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A NOVEL PROCESS FOR FABRICATING Mg₂Ni

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ABSTRACT

The alloy, Mg₂Ni, has a number of desirable properties for use as a lightweight reversible hydride for hydrogen storage applications. It has relatively good storage capacity (3.6 wt.% H₂ as Mg₂NiH₄) and a higher plateau pressure and lower operating temperature than MgH₂. A novel low temperature (<300°C) process is reported that does not require melting of the alloy constituents to achieve a single phase alloy of Mg₂Ni. The process results in smaller particle dimensions without sacrifice in product yield and eliminates the need for post processing to achieve homogenization and particle sizing. It can also be implemented *in-situ* in storage vessels to greatly simplify fabrication while providing more material predictability during the activation process. The process is described and the hydride properties of the product are reported and compared to conventionally formed alloys.

KEY WORDS: Mg₂Ni, lightweight hydride, hydrogen storage.

INTRODUCTION

Mg and Mg-based hydride-forming alloys are attractive hydrogen storage materials due to their high storage capacity relative to other hydrides. They also offer great potential as low cost hydride materials. Pure Mg in the form of MgH₂ has a theoretical capacity of 7.6 wt.% H₂; however, it requires a high operating temperature (400°C) to generate an acceptable hydrogen pressure (0.1 MPa) and the hydrogen desorption kinetics are slow. Other constituents have been successfully alloyed to Mg to lower the temperature and improve the kinetics, but at a compromise in overall capacity. The most commercially viable alloy has been the intermetallic, Mg₂Ni, that forms the hydride Mg₂NiH₄.¹ This alloy has a storage capacity of 3.6 wt.% H₂ and achieves good hydrogen performance with long-lived cycling behavior at 300°C. However, these characteristics have been demonstrated for the most part in laboratory experiments since hydride beds using this alloy for storage have not been commercially available. The ability to process and handle this hydride material in a bed configuration at acceptable costs would contribute to the development of viable lightweight hydride systems.

Often, the processing cost of making hydride materials suitable for storage applications tends to outweigh the basic alloy production costs. Two important points that relate specifically to Mg-based hydride behavior are the multiple phases produced by conventional melt-cast methods and the generally high sensitivity of Mg and Mg alloys to oxidation. Furthermore, pure Mg has a very high vapor pressure, even at temperatures well below the melt, which makes complicates alloy fabrication.

Without additional heat treatment of commercially available melt-cast alloys of Mg₂Ni, the materials generally contain a pure Mg phase as well as the binary alloy. This phase results in a loss in hydrogen capacity at lower temperatures and contributes to the brittleness of the alloy. Interfacial fractures during hydride reactions result in the breakup of particles and the formation of very fine particulate. This material decrepitation is a significant mechanism in the initial activation process for the hydride and has the positive effect of generating more active (to hydrogen) surface area thereby increasing the reaction kinetics. However, it is difficult to control and the very fine fragments must be contained to prevent their transport throughout the storage system. Accumulation of these fine particles in constrained regions of a storage system can lead to failure of the containment vessel and plumbing because of their volumetric expansion during hydriding.

Smaller particle sizes tend to have less decrepitation problems, and also minimize the activation requirements because of better hydrogen absorption and desorption properties. Thus, various methods of pre- and post-hydriding methodologies have been explored to reduce the initial particle sizes. Most of these methods concern some variation of mechanical ball milling techniques³⁻⁵ and show some promising results. However, they may introduce additional processing problems and do not address the issue of multiple phases.

Sensitivity to oxidation creates problems during final assembly of a storage system as well as with the fabrication of the alloy. In both cases, the formation of MgO impedes hydrogen absorption and can represent a substantial loss of active material, particularly in fine hydride powders. Compared to Mg, Mg₂Ni and its hydride are more resistant to oxidation at room temperature. In practice, however, even small levels of air exposure during handling will require reactivation of the material and some hydrogen capacity is always lost. If activation within the final bed assembly requires a higher gas overpressure than normal operation, the resultant containment vessel may be heavier than needed and reduces the weight advantage of the lightweight hydride material.

