

Improved Properties of Mg₂NiH₄

S. E. Guthrie and G. J. Thomas
Sandia National Laboratories
Livermore, CA 94550

The objectives of this study are (1) understanding the physical mechanisms that limit the hydrogen storage properties of the magnesium-based alloy, Mg₂Ni, and (2) improving the alloy's properties through processing or fabrication methods. This lightweight alloy is commercially produced, usually through melt-cast methods, and has relatively good hydrogen kinetics and long-lived cycling behavior. Although it has been extensively studied, our new observations on single-phase material produced by a novel vapor phase process [1] have indicated improved hydrogen storage properties over commercial material. An understanding of the mechanisms responsible for these differences could lead to lower temperature hydride materials based on magnesium.

Commercial melt-cast materials generally are two-phase, containing a pure Mg phase as well as the binary alloy. In the vapor phase process, the alloy is formed directly by a solid-state reaction at temperatures of 600 K or less, rather than by solidification from the melt [1]. The vapor phase process has been found to form single-phase alloys and, furthermore, could be used directly in large-scale production of commercial storage units. This single-phase alloy exhibits an equilibrium plateau pressure about 30% higher than commercial material at 473 K and has faster hydrogen absorption/desorption kinetics. The second lower plateau that is normally observed in commercial material due to the presence of Mg is also eliminated.

As part of this IEA activity, a collaborative exchange of samples was made with the University of Sweden to perform x-ray diffraction measurements on the vapor phase material. The sample containers included the remnants of the starting Mg material and the results indicated that our starting Mg contained almost 30% by weight oxide, somewhat higher than had been expected. Taking this factor into account indicates a process yield of about 92% by weight for forming the alloy phase. This yield was higher than our earlier estimates that were based on lower MgO levels. New starting Mg material was obtained and the high conversion efficiency was verified by our own x-ray diffraction measurements.

Additional experiments were performed in which the starting materials were partitioned rather than being mixed together. Our results indicated that acceptable yields could be obtained using only convective flow of the Mg vapor through screens that physically separated the Ni material from the remnant Mg and MgO. The effects of Ni particle size were also examined. It was found that equilibrium plateau pressures were the same in alloys formed from Ni particles with 5 nm nominal diameter (nanophase material) and from larger than 5 micron nominal diameter gas atomized particles. A lower yield of Mg₂Ni was obtained with the nanophase material, which could be attributed to a proportionally higher oxide content on the small diameter Ni.

Additional improvements in equilibrium and kinetic properties were also observed at low temperatures. D. Noréus and co-workers at the University of Sweden have established that Mg₂NiH₄ undergoes a phase change around 500 K, in which the orientation of the NiH₄ complex is quenched in a monoclinic distortion of the cubic (CaF₂) high temperature phase. This results in the formation of domains in which the lattice distortion is accommodated by microtwinning. These microtwins can be absent when the hydride is formed below the transition temperature, resulting in a more unstable structure and, hence, better hydride properties. We have measured plateau pressures and hydrogen desorption rates in hydrides that were formed above (>513 K)

and below (at 453 K) the transition temperature using commercial Mg_2Ni , as well as with material formed by our vapor phase method [2].

Hydrogen desorption isotherms at 473 K and 453 K for four different conditions are shown in Figures 1 and 2. The measurements at 453 K are believed to be the lowest temperature isotherms published for this hydride. The nomenclature used in the figure is as follows: HT refers to hydrides formed above the transition temperature, while LT corresponds to material hydrided below the transition temperature. Additionally, if the hydrides were formed from commercial melt-cast Mg_2Ni , the prefix 'M' is added and if the hydrided alloy was formed by our vapor process, then the prefix 'VP' is added. Note that the highest plateau pressures at both temperatures were for hydrides formed from the vapor process alloy. At 473 K there was no difference observed in plateau pressures between hydrides formed above and below the transition temperature. At 453 K, however, one can see that for both starting alloys, the more unstable hydrides formed below the transition temperature (denoted LT) have higher plateau pressures than the HT hydrides. At this temperature, the equilibrium plateau pressure in the vapor process low temperature hydride is more than double that of the conventional material hydrided under typical high temperature conditions.

