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Hydriding properties of a nano-/amorphous-structured Mg–Ni–H system

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Abstract

The alloys Mg−x at.% Ni (x=33, 38, 43 and 50) with nanometer-scale structures were successively synthesized by mechanical grinding of Mg_2Ni mixed with various amounts of additional Ni. The total hydrogen contents in these alloys increases from 1.7 mass% for x=33 to 2.2 mass% for x=43 and 50, while the dehydriding temperatures gradually lower from 440 K to 373 K with increasing of the Ni amounts. The value of the total hydrogen content in each alloy is reasonably explained by taking into account the hydrogen contents of the following three regions; the intra-grain region of nanostructured Mg_2Ni, its inter-grain region, and the amorphous MgNi region. The maximum hydrogen content in the amorphous MgNi region, 2.2 mass%, might imply a specific interatomic occupation of hydrogen atoms in this region.

Keywords: Magnesium–nickel–hydrogen; Nanostructure; Intra-grain; Inter-grain; Amorphous

1. Introduction

Quite recently, we have reported the hydriding properties of a nanostructured Mg_2Ni–H system [1–3]. In this system, hydrogen atoms preferentially dissolving into the inter-grain region leads to the notable hydriding properties, such as the enhanced dissolution of hydrogen up to 1.6 mass% and its low-temperature dehydriding below 440 K. Thus one of directions for a further improvement of hydriding properties in this system is to enrich non-crystalline structures like the inter-grain region.

We also have paid attention to an amorphous MgNi as one of the non-crystalline structures relating to that formed at the inter-grain region of the nanostructured Mg_2Ni(–H), although their compositions and atomistic arrangements differ from one to another [4]. The amorphous MgNi was mechanically synthesized as one of the promising electrode materials, and the electrochemical properties have been studied [5–8]. However, the structural and hydriding properties of the amorphous MgNi, especially on the gas–solid reaction, have not been clarified yet.

The aim of this work was, therefore, to investigate the hydriding properties of the alloys Mg−33, 38, 43 and 50 at.% Ni, in which the different amounts of the amorphous MgNi were partially dispersed around the nanostructured Mg_2Ni.

2. Experimental procedures

The initial compound Mg_2Ni without/with elemental Ni were first mechanically ground under an argon atmosphere, using a planetary ball mill apparatus (Fritsch P7) for 60~4800 min at ambient temperature. Elemental compositions of them are Mg−33, 38, 43 and 50 at.% Ni. Then the samples are mechanically ground under a hydrogen atmosphere to achieve complete hydrogenation. During hydrogenation the grinding time was fixed to 60 min and an initial hydrogen pressure of 1.0 MPa.

In this work, we have paid attention to avoiding impurity effects on the hydriding and structural properties of the samples as far as possible. Therefore the material and shape for the vial were carefully selected, so as to lower the amount of elemental Fe contamination during the grinding process (less than 0.03 mass% Fe after the grinding for 4800 min). In addition, the vial with the sample was directly degassed prior to the grinding and was always handled in an argon grove-box before and after the grinding, so as to minimize the oxidation effect on the sample. Details concerning the grinding conditions are described in Refs. [2,3].

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The structural and hydriding properties of the samples thus prepared were characterized by X-ray diffraction, thermal analyses, TEM observation, and measurement of hydrogen pressure–composition isotherms.

3. Results

Fig. 1 shows the X-ray diffraction profiles of Mg−x at.% Ni mechanically ground for 1200 min under an argon atmosphere. By grinding only Mg_2Ni the nanostructured Mg_2Ni with broad diffraction peaks was obtained (x=33). The amorphous MgNi was partially formed by grinding of Mg_2Ni mixed with the additional Ni (x=38 and 43), and was homogeneously formed in an equivalent composition (x=50), leaving a small amount of elemental Ni unreacted. These results indicate that the fraction of the amorphous region increases with increasing Ni content. High resolution TEM images also reveal an increase of the amorphous region, as shown in Fig. 2. The crystallite sizes of Mg_2Ni are about 10 nm for all alloys. Fig. 3 shows that the diffraction peaks corresponding to unreacted elemental Ni completely disappear in Mg−50 at.% Ni after the grinding for 4800 min, indicating the formation of pure amorphous MgNi.