The vapor phase process may alleviate some of these problems in hydride bed fabrication by allowing *in-situ* formation of the alloy. This circumvents many of the contamination problems and greatly simplifies initial material handling and component assembly. The basis for the vapor phase process is the naturally high vapor pressure of Mg and the fast interdiffusion of Mg and Ni which permit the alloy to form through a solid state reaction at low temperatures (200°C-350°C). It is the initial form of the Ni then that determines the final form of the product. This effectively gives the material designer greater control over the final hydride product by being able to specify the size and shape of the initial Ni substrate. As the reaction continues to the stoichiometric limit, the process results in a single phase product, Mg₂Ni, with no excess Mg. We have found these materials to have greater stability and much faster hydride/dehydride kinetics at low temperatures than conventional alloys.

EXPERIMENTAL METHODS

For most of the experiments reported here, commercially available powders (-325 mesh) of Mg and Ni were purchased as starting materials. The Ni powder was formed by a gas atomization technique and spherical in shape. This feature was not a necessary condition and other forms of Ni were used, including nanocrystalline (5nm) materials. The magnesium was formed from a chemical precipitation process and generally irregular in shape. Its morphology did not play a role in determining the form of the resultant alloy; however, its purity and level of oxidation were found to be very important.

The general procedure was to mix the Mg and Ni powders by simple shaking and loading them into a containment vessel. Mixing and handling were done in an Ar filled glovebox to minimize contamination. The containment vessels were constructed of stainless steel (304L) with a small diameter tube welded on for pumping and as a gas inlet. A sintered stainless steel frit (60µm pore size) was used at the inlet to contain particles during the experiments. The vessels were attached to a Sieverts' type system for determining hydride properties and evacuated using an ancillary turbo-pumped vacuum system. At a background pressure of approximately 6.0×10^{-8} Pa, the material was heated to 150°C. Using a quadrupole mass spectrometer, the dominant off-gassing species were found to be water vapor and hydrogen. The off-gassing was assisted by three cyclic exposures of the material to low pressure hydrogen followed by vacuum pumping. The hydrogen exposures were for about 5 minutes at pressures of 50 kPa and were completed in less than 45 minutes. Following these cycles, pumping was continued until the water vapor partial pressure was less than 5.0×10^{-7} Pa and the hydrogen partial pressure was less than 10^{-6} Pa.

Hydrogen was then introduced to a pressure of 1.0 MPa and the temperature of the material was increased to 300°C. It was found that these values were not critical and that the alloy could be formed with hydrogen pressures as low as 0.1 MPa and at temperatures as low as 200°C; however, these lower temperature and pressure conditions required longer times for the alloy reaction to complete. At the higher values, the material in the vessel began to absorb hydrogen in less than 15 minutes and approached a limiting value. The gas was then pumped off to approximately 10 Pa and the procedure repeated. Continual growth of the Mg₂Ni phase was

evident in each progressive cycle and after about 10-12 cycles all of the Mg had converted to Mg_2Ni .

Once converted, pressure-temperature isotherms (PCT) measurements were made to characterize the equilibrium hydrogen properties of the materials. This was done in place on the Sievert's system using the standard techniques of gas volumetry. This system is an all metal system with calibrated volumes that can provide H_2 pressures up to 20 MPa. The temperature of each sample is actively controlled to $\pm 1.0\text{ C}^\circ$.

The process was also attempted by physically isolating the Ni and Mg, either by a screen or by placing them in separate containers joined by a tube. The screen method worked well, producing high yields of the alloy which did not contain MgO remnants. The rate of conversion in the separated containers was very slow and further optimization is required to assess its viability. The process was also tried in a mixed assembly without a hydrogen overpressure. It was found that the MgO skin on the Mg feed stock prevented vaporization and no alloy was formed. Apparently, the hydrogen is absorbed by the Mg, cracking the oxide shell and allowing vaporization to occur.

