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Destabilized Magnesium Nickel Hydride

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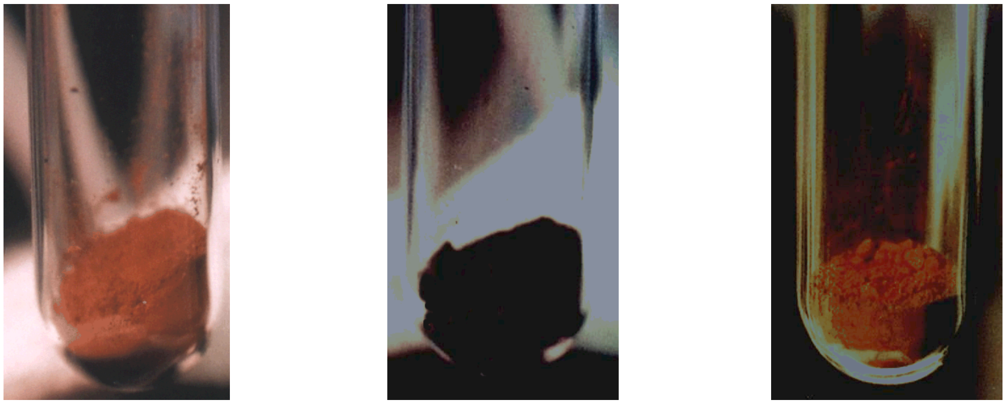
Background

Since 1968 when Reilly and Wiswall [1] discovered the reversible hydrogen absorption ability of the alloy Mg_2Ni to form the ternary hydride Mg_2NiH_4, its hydriding-dehydriding, structural, electric, thermal and kinetic properties have been investigated by many research groups. During the years, Mg_2NiH_4 has continued to surprise the researchers by exhibiting structural changes, colour [2] and resistivity anomalies [3], seemingly unpredictably dependent on sample preparation and sample history.

Mg_2NiH_4 has been regarded as a promising metal hydride for hydrogen storage and for increasing the negative electrode capacity in nickel metal hydride (NiMH) batteries. However, under normal conditions Mg_2NiH_4 is too stable, i.e. at room temperature the equilibrium pressure is so low that Mg_2NiH_4 practically does not desorb hydrogen. Therefore, it is essential that the stability of Mg_2NiH_4 be decreased to produce a suitable material for practical hydrogen storage.

Results and discussion

On heating and cooling, Mg_2NiH_4 exhibits a reversible phase transformation at about 510 K accompanied by a distinct colour change from orange ← → grey-black (Figure 1). Below 510 K, Mg_2NiH_4 exhibits a monoclinic distorted low-temperature (LT) modification of a cubic high-temperature (HT) phase, where magnesium ions form a cube around zerovalent NiH_4-complexes in an antifluorite arrangement. In the HT phase the hydrogen atoms perform a rapid reorientational motion around the central nickel atom [4]. In the LT phase this motion is “frozen” and an ordered arrangement of slightly distorted tetrahedral NiH_4-complexes is observed by neutron diffraction [5]. In addition to this, a frequently occurring stacking fault or microtwinning on unit cell level is introduced into the lattice [5, 6]. If the microtwinning is suppressed the stability of the hydride is decreased, making it more practical for hydrogen storage [7].



(a) Room Temp. (LT2)

(b) Transition Temp. 510 K (HT)

(c) Cooled to Room Temp. (LT2)

Figure 1 - Color changes associated with heating and cooling through the 510 K phase transition of Mg_2NiH_4

The stability of a series of related zerovalent palladium complexes in Na_2PdH_2, $NaBaPdH_3$ and Ba_2PdH_4 could be explained by a substantial bonding interaction between the complexes and the electropositive counter ion matrix as an alternative to conventional "back bonding" [8-10]. By adopting a similar approach to Mg_2NiH_4, containing a nickel analogue of the PdH_4-complex, the peculiarities of Mg_2NiH_4 can be better understood and suggest ways to increase the hydrogen release pressure from Mg_2NiH_4.

During the project four different Mg_2Ni starting alloys for synthesizing the Mg_2NiH_4 hydride were used. Mg_2Ni prepared by bulk mechanical alloying from Mitsui Mining and Smelting in Japan (Mg:Ni is 2:1); a vapor phase deposited Mg_2Ni from Sandia Laboratory (also Mg:Ni is 2:1); and two Mg_2Ni alloys prepared by conventional casting techniques, supplied from JMC in Japan and by MPD-Technology Corporation (Mg:Ni is >2:1). The significant difference between the alloys is the extra amount of free magnesium, which varies from none to more. The results from the study can be summarized as follows: [11]

- The presence of more Mg in the starting alloy stabilizes the hydride, decreases the amount of microtwinning and gives the hydride an orange or rust color.
- Microtwinning is a stabilization mechanism in Mg_2NiH_4. If the microtwinning is suppressed, the hydride becomes less stable [7] (see Project 2).
- Microtwinning and the presence of Mg are competing stabilization mechanisms. If both can be avoided, the hydride is further destabilized.
- The stabilization mechanism is connected to a change of electric properties of the hydride. When a static pressure is applied to a sample containing microtwinning from the start, the conductivity will increase as the microtwinning disappears (Figure 2).

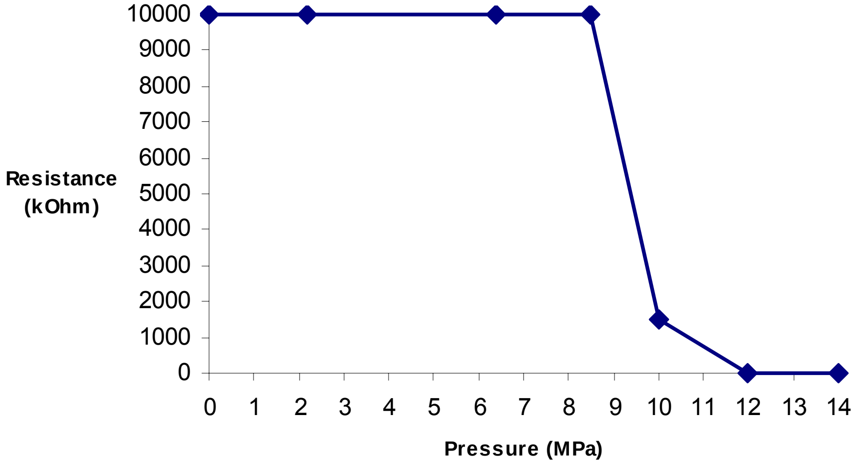


Figure 2 - Resistivity Change of LT2 Mg_2NiH_4 at High Pressure

Conclusions

To make Mg_2NiH_4 less stable and more suitable for hydrogen storage it is essential to:

1. Avoid the presence of Mg/MgH_2 by using a starting alloy prepared by other methods than conventional casting.
2. Suppress microtwinning by using a lower synthesis temperature or by applying a static pressure or mechanical work on the powder after the synthesis.
3. Metal hydride electrodes have been made with the destabilized hydrides giving a very high storage capacity of 550 mAh/gram of active electrode material. Poor corrosion stability, however, still limits use to a few electrochemical cycles. The corrosion stability versus the alkaline electrolyte must be improved.

References

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