The alloys Mg−x at.% Ni mechanically ground for 1200 min under an argon atmosphere were then sequentially ground for 60 min under a hydrogen atmosphere of 1.0 MPa in order to achieve complete hydrogenation. The structural properties seem not to be dominantly affected in this hydrogenation process. Thermogravimetric profiles of the hydrogenated samples with different Ni amounts are shown in Fig. 4. The dehydriding reactions of all alloys are completely finished below 520 K, although that for Mg−33 at.% Ni proceeds slower than that for the alloy ground under hydrogen atmosphere [1–3]. With increasing the Ni content, the starting temperatures of the dehydriding reaction is gradually lowered from 440 K to 373 K. It is noteworthy that the total hydrogen content increases with increasing Ni content, and that it reaches nearly 2.2 mass% in Mg−43 and −50 at.% Ni.

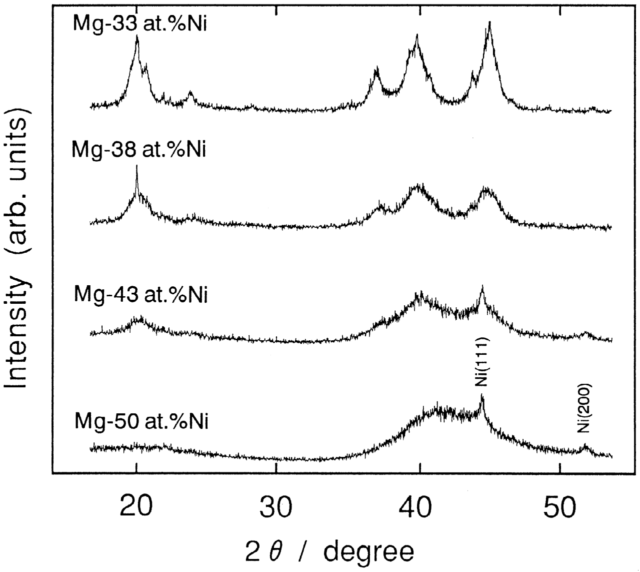

Fig. 1. X-ray diffraction profiles of Mg−x at.% Ni (x=33, 38, 43 and 50) mechanically ground for 1200 min under an argon atmosphere. The major diffraction peaks, except those of elemental Ni, correspond to Mg_2Ni.

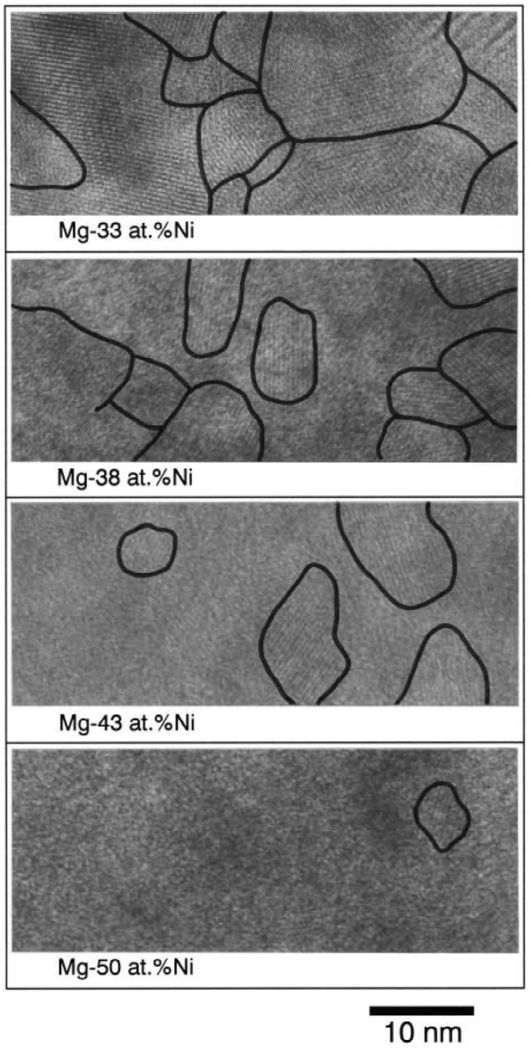

Fig. 2. High resolution TEM images of Mg−x at.% Ni (x=33, 38, 43 and 50) mechanically ground for 1200 min under an argon atmosphere. The border contrast of the Mg_2Ni crystallites has been enhanced in the images.