RESULTS

Samples of material which were reacted were removed from the containment vessels, encapsulated in an epoxy mount, mechanically polished and examined by electron microscopy. The polishing results in random degrees of cross-section on individual particles. Figure 1 is a backscattered electron image of a sample which contained excess Ni and shows an intermediate stage of alloy formation. Each of the numbered areas were analyzed for elemental composition using quantitative x-ray spectroscopy. However, different compositions are clearly delineated because the contrast observed in the image is due largely to differences in effective atomic number. Thus, the darkest areas are the epoxy mount, while MgO appears slightly brighter. The next brighter intensity level is from the Mg_2Ni and the brightest areas are Ni. No pure Mg phase is present in the region shown. One can see the hollow MgO shell of an original Mg particle in the center of the image. Areas 4 and 5 were verified to be the oxide by elemental analysis. Area 3 shows the unreacted core of a Ni particle, and the regions numbered 1 and 2 were determined to have the correct ratio of Mg to Ni for the alloy. One can also observe that the roughly spherical shape of the Ni particles is retained, although chains of intermetallic particles have also formed. It may be possible to form an interconnected alloy structure if the Ni powder were compressed prior to reacting with the Mg. Such a structure may be advantageous in hydride beds because of improved thermal conductivity properties. Finally, note that small particle sizes are formed during the fabrication process and further activation cycles are not needed to produce material with fine particles suitable for hydriding.

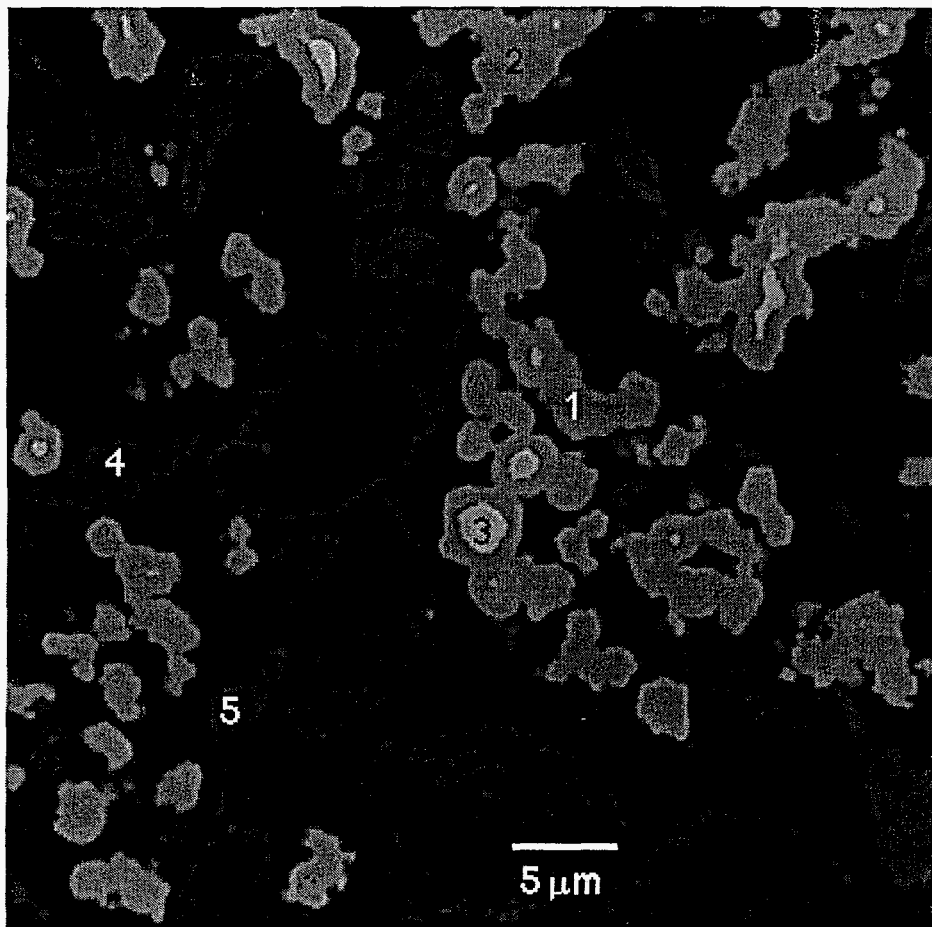


Figure 1.

