Improved hydrogenation-dehydrogenation characteristics of nanostructured melt-spun Mg-10Ni-2Mm alloy processed by rapid solidification

Na XING, Ying WU, Wei HAN, Shao-xiong ZHOU
China Iron & Steel Research Group, Advanced Technology & Materials Co., Ltd., Beijing 100081, China

Received 23 August 2010; accepted 23 October 2010

Abstract: The as-cast Mg-10Ni-2Mm (mole fraction, %) alloy was prepared by a simple and low-cost two-step method of pre-alloying and vacuum induction melting. The nanocrystalline alloy was obtained by the melt-spun process with the surface velocity of copper wheel of 10.5 m/s. The hydrogen storage properties were examined by PCT measurement. The enthalpy (ΔH) and entropy (ΔS) of the alloy determined by van’t Hoff plots indicate that the thermodynamic performance of the nanocrystalline alloy is improved by fast diffusion ability of hydrogen in the nanocrystalline microstructure embedding nano-particles of intermetallics compounds Mg2Ni and MmMg12. The reaction kinetics of the melt-spun alloy is greatly improved due to short diffusion path of hydrogen in the nanocrystalline microstructure, resulting in better overall hydrogen storage properties. The hydrogen storage capacity is 5.09% (mass fraction, hereinafter the same), and the amount of hydrogen desorption is 4.86%. The hydrogen desorption rate of 95.5% in the alloy is available.

Key words: Mg-10Ni-2Mm alloy; vacuum induction melting; melt-spun; hydrogen storage properties; enthalpy; entropy; kinetics

1 Introduction

Among many hydrogen storage material systems, Mg-based hydrogen storage alloys have received considerable interest in the last few years due to their low cost, high hydrogen storage capacity (7.6% for MgH2 and 3.6% Mg2NiH4), lightweight, and great abundance[1–3]. However, their high desorption temperature and relatively slow hydrogen absorption/desorption kinetics make them still inapplicable for practical application. It was reported that alloying Mg with transition metal elements, such as Ni, Cu, Fe, Ti, and rare earth elements such as La, Ce, Y as well as adding metal oxide such as Nb2O5 and Fe2O3, into pure Mg had been attributed to hydrogenation kinetics significantly and the storage capacity of the alloy[4–10]. SPASSOV et al[6], for Mg-Ni-RE (RE=Y or Ce), reported that Mg73Ni15Mm12 exhibited best performance. ORIMO et al[11] reported that nanocrystalline and amorphous phases contained materials showed faster kinetics performance and lower reaction temperature. In our previous studies, hydrogen absorption/desorption rates in Mg-based alloys are dramatically enhanced by nanoprocessing[12–16]. The present paper, therefore, is devoted to an study on the hydrogenation-dehydrogenation characteristics of the melt-spun Mg-10Ni-2Mm alloy focusing on the effect of nanocrystalline microstructure on the thermodynamics and reaction kinetics.

2 Experimental

The as-cast alloy was prepared by induction melting of a mixture of 99.99% (mass fraction) pure magnesium, 99.95% pure nickel, 99.7% cerium and lanthanum rich mischmetal (La 36.98%, Ce 63.00%). Because of the large difference in the melting point of Mg (650 °C) and Ni (1 455 °C), and the high vapor pressure of Mg, the pre-alloying process for the Ni-Mm was firstly applied, and then the pre-alloy with pure Mg was remelted in a vacuum furnace under an argon atmosphere at 670 °C. Nanocrystalline alloy were obtained by a melt-spun method with the surface velocity of the copper wheel of 10.5 m/s[12–16].

The chemical composition of the Mg-10Ni-2Mm
(Mm=Ce, La-rich mischmetal) alloy was confirmed by XRF (X-ray fluorescence): 74.32% Mg, 18.1% Ni, 3.46% La, 4.07% Ce. The structure and morphology of the phases in the non-hydrogenated and hydrogenated samples were examined by X-ray diffractometry (XRD) with Cu Kα radiation, scanning electron microscopy (SEM, Hitachi s-3400se) and transmission electron microscopy (TEM, JEM−2010) equipped with an energy dispersive X-ray spectrometer (EDS).