By hydrogenation of Mg−50 at.% Ni mechanically ground for 4800 min under an argon atmosphere, a shift of the halo to low angles is observed in the X-ray diffraction profile shown in Fig. 5. The diffraction profiles examined after the heat treatments at various temperatures indicate that the structural relaxation to form Mg_2Ni starts to occur around 573 K. Hydrogen pressure–composition isotherms in the dehydriding processes of Mg−50 at.% Ni (the amorphous MgNi) mechanically ground for 1200 min are shown in Fig. 6. Even at 433 K, the dehydriding reaction

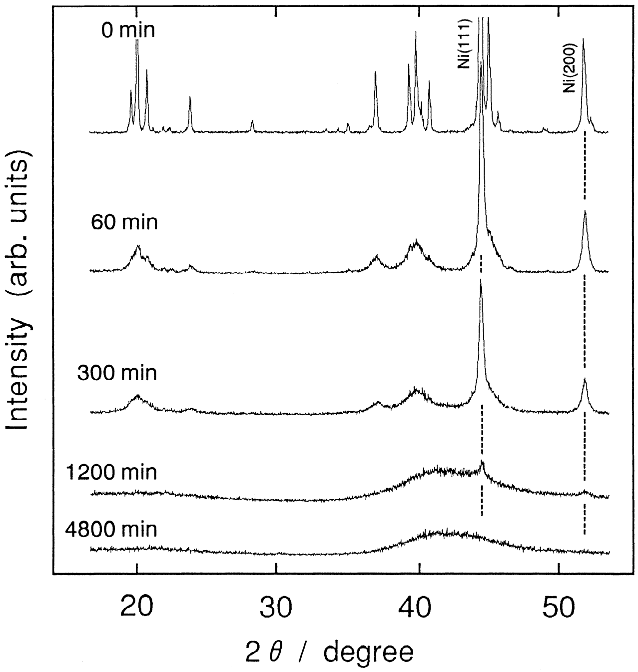

Fig. 3. X-ray diffraction profiles of Mg−50 at.% Ni during mechanical grinding under an argon atmosphere.

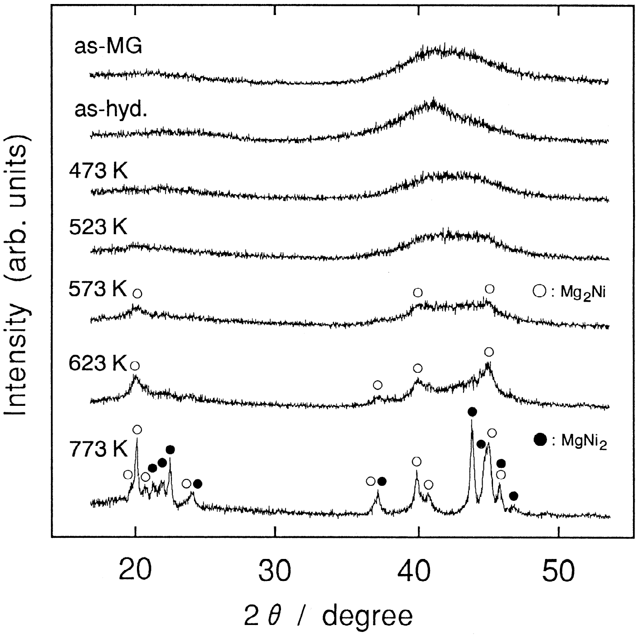

Fig. 5. X-ray diffraction profiles of Mg−50 at.% Ni; after grinding for 4800 min under an argon atmosphere, after sequential hydrogenation, and after heat treatments at various temperatures.

proceeds below 0.1 MPa. The pressure dependence of the hydrogen content is small, compared to the other amorphous alloys with broad site energy distribution for hydrogen atoms, like Zr–Ni system [9–12]. This suggests that the site energy distribution is more narrow in amorphous MgNi.