In Figure 2 are shown two PCT plots which show the progression of Mg_2Ni formation and the depletion of Mg with cycling. The plots are pressure-composition isotherms where the equilibrium hydrogen desorption pressure is plotted against the hydrogen weight fraction in the solid at a given temperature. The higher plateau pressure is due to Mg_2Ni while the lower is from Mg. Thus, the measurements can be used to determine the relative amounts of each phase. As can be seen, a significant fraction of Mg remains after eight cycles. However, by the twelfth cycle, essentially all of the Mg has been alloyed with the Ni to form Mg_2Ni . The plots also show that the oxide (which is inert to hydrogen) in the starting material remains as dead weight in the total sample weight. That is, the overall weight percentage does not reach 3.6wt %, the value for Mg_2Ni , but stops at 3.2wt %. This is also reflected in Figure 3, where the hydrogen content is plotted as a ratio of the total Mg in a fully converted sample at two different temperatures. If all of the Mg initially loaded were participating, this ratio would reach the stoichiometric value of 2.0. The observed loading ratio of approximately 1.7-1.8 H/Mg corresponds to an oxide content of about 7-10% in the initial material. For spherical particles, the oxide skin thickness would be about 3-4% of the particle radius. Microscopy observations of remnant MgO material are in reasonable agreement with these estimates. However, the sample shown in Figure 1 is for earlier material which had greater oxide content and, consequently, the shell thickness in these particles is somewhat greater.

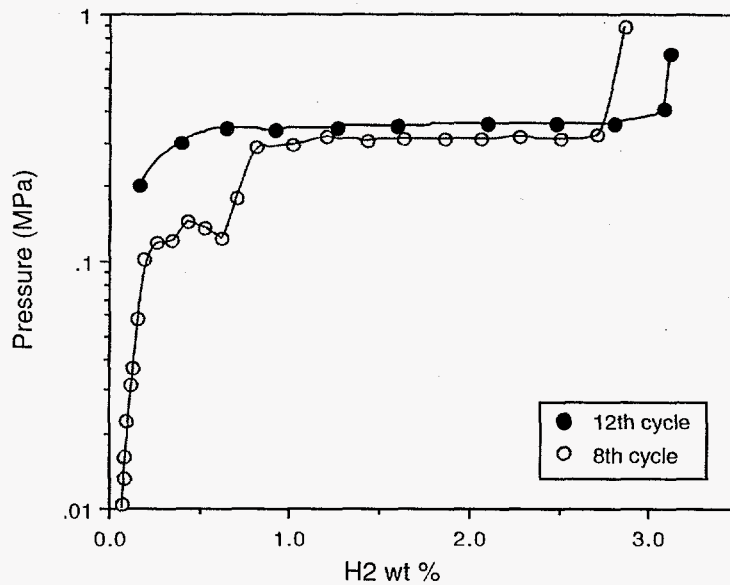


Figure 2.

It should also be mentioned that the 200° C isotherm in Figure 3 demonstrates that this material has very rapid hydrogen kinetic properties. Most published data on this alloy, using conventional material, is at 300° C and above. Low temperature data, particularly in desorption, is uncommon for Mg_2NiH_4 and is almost nonexistent at 200° C due to the times required to reach equilibrium between the hydride and the gas phase. The kinetic properties of the vapor phase alloys relative to conventional material can be seen in Figure 4, where the hydriding rates are compared at 300° C. Here, the hydrided fraction is plotted as a function of time for loading the two materials under the same conditions of hydrogen pressure and volume of gas. The conventional meltcast alloy was well activated and representative of measurements on these alloys. Note that the time to reach 90% of full hydride loading is longer by more than an order of magnitude in the conventional alloy.

The relative rates of absorption and desorption in the vapor phase material can be seen to be comparable, as shown in figure 5. This data, taken at 300° C, shows most of the gas (about 90% or more) being absorbed or desorbed within 10 minutes. In the absorption measurement, the total amount of hydrogen absorbed amounted to half of the total capacity of the sample. The quantity of hydrogen in the desorption measurement was somewhat less, about 30% of the total sample capacity, but still significant. Thus, these materials are capable of very rapid delivery and filling rates in applications.

