca}_3\text{Mg}_2\text{Ni}_{13}$ alloy show that even after complete hydrogenation at room temperature, part of H remains in CaNi_5 gap and can not be released, resulting in capacity failure. c). Partial phase decomposition and amorphization of Alloys.²⁶⁾ From the Fig. 4, there is no new phase or amorphous formation after hydrogen absorption and desorption. The broadening of diffraction peaks is usually caused by the strain and size factors.²⁷⁾ In Rietveld software U and Y_e are the related parameters of strain.²⁸⁾ Figure 6 shows the lattice strain of RMgNi_4 after hydrogenation cycles, which displays the lattice strain increases with the decrease of the radius of the rare earth element. It can be concluded that accumulation of lattice strain is a principal consideration for decreased cyclic performance. In hydrogen atmosphere, surface defects are induced by high concentration of hydrogen atoms on the surface because a

Fig. 5 XRD patterns of RMgNi_4 after 50 cycles. (a) NdMgNi_4 , (b) GdMgNi_4 , and (c) ErMgNi_4 .

Fig. 6 Lattice strain after 50 cycles in RMgNi₄.

concentration gradient must exist from the surface to the center of sample powder particles. After complete hydrogen absorption and desorption cycle, high-density dislocation and other lattice defects will occur in the lattice of alloys.^{21–23} Therefore, reduced hydrogen absorption capacity is mainly caused by the lattice stress resulting from dislocation accumulation during hydrogen absorption and desorption cycles. In general, hydrogen-induced amorphous structures are most likely to occur in AB₂ compounds with C15 structure when $r_A/r_B > 1.37$. NdMgNi₄, GdMgNi₄, and ErMgNi₄ feature $r_{(R,Mg)}/r_{Ni}$ ratios of 1.379, 1.37, and 1.35, respectively, which are larger, equal to, or less than 1.37. Furthermore, the structures remained crystalline after hydrogenation cycles. However, NdMgNi₄ with an $r_{(Nd,Mg)}/r_{Ni}$ of 1.379, which is slightly larger than 1.37, still existed in crystalline state after hydrogenation cycles. These results were consistent with those of Zhang,²⁴ who showed that although $r_A/r_B > 1.37$, Sm_{2–x}Mg_xNi₄ compounds still showed increased stability, and their hydrides retained a crystalline state when Mg content was increased to $x = 0.75$.²⁴

4. Conclusions

This paper discussed hydrogen absorption/desorption cycle persistence of RMgNi₄ (R = Nd, Gd, Er) alloys prepared by sintering. RMgNi₄ (R = Nd, Gd, Er) with different r_A/r_B values (1.38, 1.37, and 1.34, respectively) showed that RMgNi₄ alloys possess a stable structure without hydrogen-induced amorphization nor component decomposition during hydrogen absorption/desorption cycles. The hydrogen-induced amorphous criterion r_A/r_B of pseudo-binary RMgNi₄ alloys should be > 1.37 at fixed R/Mg equal to 1.

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