The impact of metal hydride material activation to storage percentage of hydrogen in this material

Ľubica Bednárová[1], Tomáš Brestovič[1], Natália Jasminská[1], Marián Lázár[1], Romana Dobáková[1], Lukáš Tóth[1]
[1]Department of Power Engineerng, Technical University of Košice, Vysokoškolská 4, 040 01
Email: lubica.bednarova@tuke.sk

Abstract

Currently, a lot of focus is dedicated to metal hydride alloy and options of their utilization. Mankind must solve energy problems due to constant population growth and use of non-renewable energy sources. The World resources of oil are limited and therefore the mankind must start utilizing the alternative energy sources for example hydrogen. Its known that the hydrogen can be stored by metal hydride alloys what it represents the safety way of storage with absence high pressure and temperature. The process by produce of the alloy with good absorption properties the research does not end. Some alloy absorbs the hydrogen after they produce immediately, however a lot of them need the activation for improvement or starting absorption process. Process of activation is very important for achieving the maximum capacity at moderate temperature.

Keywords: Metal hydride, hydrogen storage, hydrogen activation

1. Introduction

In recent years, many new trends have emerged in metal hydrides with the introduction of new, unconventional production methods, surface treatments, and the discovery of new hydride phases. Their excellent properties are the result of combined engineering a lot of factors: the alloy composition, surface properties, microstructure, grain size etc. In development of nanocrystal hydride is not just the aim improvement of operating characteristics of existing hydrides but too, it is important the create the new generation of materials, those the properties will be proposed and controlled so that it meet the specific requirements of different applications.

2. Activation of alloy

We start with the problem about hydrogen diffusion into intermetallic areas of alloy. For better hydrogen diffusion it should evolve the special microstructure of material. In the case of nanocrystalic material provides a very small grain size enormously increased grain boundaries in the material. Although grain boundaries can act as hydrogen beds with very small amounts of hydrogen, due to the higher hydrogen content, the diffusion coefficient of hydrogen in nanocrystalline Pd has been shown to be higher than that of single crystalline palladium. Hydrogenation begins by filling easily accessible sites at the disordered (or amorphous) grain boundaries. This leads to easier access of hydrogen atoms to nano-grains by avoiding long-range hydrogen diffusion through the already formed hydride phase, which is one of the most difficult phases of absorption. The second factor that can significantly improve hydrogen absorption is the surface to volume ratio. The large surface to volume ratio of the powders obtained by spherical grinding increases the accessibility of the hydrogen penetration material. In addition, ball milling creates a specific surface condition, with special surface defects and imperfections. All of this supports the hydrogen uptake reported in various documents. Nanocrystalline spherical grinding materials appear to have an ideal microstructure for hydrogen absorption. The microstructure of the Mg_2Ni spherical ground powder is shown in Fig. 1. Powder (20-50 μm) consists of very small grains (20-30 nm) which are randomly oriented in powder particles. As expected, the hydrogen uptake of the nanocrystalline material significantly exceeds the absorption rates for a conventional alloy [1-3].

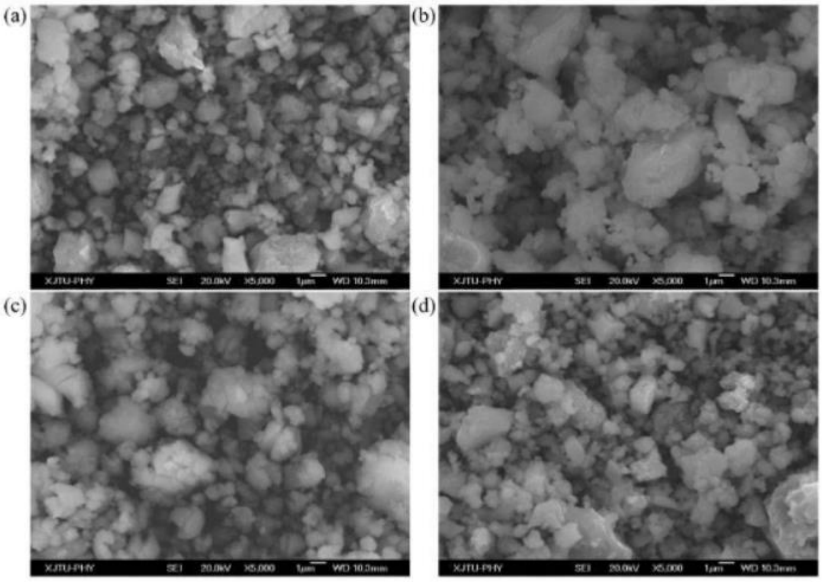

Figure 1. (SEM) of Mg2Ni powder prepared by different milling methods [1]