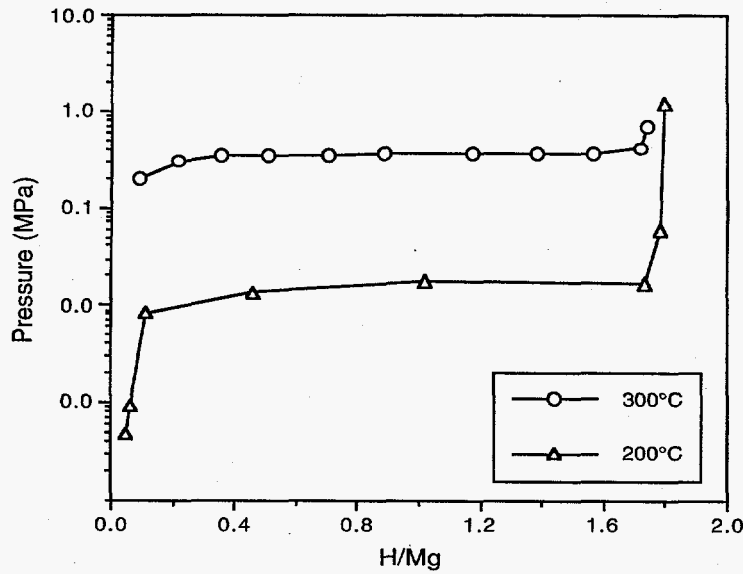


Figure 3.

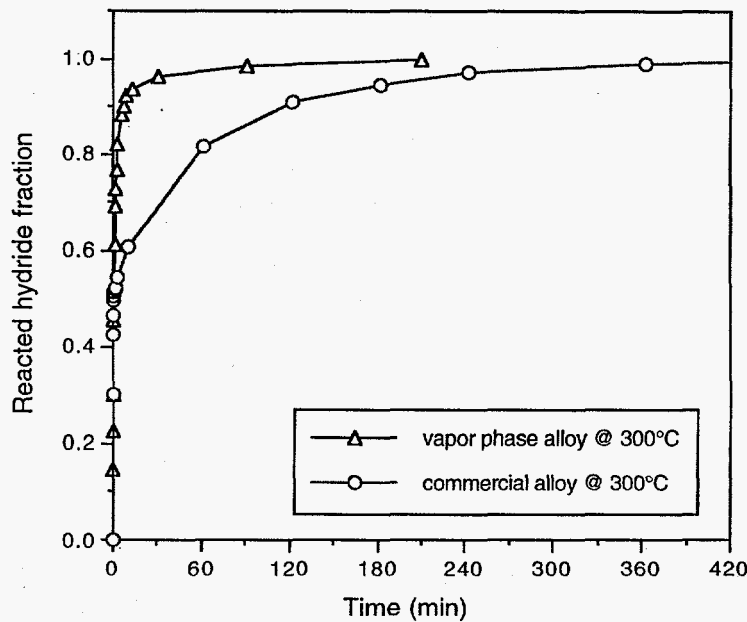


Figure 4.

The 300°C desorption data is re-plotted in figure 6 in terms of the fraction :

$$\Delta P/P = (P(t) - P(eq)) / P(eq)$$

where $P(t)$ is the instantaneous pressure and $P(eq)$ is the equilibrium pressure. This is compared to 200°C desorption data on the same material. As can be observed in the plot, even at 200° C approximately 75% of the gas is desorbed in about an hour. As at 300° C, the 200° C rate would be adequate for many applications.