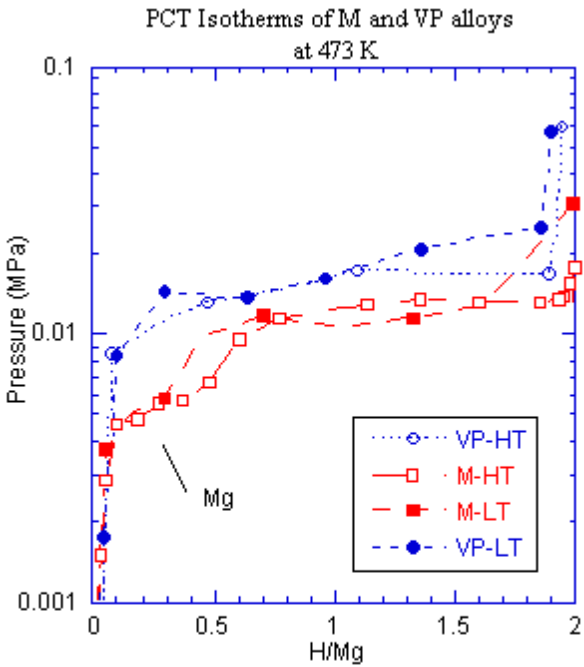


Figure 1. Isotherms at 473 K do not show differences between LT and HT hydrides. Mg impurity phase is present. at low concentrations.

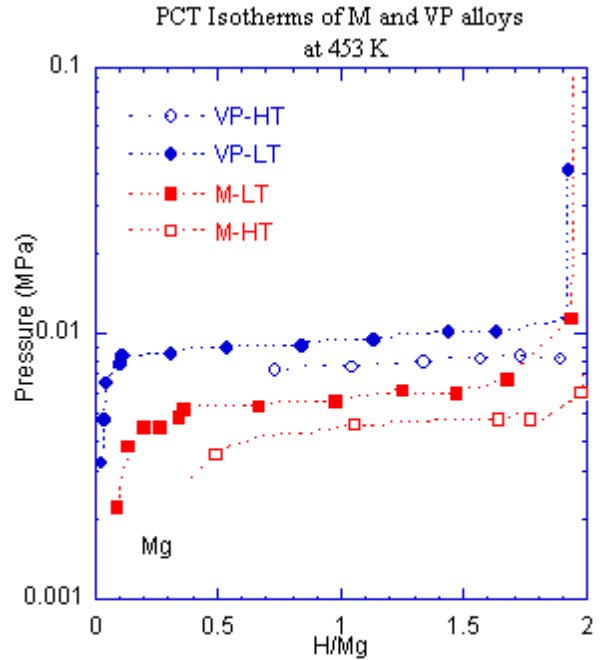


Figure 2. Isotherms at 453 K indicate LT and HT hydride differences. The impurity effect was still evident in M-LT hydride. HT kinetics were slow at low H/Mg in both materials.

Additional isotherms were measured at higher temperatures up to 570 K. Several different samples were used to repeat select measurements. Thus, vapor process (VP) alloy samples were first cycled as HT hydrides, then as LT hydrides. Two samples each of LT and HT hydrides were used for the melt-cast (M) alloy. In general, the VP material always exhibited higher plateau pressures. Hydrogen desorption kinetics were also measured for the four different conditions shown in Figures 1 and 2 at 453 K and 457 K. Again, the VP material had somewhat faster desorption kinetics. These measurements are described in detail in reference [2].

References

- [1] S. E. Guthrie and G. J. Thomas, "A Novel Process for Fabricating Mg_2Ni ", Proceedings of the Society for Advanced Material Processing and Engineering (SAMPE), Anaheim, CA, June 1998. (See also U. S. Patent No. 5, 895,518)
- [2] S.E. Guthrie, G.J. Thomas, D. Noréus and E. Rönnebro, "Properties of Mg_2NiH_4 at 450-570 K", Proceedings of the Materials Research Society (MRS) 1998 Spring Meeting, San Francisco, CA, April 1998, MRS Vol. 513 (1998), pp. 93-98.