The hydrogen storage properties of the alloys were examined by pressure—composition—temperature (PCT) characteristics measurement system (Suzuki, PCT−1SPWIN). Before measuring the PCT diagram, the samples were hydrogenated at 300 °C with a hydrogen pressure of 1.8MPa, and then were activated by five hydrogen absorption/desorption cycles. The PCT diagram of the samples was measured with pressure range of 0−2.5 MPa after 30 min vacuum. The data points on PCT curves were collected under equilibrium conditions. The rate of desorption from the sample fully saturated with hydrogen was measured after determining the PCT.

3 Results and discussion

The as-cast master alloy has a typical dendritic microstructure. As shown in Fig.1(a), the microstructure consists of mainly Mg$_2$Ni with a size of 2–80 μm and a minor mischmetal-rich Mg-containing phase in a matrix of Mg. The mischmetal-rich phases were determined to be MmMg$_{12}$ (bright contrast in the micrograph). The phase constitutes can be explained from the Mg-Ni-La ternary phase diagram. There are three phases present in the alloy, pure Mg, and, because of low solubility of Ni and La in Mg, the intermetallic phases Mg$_2$Ni and LaMg$_{12}$. From the results of XRD in Fig.2, three phases, i.e., Mg, Mg$_2$Ni and MmMg$_{12}$ phases, are confirmed. The two former phases, Mg and Mg$_2$Ni, because of their significantly higher content in the material, show stronger peak intensities than the MmMg$_{12}$, giving an indication of the relative amounts of the phases. Rapid solidification remarkably results in the grain refinement of the melt-spun sample without changing constitutes of the alloy. Applying for a surface velocity of the copper wheel of 10.5 m/s, nanocrystalline alloy was obtained consisting of a considerable amount of nanocrystalline Mg and Mg$_2$Ni particles. This is illustrated in Fig.1 (b). Nanocrystalline Mg and Mg$_2$Ni phases are confirmed in Fig.2. Strong diffraction peaks of Mg and Mg$_2$Ni phases appear, and a small amount of MmMg$_{12}$ with weak peaks is also detected. From the previous studies[12−16], Mg, Mg$_2$Ni and a minor mischmetal-rich Mg-containing phase changed to MgH$_2$, HT-Mg$_2$NiH$_4$ and Mm-based hydride. The latter hydride formed during decomposition of MmMg$_{12}$ to form MmH$_{1−x}$ and MgH$_2$. The desorbed material contained Mg, Mg$_2$Ni and MmH$_2$, which is a highly stable hydride up to 600−700 °C[9]. In addition, Mg$_2$NiH$_{0.3}$ phase, Mg$_2$Ni containing hydrogen in interstitial solid solution, is detected in the hydrogenated melt-spun alloy due to the incomplete hydrogenation of the melt-spun alloy and partial hydrogen release during alloys handling. However, the as-cast alloy is reported to

![Fig.1](image1)

![Fig.2](image2)
contain hydrides of MgH$_2$, LT-Mg$_2$NiH$_4$, HT-Mg$_2$NiH$_4$, and MmH$_3$[13−15]. In the as-cast alloy, the LT-Mg$_2$NiH$_4$ hydride appears instead of the Mg$_2$NiH$_{0.3}$ phase.

Nanoprocessing of the melt-spun alloy resulted in faster hydrogen absorption/desorption kinetics. Fig. 3 shows the hydrogen absorption/desorption kinetic curves of the as-cast and the melt-spun Mg-10Ni-2Mm alloy at 325 °C under 1.0 MPa. The amounts of hydrogen absorption within 4 min are 3.72% (mass fraction) and 3.84% for the as-cast and nanocrystalline alloys, respectively. The fast initial hydrogen absorption kinetics for nanocrystalline alloy was believed to be due to fine particle size and the crystal defects produced during the rapid solidification, which contributes to a significant promotion of the nucleation and diffusion of hydrogen. The capacity of hydrogen absorption for nanocrystalline alloy (5.09%) is higher than the as-cast alloy (4.67%), the large number of interfaces and grain boundaries available in the nanocrystalline alloy provide easy pathways for hydrogen diffusion and promote the absorption of hydrogen. The amount of hydrogen desorption has the same characteristics, they are 4.46% and 4.86% for the as-cast and nanocrystalline alloy, respectively. For the latter, the hydrogen desorption rate of about 95.5% is obtained. The hydrogen released completely within 10 min for the two samples. Therefore, the nanocrystalline alloy achieved the better overall hydrogen storage properties.

