

Hydriding and Dehydriding Properties of Amorphous Magnesium–Nickel Films Prepared by a Sputtering Method

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Metal/alloy hydride films have attracted much attention during the past decade, owing to their various uses in the areas of hydrogen storage,^{1,2} electrochemical electrodes,^{3,4} hydrogen permeation,^{5,6} switchable mirrors,^{7–12} and field emission displays.¹³ In comparison with the bulk powders, the hydride films show novel properties such as excellent durability with regard to hydriding–dehydriding cycles. The film preparation mainly includes thermal vapor deposition and sputtering techniques.¹⁴ With the former method, it is generally difficult to control the chemical composition of the layer deposited, whereas with the latter one, it is relatively easy to obtain a homogeneous distribution. On the other hand, among the hydrogen storage materials known, the magnesium–nickel hydride phases are promising candidates because of their high hydrogen storage capacity and low cost.¹⁵ However, most of the studies for the Mg–Ni system has been performed on bulk powders, and to our knowledge there is only one about Mg–Ni thin films (on switchable mirrors).¹²

In the present work we report the preparation of amorphous Mg–Ni films deposited on molybdenum

substrate by an ion-beam sputtering method. The composition, structure, and hydriding–dehydriding properties of these films were also investigated. The results obtained provide us with new possibilities to further understand their applications in the fields of reversible hydrogen storage and hydrogen sensors.

Magnesium–nickel films were prepared using an ion-beam sputtering apparatus with a Kaufman-type ion gun. Mg and Ni plates, supplied by Japan Metal Chemical Company with the purity higher than 99.9%, were used for the sputtering targets. Prior to the sputtering deposition, the chamber was vacuumed to 10^{-6} Pa. The Mo substrate, which shows rather low solubility of hydrogen at the normal conditions¹⁶ and better heat conductivity than that of glass/quartz, was attached to a water-cooled holder. Adjusting the sputtering parameters such as the Ar pressure, the cathode–anode, and the ion beam power resulted in the Mg–Ni films with a deposition rate of ≈ 1.0 nm/s. We also obtained nominal Mg_2Ni and $MgNi_2$ films by changing the conditions, but their results will not be reported here. The as-prepared Mg–Ni films, which were in some cases peeled from the substrate, were characterized by means of several analytical techniques including X-ray diffraction (XRD, Rigaku INT-2000, Cu $\text{K}\alpha$ radiation), scanning electron microscopy (SEM, JEOL JSM-5600 apparatus) equipped with energy-dispersive X-ray spectroscopy (EDXS, Kevex Super 8000 detector), transmission electron microscopy (TEM, JEOL JEM 2000EX II microscope), and differential scanning calorimetry (DSC, Rigaku Thermo-Plus DSC 8230HP calorimeter). The instrumental measurement conditions have been described previously.^{17–19}

The thickness of the Mg–Ni films was found to be directly proportional to the sputtering time. Figure 1a shows the SEM image of the cross section of the film deposited on the Mo substrate. In the area measured, the compositions of the film were determined to be $Mg_{1.2}Ni_{1.0}$. Parts b and c of Figure 1 are the EDXS maps in the same field of Mg and Ni, respectively, from which it can be seen that the Mg and Ni compositions are evenly distributed in the whole layer, suggesting that the as-prepared film could achieve a uniform structure.

Figure 2a shows the XRD patterns of the Mg–Ni films obtained at different sputtering times and the 10-min deposited film after hydriding (vide infra). The presence of only one broad peak at $2\theta \sim 41^\circ$ illustrates that amorphous $Mg_{1.2}Ni_{1.0}$ was formed: $1.2\text{Mg} + \text{Ni} \rightarrow Mg_{1.2}Ni_{1.0}$. This is further confirmed by the analysis of TEM electron diffraction (Figure 2b). The halo pattern centered displays the strong incoherent scattering of the beam electrons in the amorphous state of the $Mg_{1.2}Ni_{1.0}$ film, while the outer rings reveal the state of coexistence with some other phases (possible for Mg, Ni, and their

