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High-Pressure Synthesis of Amorphous $MgNi_{1.02}H_{2.2}$

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The use of hydrogen storage materials is an attractive proposition for applications in clean electric vehicle systems.[1] One of the most important achievements in this area would be the creation of lightweight hydrogen storage materials with high capacity and low desorption−absorption temperatures.[2,3] Among the different hydrogen storage materials, magnesium−nickel-based metal hydrides are promising candidates for reversible hydrogen storage because of their high capacity and relatively low cost.[4] It is known that in the phase diagram of the Mg−Ni system, two intermetallic compounds are formed: Mg_2Ni and $MgNi_2$.[5] Within the limits of a maximum temperature of 350 °C and a maximum pressure of 4 MPa, Mg_2Ni reacts readily with hydrogen to form Mg_2NiH_4, whereas $MgNi_2$ does not react with hydrogen.[6] These conditions limit their practical utilization in view of the high desorption temperature in the former case, and the small content of hydrogen in the latter. Recent effort has been devoted to improving the hydriding and dehydriding properties of Mg−Ni based alloys using techniques such as element substitution,[7,8] ball-milling,[9−11] and high-pressure treatment.[12,13] These results showed that the hydrogenation behavior was greatly changed, mainly due to the formation of amorphous phases or/and nanocrystallines. However, since the Mg−Ni system is still premature, less stable hydrides need to be developed. At present, new hydrides can be successfully synthesized by using high-pressure technology that can reach gigapascals (GPa).[14,15] More importantly, the application of the high hydrogen pressure techniques to a number of metal−hydrogen systems has given clear evidence of further absorption of hydrogen, of which various novel properties can be expected.[16] Here we report an interesting finding that the homogeneous hydride phase $MgNi_{1.02}H_{2.2}$, which was synthesized by heating a stoichiometric mixture of $2MgH_2 + Ni$ at a pressure of 6 GPa, can desorb−absorb hydrogen reversibly in the temperature range 80−200 °C.

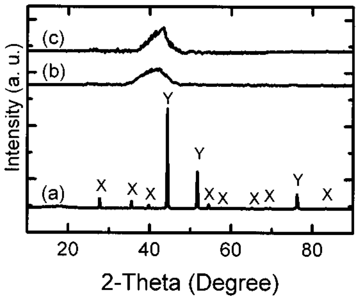

Figure 1. X-ray diffraction (XRD) patterns of (a) the initial $MgH_2 + Ni$ mixture, (b) the sample recovered from 6 GPa and 600 °C, and (c) the recovered sample cooled after TG measurement (300 °C): (X) MgH_2, (Y) Ni. A Rigaku RU-200 diffractometer was used.

In a glovebox filled with pure argon gas, a powder mixture (≤30 μm) of MgH_2 and Ni having a molar ratio of 1:1 was pressed into pellets and put into a sodium chloride crucible together with the internal hydrogen source $LiAlH_4$, which supplied hydrogen after heat-decomposition. The sample and $LiAlH_4$ were separated by a boron nitride disk, which only allowed hydrogen to diffuse freely and therefore protected the sample from pollution.[17] The NaCl container was surrounded by a graphite heater and placed in an octahedral pyrophyllite, a pressure transmitting medium with an edge size of 20 mm. Heat treatments were carried out by using an UHP-2000 oil machine with a multi-anvil device (tungsten carbide) at 6 GPa and 600 °C for 90 min.[18] After heating, the sample was quenched in liquid nitrogen, yielding the new phase as a dark-gray powder.

Figure 1 shows the X-ray diffraction (XRD) patterns of the recovered samples along with a profile of the initial $MgH_2 + Ni$ mixture. From the XRD patterns, different phases can be identified. In the initial mixture (Figure 1a), the presence of MgH_2 and Ni was verified. However, in the case of the as-prepared sample (Figure 1b), the characteristic peaks of initial MgH_2 and Ni were not detected, indicating the formation of a new phase. In addition, a broad diffraction peak was also observed, showing that an amorphous structure is obtained by means of mechanical milling.[19,20]

We were surprised by this new phase change and interested in its possibility of hydrogen desorption. The TG and DTA results (Figure 2) revealed that hydrogen desorbed from the above two samples with rather distinct characteristics. In the case of the initial MgH_2 and Ni mixture (Figure 2a), the desorption of hydrogen started at 400 °C and ended at 480 °C, giving a total loss value of 2.3 wt % H_2. This desorption process was confirmed by a thermal reaction that showed one endotherm with an onset temperature of about 430 °C, owing to the decomposition of MgH_2 to Mg and hydrogen.[21] In the case of the recovered sample (Figure 2b), hydrogen started to desorb at about 80 °C, and the dehydriding reaction was complete at about 200 °C, reaching a hydrogen content of 2.6 wt %. The corresponding DTA result showed that there was only one endotherm with an onset temperature of 120 °C, suggesting that this dehydriding process occurs over a much lower temperature range than that of MgH_2.

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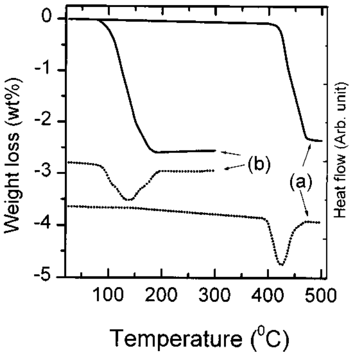

Figure 2. TG (full curves) and DTA (dotted curves) of (a) the $MgH_2 + Ni$ mixture and (b) the sample recovered from 6 GPa and 600 °C. A Rigaku TG8120 analyzer was used and the temperature was linearly increased to 500 °C with a ramp of 2 °C per minute in a slow stream of argon.