The thermodynamic performance of the Mg-10Ni-2Mm alloy is improved by introducing nano-particles of Mg$_2$Ni and MmMg$_{12}$ intermetallics phases, which acts as catalysts to promote the formation of MgH$_2$. The larger pressure hysteresis for the higher Mg$_2$NiH$_4$ plateau occurs. The hydrogen absorption/desorption equilibrium characteristics of the as-cast alloy are determined to be the ones for MgH$_2$ (lower plateau) and Mg$_2$NiH$_4$ (upper plateau). As shown in Fig. 4, PCT dependencies measured for the two samples show the presence of two plateaus. According to Ref.[9], the lower plateau corresponds to a transformation Mg$\rightleftharpoons$MgH$_2$ and the upper plateau belongs to Mg$_2$Ni$\rightleftharpoons$Mg$_2$NiH$_4$. The lower plateau has no big hysteresis, and practically no slope, while the upper plateau has a pronounced hysteresis and slope, especially for the melt-spun sample. The strain and chemical inhomogeneity of the supersaturated solid solution of Ni in Mg result in the slope of Mg$_2$NiH$_4$ phase. In the as-cast alloy, the latter deformation by addition of Ni and Mm was responsible for the slope in the high pressure plateau during the equilibrium the hydrogen absorption and desorption processes. It is known that Ni weakens the Mg-H bond, which is the reason why hydrogen absorption and desorption pressure plateaus for Mg$_2$NiH$_4$ are higher than those for MgH$_2$[4]. It is generally accepted that the hydrogen storage alloys with larger unit cell volumes would result in more sites available for hydrogen storage[1]. Mg$_2$Ni is easier to react with hydrogen than MgH$_2$.

In the nanocrystalline alloy, the specific surface areas and grain boundary densities increase, which is beneficial for nucleating and reducing the distance of diffusion of hydrogen, and the diffusion rate of hydrogen absorption/desorption is therefore improved. The larger pressure hysteresis between the absorption/desorption curve and smaller slope for the higher Mg$_2$NiH$_4$ plateau are obviously observed in the nanocrystalline alloy. This is attributed to the lattice stress resulted from the change of lattice constants and cell volumes during the rapid solidification and subsequent cycles of dehydrogenation-hydrogenation. The well diffusion capacity for hydrogen in the nanocrystalline alloy can be one reason why the upper plateau has smaller slope. It was thought that the final capacity was related to the speed of hydrogen diffusion in the alloy. According to the JMA model of metal-hydrogen interaction, there was a big difference in the kinetic parameters between the two hydrides MgH$_2$ and Mg$_2$NiH$_4$[9]. The formation and decomposition of Mg$_2$NiH$_4$ have rate-constants that were much lower than the corresponding values for MgH$_2$, resulting in much slower formation and decomposition of Mg$_2$NiH$_4$ compared to MgH$_2$. The absorption seems to be rate-limited by diffusion, one-dimensional growth. The desorption had not a unique rate-limiting process, but it was reasonable to believe that the diffusion was the main rate-limiting process[9].
The midpoints of the pressure plateaus in the PCT curves are taken as the data of the plateaus pressure in the van’t Hoff plot. The formation enthalpy and entropy are calculated according to the van’t Hoff equation[12]:

$$\ln \left( \frac{p_H}{p^0} \right) = \frac{\Delta H_f}{RT} - \frac{\Delta S_f}{R} \tag{1}$$

The values of enthalpy and entropy are listed in Table 1. $\Delta H = -61.5 \text{ kJ/mol}$, $\Delta S = -118.6 \text{ J/mol}$, and $\Delta H = -55.6 \text{ kJ/mol}$, $\Delta S = -109.1 \text{ J/mol}$ for Mg$_2$NiH$_4$ phase of the as-cast and melt-spun alloy are determined, respectively, indicating that the thermodynamic performance of the melt-spun alloy is slightly improved. The difference of values of enthalpy and entropy of the Mg-10Ni-2Mm alloy with different microstructures is associated with the ability of the diffusion of hydrogen and the stability of constituents in the alloy. Fine microstructure with much more reactive surface areas easily reacts with hydrogen, and the diffusion distance of hydrogen is reduced. In addition, Mg$_2$Ni and MmH$_{3-x}$ is thermodynamically less stable than MgH$_2$. Thus, the thermodynamic performance of the alloy was ameliorated.