CONCLUSION

The vapor phase process has been shown to be a useful alternative process for producing the alloy, Mg₂Ni, and results in superior product for energy storage applications. The process utilizes the high vapor pressure of Mg, the condensation of Mg vapor on Ni particles and subsequent low temperature solid state reaction to form the alloy. The morphology of the Ni stock determines, to first order, the final material morphology. This extra control available during fabrication eliminates the necessity for additional processing steps when particle size, size range and shape are important alloy parameters in an application. Even monolithic structures could be generated. The process could also be used for *in-situ* fabrication of the alloy within a storage system which would minimize contamination during assembly and, perhaps, lend itself to automated assembly. The resulting single phase material has not been observed to fracture and break apart as in multi-phase commercial materials. This mechanical integrity could relieve some of the filtration problems common to hydride beds.

Finally, the material has much better kinetic properties than conventional alloys. Equilibrium hydride data could be obtained at 200° C and release rates at this low temperature indicate that the material could be used in some low temperature applications.

ACKNOWLEDGEMENT

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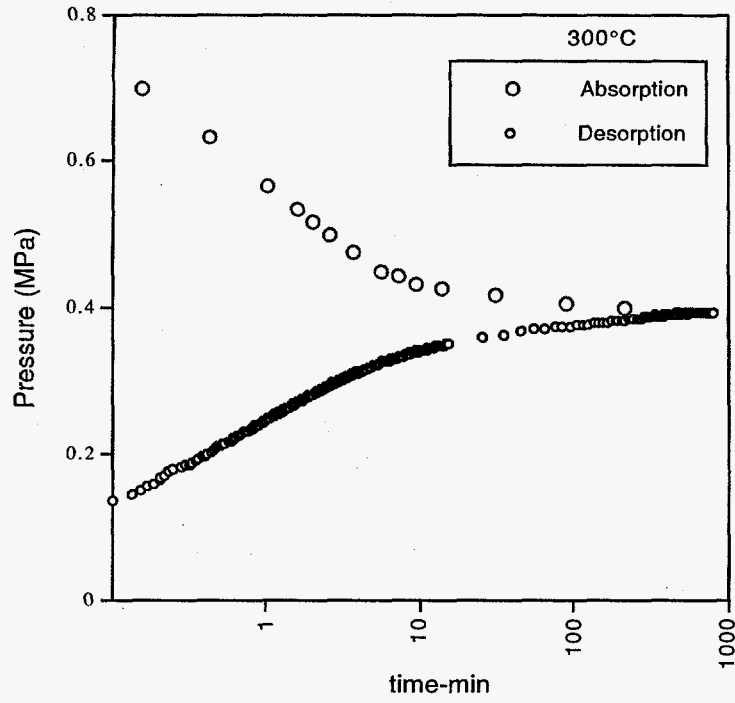


Figure 5.

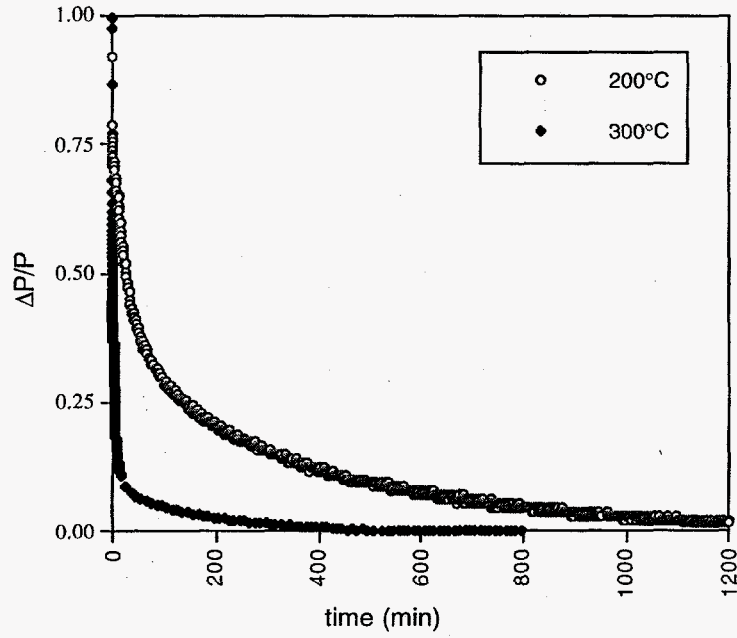


Figure 6.