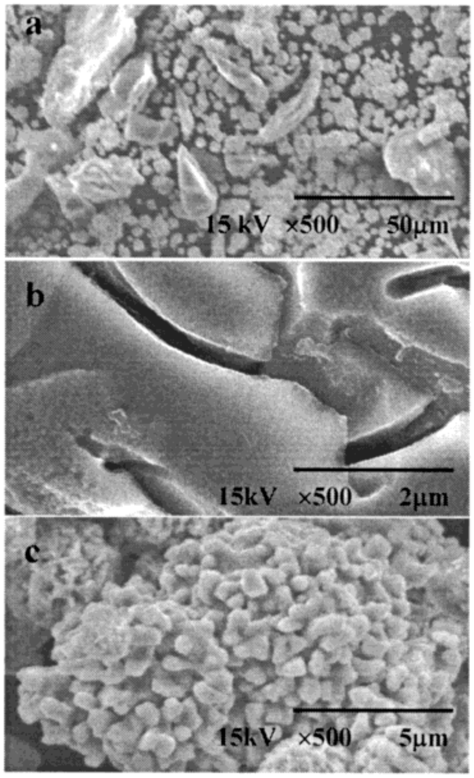

Figure 3. SEM images of (a) the $MgH_2 + Ni$ mixture, (b) the sample recovered from 6 GPa and 600 °C, and (c) the recovered sample cooled after TG measurement (300 °C). A JEOL JSM-5600 microscope equipped with EDXS, operating at 15 kV, was used.

Furthermore, it is worth mentioning that powder XRD analysis of the recovered sample after the TG measurement (under Ar and at 300 °C) still showed a single broad peak (Figure 1c), showing that the crystallization to Mg_2Ni and $MgNi_2$ does not occur. This result demonstrates that the dehydrided phase is stable.

Morphological changes of three kinds of powders, the starting $MgH_2 + Ni$ mixture, the recovered sample, and the recovered sample after TG measurement, were examined by scanning electron microscopy (SEM) (Figure 3). In the initial mixture the particles consist of visibly separated MgH_2 and Ni (the larger and smaller portion in Figure 3a, respectively). In contrast, only one homogeneous phase was found for the recovered sample (Figure 3b). This phase was further analyzed by energy-dispersive X-ray spectroscopy (EDXS), and the chemical composition was found to be $Mg_{1.0}Ni_{1.02}$. Considering the hydrogen concentration determined by TG as shown in Figure 2b, it is deduced that the composition of the recovered phase is $Mg_{1.0}Ni_{1.02}H_{2.2}$. Powder microstructures of the recovered sample cooled after TG measurement (Figure 3c) reveal a characteristic of nanocrystallites, agglomerated with a subsurface layer.

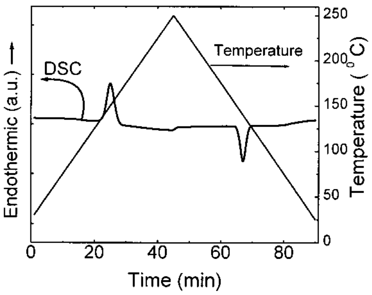

Figure 4. DSC trace of amorphous $Mg_{1.0}Ni_{1.02}H_{2.2}$ showing that the dehydrogenation−rehydrogenation is reversible at a pressure of 3.3 MPa of H_2. A Rigaku DSC 8230HP calorimeter at a heating and cooling rate of 5 °C per minute was utilized.

The reversibility of the hydrogen desorption−absorption for the recovered sample is demonstrated in Figure 4. The DSC heating curve shows one endothermic peak around 150 °C, which results from the dehydrogenation of $Mg_{1.0}Ni_{1.02}H_{2.2}$ to $Mg_{1.0}Ni_{1.02}$. During the DSC cooling process, an exothermic peak was observed at 140 °C, signaling the hydride formation of $Mg_{1.0}Ni_{1.02}H_x$ from $Mg_{1.0}Ni_{1.02}$. On the basis of the DSC peak areas, the enthalpies associated with the transitions for hydrogen desorption−absorption were calculated to be -40.5 and -38.2 kJ/mol of H_2, respectively. These data illustrate that the strength of M−H bonding in $Mg_{1.0}Ni_{1.02}H_{2.2}$ is much weaker than it is in Mg_2NiH_4. It is noteworthy that different hydrogen occupation in these two hydrides should be responsible for such entholpic differences. In the former case, hydrogen occupies the tetrahedral site composed of nearly 2Mg2Ni,[22] whereas in the latter case, hydrogen occupies the 4Mg1Ni site[23] due to the formation of stable covalent-type bonds that may be described as Mg^{2+} and the $[NiH_4]^{4-}$ complex.[24]

In summary, using a high-pressure technique we have prepared amorphous magnesium−nickel hydride $Mg_{1.0}Ni_{1.02}H_{2.2}$ (2.6 wt % of hydrogen) exhibiting a dehydriding temperature range of 80−200 °C. In addition, this hydride phase underwent reversible hydrogen desorption−absorption at a hydrogen pressure of 3.3 MPa and a temperature around 150 °C. Because the melting point of metals is reduced appreciably at high pressures by dissolution of H_2,[25] we believe that hydride complexes such as a NiH_2 complex counterbalanced by a disordered Mg-cation arrangement[26] are possibly formed due to an electronic structure change.[27] In other words, high pressure with heating results in a new hydride phase, and the quenching process from high pressures and temperatures yields a less stable hydride phase owing to the sudden elimination of H_2. This allows for the possibility of synthesizing magnesium-based hydrides with high capacity and a low desorption temperature. Further investigations into the potentially interesting properties of this system are currently underway.

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