TEM micrographs in Fig.5 shows the hydrogenated microstructures of the as-cast and the melt-spun alloys after 5 cycles of hydrogenation-dehydrogenation. The coarse grains about 0.5 $\mu$m in size including hydrides of MgH$_2$ and Mg$_2$NiH$_4$ are retained in the as-cast sample as shown in Fig.5(a). Regarding the melt-spun sample in Fig.5(b), in addition to nanocrystalline equiaxed MgH$_2$ particles of about 20 nm in size, a considerable amount of nanocrystalline particles of Mg$_2$NiH$_4$-type form. Particularly, the rod-shaped Mg$_2$Ni-type hydrides are distorted, indicating higher strains within the grains during the rapid solidification processing and the subsequent hydrogenation-dehydrogenation cycles. Thus, the grains remained nano-sized in the melt-spun sample.

### Table 1 Values of $\Delta H$ and $\Delta S$ in as-cast and melt-spun Mg-10Ni-2Mm alloys

<table>
<thead>
<tr>
<th>Sample</th>
<th>Slope, $K$</th>
<th>$\Delta H_f$(kJ·mol$^{-1}$)</th>
<th>$\Delta S_f$(J·mol$^{-1}$·K$^{-1}$)</th>
<th>Intercept, C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgH$_2$, as-cast</td>
<td>$-9 168.14$</td>
<td>$-76.2$</td>
<td>$-74.5$</td>
<td>$-136.7$</td>
</tr>
<tr>
<td>MgH$_2$, melt-spun</td>
<td>$-9 257.07$</td>
<td>$-77.0$</td>
<td>$-74.5$</td>
<td>$-138.1$</td>
</tr>
<tr>
<td>Mg$_2$NiH$_4$, as-cast</td>
<td>$-7 391.34$</td>
<td>$-61.5$</td>
<td>$-64.4$</td>
<td>$-118.6$</td>
</tr>
<tr>
<td>Mg$_2$NiH$_4$, melt-spun</td>
<td>$-6 682.14$</td>
<td>$-55.6$</td>
<td>$-64.4$</td>
<td>$-109.1$</td>
</tr>
</tbody>
</table>

Fig.5 TEM micrographs showing hydrogenated microstructures after 5 cycles of hydrogenation-dehydrogenation: (a) Coarse grains of MgH$_2$ in as-cast Mg-10Ni-2Mm alloy; (b) Nanograins of MgH$_2$ and Mg$_2$NiH$_4$-type in melt-spun Mg-10Ni-2Mm alloy.
after several cycles of hydrogen absorption/desorption, which ensured the fast diffusion of hydrogen.

4 Conclusions

1) The thermodynamic performance of the melt-spin Mg-10Ni-2Mm alloy was improved due to an introduction of intermetallics compounds Mg$_2$Ni and MmMg$_{12}$ and increased crystal defects as the nucleation center of hydrides as well as short diffusion path of hydrogen in nanocrystalline microstructure. The values of enthalpy and entropy for Mg$_2$NiH$_4$ phase of the hydrogen in nanocrystalline microstructure. The values of enthalpy and entropy for Mg$_2$NiH$_4$ phase of the hydrogen in nanocrystalline microstructure. The values of enthalpy and entropy for Mg$_2$NiH$_4$ phase of the hydrogen in nanocrystalline microstructure. The values of enthalpy and entropy for Mg$_2$NiH$_4$ phase of the hydrogen in nanocrystalline microstructure.

2) The melt-spin alloy shows the better hydrogen absorption/desorption kinetics than that for the as-cast one due to short diffusion distance of hydrogen and increased nucleation sites in the nanocrystalline microstructure. The hydrogen storage capacity was 5.09%, and the amount of hydrogen desorption was 4.86%. The hydrogen desorption rate of 95.5% was attained.

Acknowledgments

The authors are grateful to the International S&T Cooperation Project (2007DFA50590) and the National Hi-Tech Research and Development Program of China (2009AA03Z230) for the financial support. This work was partly supported by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry, China.

References