The rate of absorption can be improved even more radically when other kinetic constraints are reduced. Hydrogen dissociation is one of the critical factors of hydrogen absorption. For example, pure Mg surfaces do not have the ability to adsorb and dissociate hydrogen molecules to allow atomic diffusion within the metal. However, magnesium oxides can help dissociate the hydrogen molecules, but on the other hand the oxide layer significantly slows down the overall absorption rate. The oxide layer almost completely reduces the dissociative chemisorption of hydrogen. Therefore, a likely mechanism of activation is that the oxide layers are divided to expose clean metal surfaces, so that the overall absorption rate is increased [4, 5].

3. Activation to remove oxidation layer

V Most materials are highly reactive and easily form surface oxides and hydroxides that prevent hydrogen uptake. Typically, metal hydrides require activation, which typically involves a slow and complicated high temperature and high hydrogen annealing process.

Hydrogenation, i. formation of metal hydrides by hydrogen absorption is determined by both thermodynamics and reaction kinetics. The following describes the basic mechanisms that govern these two aspects and also show possible ways of using them to improve the properties of metal hydrides. The following alloy activation process with composition $Zr_{0.5}Ti_{0.5}Fe_{1.2}Ni_{0.4}V_{0.4}$ is according to E.D. Koultoukis. For the activation process, all samples were placed in the sample holder at room temperature and under ambient atmosphere. To ensure the best degassing procedure, the samples were kept under vacuum at 350 ° C for two hours. However, this type of alloys requires high-energy activation to react effectively with hydrogen. Therefore, six to eight activation cycles were performed using the following procedure: as soon as the sample temperature reached 350 ° C after the previous degassing step, a pressure of 40 bar hydrogen gas was applied to the sample holder. Then the temperature was lowered to approximately 2 ° C - 5 ° C and the sample was allowed to absorb hydrogen until equilibrium was reached. The temperature was then raised once more to 350 [deg.] C. until the equilibrium was reached again. This procedure is repeated 6 to 8 times, each time the hydrogen pressure is applied to the sample holder. Fig. 2 shows an experimental procedure for such high energy activation for alloy-2. The hydrogen gas used in the present work is a purity of 99.999% [3,4].

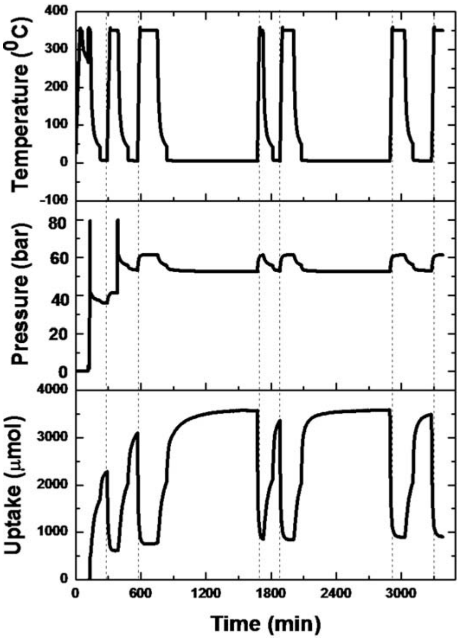

Figure 2. Alloy activation procedures [4]

ion can change dramatically using catalysts. The correct catalyst allows rapid and efficient dissociation of the hydrogen molecules. The efficiency of a catalyst is determined by its ability to "flood" the metal surface with hydrogen atoms to such an extent that the kinetic barrier of the oxide layer is reduced. As a result, activation becomes unnecessary and powders readily absorb hydrogen in the ready state, even after exposure to air [5].