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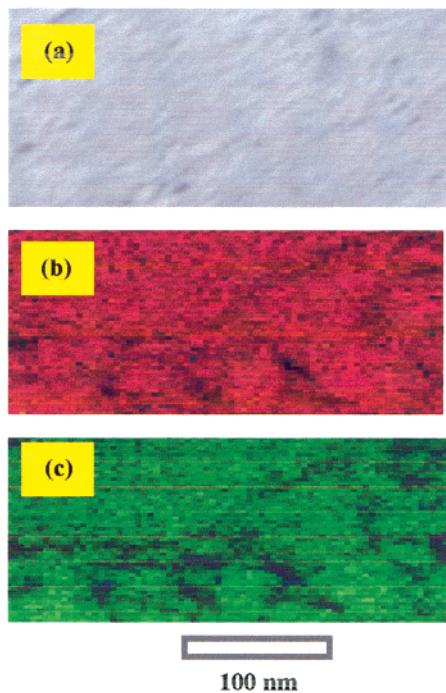


Figure 1. SEM images: (a) the cross section of $\text{Mg}_{1.2}\text{Ni}_{1.0}$ film (after 10-min deposition) and EDXS mapping of (b) Mg and (c) Ni.

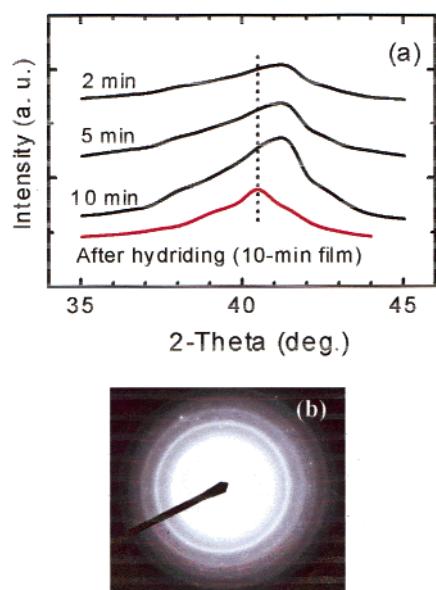


Figure 2. (a) XRD patterns of the Mg–Ni films deposited on a Mo substrate at different sputtering times and the 10-min deposited film after hydriding. (b) TEM electron diffraction pattern of the $\text{Mg}_{1.2}\text{Ni}_{1.0}$ film.

alloys). The density of this $\text{Mg}_{1.2}\text{Ni}_{1.0}$ film was measured, by using water and an electronic balance (Mettler AE 240) of the Archimedean method, to be 4.526 g/cm^3 , which is between that of Mg_2Ni (3.438 g/cm^3) and MgNi_2 (5.910 g/cm^3).²⁰

In DSC analysis of the amorphous $\text{Mg}_{1.2}\text{Ni}_{1.0}$ film in an Ar atmosphere (Figure 3a), a distinct exothermic peak around 310°C was observed. This can be attributed to a heat of crystallization that was demonstrated by XRD analysis (Figure 3b). The XRD pattern

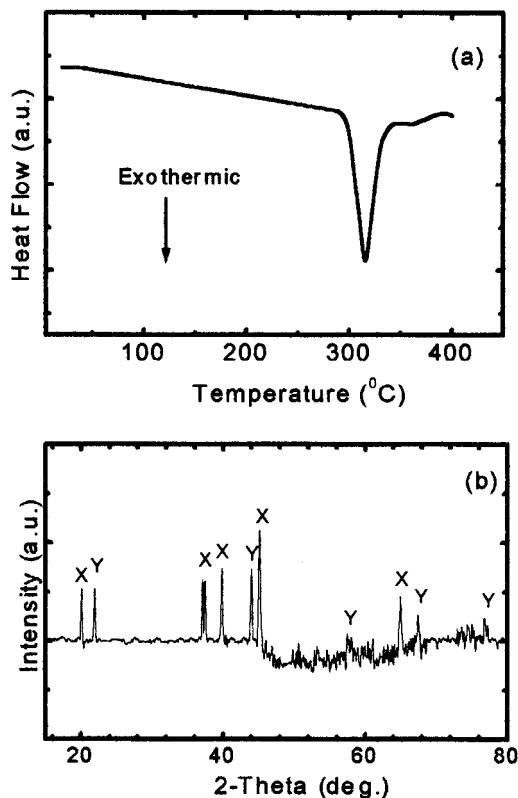


Figure 3. (a) DSC trace of amorphous $\text{Mg}_{1.2}\text{Ni}_{1.0}$ film under an argon atmosphere with a heating rate of $5^\circ\text{C}/\text{min}$. (b) XRD patterns showing the crystallizing process where X and Y are related to crystalline Mg_2Ni and MgNi_2 , respectively.