4. Discussion

We emphasize that there are substantially three regions (excluding unreacted elemental Ni) in Mg−38 or −43 at.% Ni; the intra-grain region of the nanostructured Mg_2Ni, its inter-grain region, and the amorphous MgNi region. Here, the word "inter-grain" includes both an interface between the Mg_2Ni crystallites, and an interface between the Mg_2Ni crystallite and the amorphous MgNi region. The maximum hydrogen contents in the three regions have been experimentally recognized to be 0.3 [13–15], 4.0 [2,3] in case of the interface between the Mg_2Ni crystallites, and 2.2 mass% [16], respectively. Assuming that the lever relation is valid between Mg_2Ni and MgNi in the Mg–Ni phase diagram, the volume

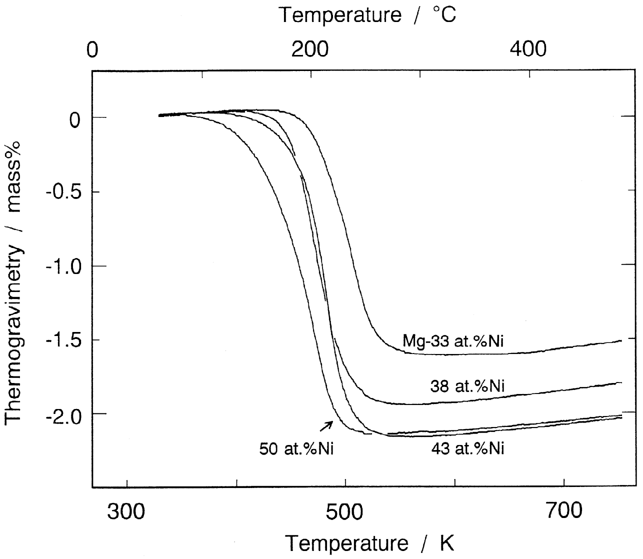

Fig. 4. Thermogravimetric profiles of the hydrogenated Mg−x at.% Ni (x=33, 38, 43 and 50).

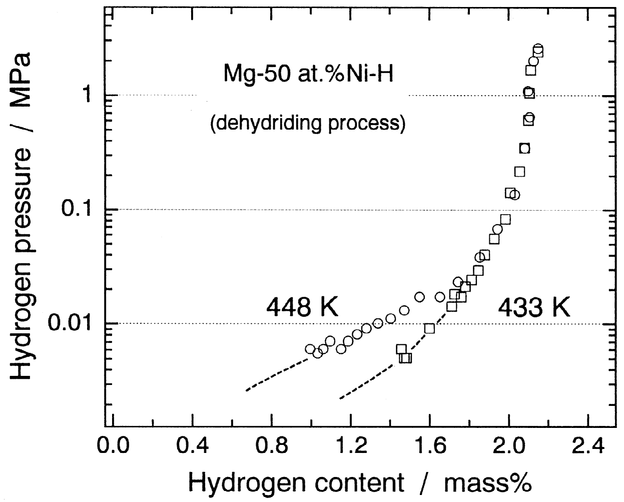

Fig. 6. Hydrogen pressure–composition isotherms in the dehydriding processes of the completely hydrogenated Mg−50 at.% Ni.

Table 1
Experimental results and their itemization on the total hydrogen contents of mechanically ground Mg−33 at.% Ni (the nanostructured Mg_2Ni), Mg−38 and −43 at.% Ni (intermediate structures of nanostructured Mg_2Ni and amorphous MgNi), and Mg−50 at.% Ni (amorphous MgNi)

Ni content (at.%)	Total hydrogen content experimentally obtained (mass%)	Maximum hydrogen content times volume fraction of each region (mass%×*vol. fraction*)		
		Nanostructured Mg_2Ni		Amorphous MgNi
		Intra-grain	Inter-grain	
33	1.7	0.3×*0.6*	4.0×*0.4*	–
38	2.0	0.3×*0.4*	4.0×*0.3*	2.2×*0.3*
43	2.2	0.3×*0.2*	4.0×*0.2*	2.2×*0.6*
50	2.2	–	–	2.2×*1.0*

The maximum hydrogen contents of the three regions are 0.3, 4.0 and 2.2 mass%, for the intra-grain region of the nanostructured Mg_2Ni, its inter-grain region, and the amorphous MgNi region, respectively.

fractions of the amorphous MgNi region should be nearly 0, 0.3, 0.6 and 1.0 for x=33, 38, 43 and 50, respectively.