The kinetic factors of hydrogen desorption are analogous to absorption and require similar considerations. The rate of desorption can be limited by diffusion of hydrogen in the material and recombination to hydrogen molecules on the surface. Thus, an increase in desorption can be achieved by methods similar to those used in absorption.

The above processes can be successfully applied to various hydrides, providing in any case an exceptional improvement in hydrogen sorption, as shown for example for $LaNi_5$ in Fig. 3.

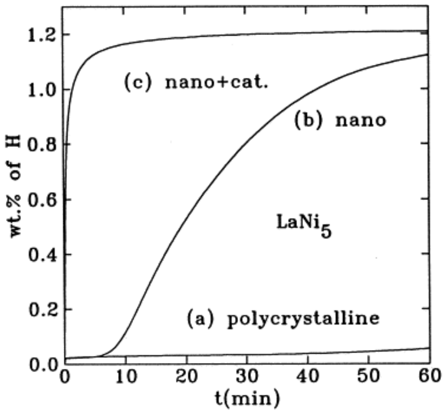

Figure 3. Hydrogen uptake rate $LaNi_5$: polycrystalline (a), nanocrystalline (b) and nanocrystalline with catalyst (c); without activation, temperature 40 ° C, pressure 15 bar [6]

The same is true for magnesium-containing light alloys, which combine two important advantages: high hydrogen capacity and low cost. Examples of the efficiency of light nanocrystalline alloys are shown in Fig. 4 and Fig. 5.

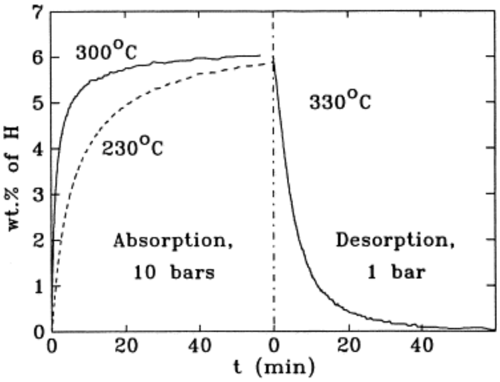

Figure 4. Absorption and desorption for nanocrystalline Mg-based alloy [7]

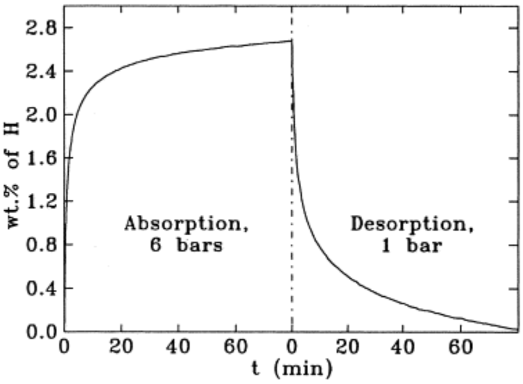

Figure 5. Absorption and desorption for a nanocrystalline light alloy at 235 °C.

Fig. 6 shows the absorption of a light alloy at low temperature. In all cases, nanocrystalline powders were exposed to air between production and hydrogenation and showed no pyrophoric tendency. After exposure to air (in some cases of the order of weeks), kinetic hydrogenation curves were measured without prior activation or treatment of hydrogen and found to be unchanged. Finally, nanocrystalline powders do not disintegrate after absorption / desorption [8].

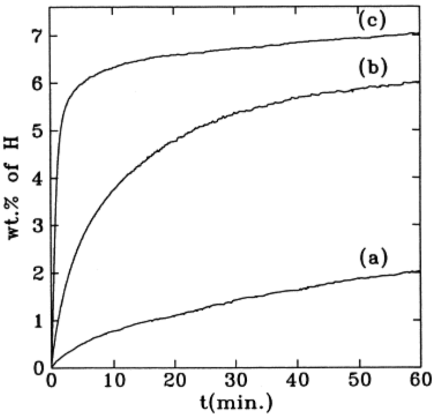

Figure 6. Low temperature absorption of light nanocrystalline alloy: 110 ° C (a), 170 ° C (b), 190 ° C, (c) (20 bar) [5]

4. Activation to change the phase structure of the alloy matrix

The activation properties of hydrogen storage alloys are generally determined by two main factors: the oxide layer on the surface and the phase structure of the alloy matrix. In the initial stage of activation, hydrogen atoms must penetrate the oxide film on the alloy surface and are absorbed by the volume of the alloy.