of the sample heated to 310°C in Ar shows that crystalline Mg_2Ni and MgNi_2 are formed owing to structural relaxation (eq 1). We also found that the Mg–Ni films deposited with Ni excess have similar transformation, as expressed in eq 2. Consequently, the



amorphous Mg–Ni phase obtained after the sputtering underwent decomposition to form crystalline phases during the heating process up to 310°C . The heat of crystallization was calculated to be 28 kJ/mol for the amorphous $\text{Mg}_{1.2}\text{Ni}_{1.0}$ film. Because crystalline Mg_2Ni forms stable Mg_2NiH_4 , MgNi_2 does not react with hydrogen within 350°C and 4 MPa H_2 ,²¹ and our target is to investigate the hydriding–dehydriding properties of amorphous Mg–Ni films, the temperatures heated in the following measurements were always controlled to be $<250^\circ\text{C}$ to prevent the decomposition of the amorphous phase.

The striking feature of the $\text{Mg}_{1.2}\text{Ni}_{1.0}$ film is the reversible hydriding–dehydriding characteristics under moderate conditions (Figure 4). An exothermic peak upon heating and an endothermic peak upon cooling were noted. This behavior is quite similar to that of the amorphous $\text{MgNi}_{1.02}\text{H}_{2.2}$ obtained by gigapascal high-pressure synthesis,¹⁷ indicating the occurrence of reversible hydrogen absorption (exothermic) and desorption (endothermic) of the amorphous alloy film. After

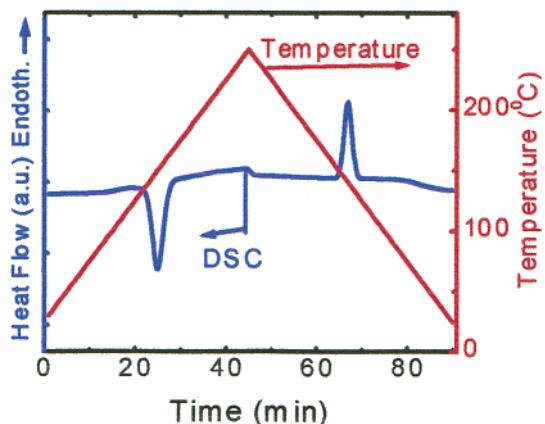


Figure 4. DSC curve of the amorphous $\text{Mg}_{1.2}\text{Ni}_{1.0}$ film at the first heating–cooling cycle with $5\text{ }^{\circ}\text{C}/\text{min}$ and 3.3 MPa of H_2 .

the hydriding reaction, the XRD pattern of the $\text{Mg}_{1.2}\text{Ni}_{1.0}$ –H film shifted to lower angles (the bottom curve in Figure 2a), indicating a large intake of hydrogen in the film. After five consecutive DSC cycles (another piece of this film), the XRD pattern shows the presence of a broad peak, which is consistent with the 10-min deposited pattern in Figure 2a, suggesting that the amorphous $\text{Mg}_{1.2}\text{Ni}_{1.0}$ phase is stable. On the basis of the peak areas of this DSC measurement, the

enthalpies associated with the hydriding–dehydriding reactions were found to be -39.8 and 42.0 kJ/mol H_2 , respectively. The absolute values of these data are much smaller than that in crystalline Mg_2NiH_4 (around 64.0 kJ/mol H_2 for hydride formation),²¹ but some larger than those in bulk amorphous $\text{MgNi}_{1.02}\text{H}_{2.2}$ (38.2 – 40.5 kJ/mol H_2).¹⁷ These results could reveal that the strength of M–H bonding in amorphous $\text{Mg}_{1.2}\text{Ni}_{1.0}$ hydride film is much weaker than it is in polycrystalline Mg_2NiH_4 , but some stronger than it is in bulk amorphous $\text{MgNi}_{1.02}\text{H}_{2.2}$.

In conclusion, amorphous $\text{Mg}_{1.2}\text{Ni}_{1.0}$ film with a layer of about 600-nm thickness was prepared by an ion-beam sputtering technique. More importantly, at about $150\text{ }^{\circ}\text{C}$ and 3.3 MPa of H_2 , this amorphous film shows reversible hydriding–dehydriding reactions. This information provides new insight for the applications of Mg–Ni-based hydride films.

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