The dependence of total hydrogen content on the Ni content can therefore be well explained as shown in Table 1. The volume ratios of the amorphous MgNi region to the intra-grain region listed in this Table are 0.3 to 0.4 and 0.6 to 0.2 for x=38 and 43, respectively, and are confirmed by an area-separation method of the peak/halo ratio in the X-ray diffraction profiles shown in Fig. 1. The volume ratio of the inter- to intra-grain regions in the nanostructured Mg_2Ni that was ground longer than 1200 min, seem to be nearly equivalent [2,3].

The value of the maximum hydrogen content in the amorphous MgNi region (Mg−50 at.% Ni), 2.2 mass%, corresponds to the formula $MgNiH_{1.9}$. This means that one hydrogen atom belongs to nearly one metal atom, as in $LaNi_5H_6$ and $TiFeH_2$. Thus this hydrogen-to-metal ratio in the amorphous MgNi region might imply a specific interatomic occupation of hydrogen atoms in this region.

5. Conclusions

The alloys Mg−x at.% Ni (x=33, 38, 43 and 50) with nanometer-scale structures were successively synthesized, and then completely hydrogenated. The total hydrogen contents' dependance on Ni content, 1.7~2.2 mass%, are well explainable by estimating both the volume fractions and maximum hydrogen contents of the following three regions in each alloy; the intra-grain region of nanostructured Mg_2Ni, its inter-grain region, and the amorphous MgNi region. The dehydriding temperatures decrease gradually from 443 K to 373 K as the Ni content increases. The value of the maximum hydrogen content in the amorphous MgNi region might imply some specific interatomic occupancy of hydrogen.

Acknowledgments

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References

[1] S. Orimo and H. Fujii, *J. Alloys Comp., 232* (1996) L16.
[2] S. Orimo, H. Fujii and K. Ikeda, *Acta Mater., 45* (1997) 331.
[3] S. Orimo, H. Fujii, K. Ikeda and Y. Kitano, *J. Jan. Inst. Metals*, 60 (1996) 685. In Japanese.
[4] T. Haubold, R. Birringer, B. Lengeler and H. Gleiter, *J. Less-Common Met., 145* (1988) 557.
[5] Q.M. Yang, Y.Q. Lei, C.P. Chen, J. Wu, Q.D. Wang, G.L. Lu and L.S. Chen, *Z. Phy. Chem., 183* (1994) 141: Y.Q. Lei, Y.M. Wu, Q.M. Yang, J. Wu and Q.D. Wang, *Z. Phy. Chem., 183* (1994) 379.
[6] D.L. Sun, Y.Q. Lei, W.H. Liu, J.J. Jing, J. Wu and Q.D. Wang, *J. Alloys Comp., 231* (1995) 621.
[7] C. Iwakura, S. Hazui and H. Inoue, *Electrochim. Acta, 41* (1996) 471.
[8] C. Iwakura, S. Nohara, H. Inoue and Y. Fukumoto, *Chem. Commun., 15* (1996) 1831.
[9] F.H.M. Spit, J.W. Drijver and S. Radelaar, *Scr. Metall., 14* (1980) 1071.
[10] R. Kirchheim, F. Sommer and G. Schluckebier, *Acta Metall. 30* (1982) 1059.
[11] K. Aoki, M. Kamachi and T. Masumoto, *J. Non-cryst. Solids, 61/62* (1984) 679.
[12] J.H. Harris, W.A. Curtin and M.A. Tenhover, *Phys. Rev. B, 16* (1987) 5784.
[13] J. Schefer, P. Fischer, W. Hälg, F. Stucki, L. Schlapbach, J.J. Didisheim, K. Yvon and A.F. Andresen, *J. Less-Common Met., 74* (1980) 65.
[14] D. Noréus and P. Werner, *Acta Chem. Scand. A, 36* (1982) 847.
[15] J.L. Soubeyroux, D. Fruchart, A. Mikou, M. Pezat and B. Darriet, *Mat. Res. Bull., 19* (1984) 895.
[16] S. Orimo, H. Fujii, K. Ikeda, Y. Fujikawa and Y. Kitano, *J. Alloys Comp., 253–254* (1997) 80–83.