Activation of the phase structure of the alloy matrix is accomplished by sequentially hydrating and dehydrating the metal several times in a pulsed manner until the desired degree of activation is achieved. The metal is pulsed by alternately subjecting the metal to a hydrating and dehydrating force. The pulsation cycle is then repeated several times until the metal is activated to the desired degree. For the purpose of pulsating cycle activation, the hydridation and dehydration forces may be applied in any order, i. a dehydration force followed by a hydration force or vice versa.

The extent to which the metal is activated depends on the duration of the individual pulses in the pulse cycle, the switching times between pulses and the number of such pulses. In this regard, it is preferred that the metal in each pulsating cycle is hydrated to a significant extent, i. j. at least about one-tenth of one percent of its total capacity, but no more than about ten percent of its total capacity. To achieve this, the time of each hydration force pulse and the dehydration force pulse in each cycle will vary from metal to metal, but is typically about 10 to about 1000 seconds. From the processing point of view, it is advantageous if the hydration pulse time is the same as the dehydration pulse time [8].

Figure 7 shows experimental isotherms measured at 298 K in a low hydrogen concentration region (H / M <1.5) during the activation procedure. It is known from the literature that during the first hydration cycles decrepitations occur: precipitation of the hydride phase creates internal defects, which in turn induce crushing of the sample into a fine powder. From Figure 7 it is evident that the equilibrium absorption pressure decreases with increasing number of hydration / dehydration cycles (whole isotherms up to H / M6 not shown). The question is to find out whether or not there is any relationship between thermodynamic states and sorption kinetics. If so, what is the reaction step (surface chemisorption of bulk hydrogen transport by diffusion) that is most affected by this development. To answer this question, experimental impedance diagrams must be measured during activation (Fig. 7) [9-11].

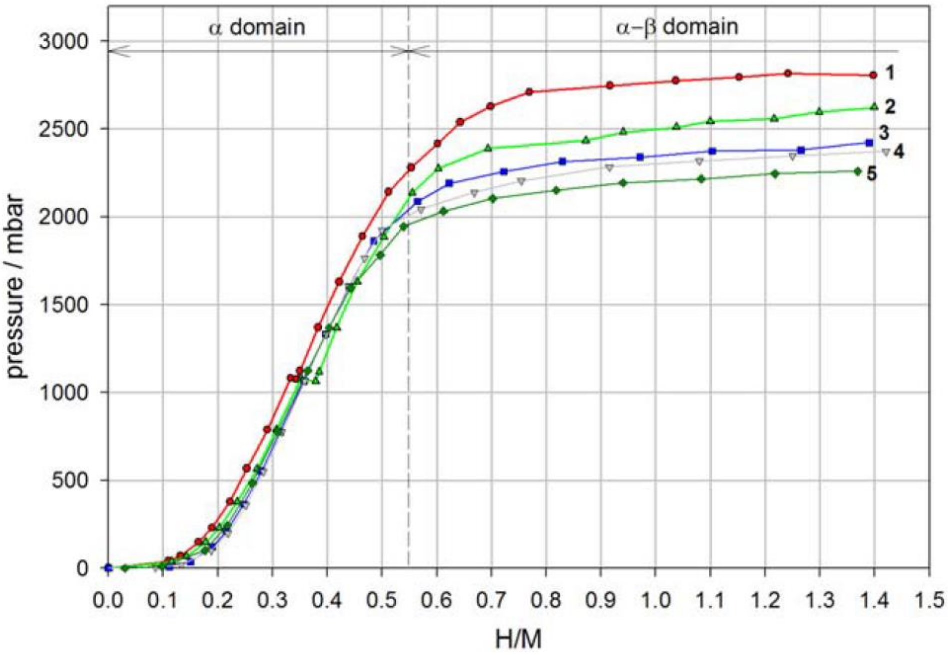

Figure 7. isotherms of the $LaNi_5$-H_2 (g) system measured at 298 K in a low hydrogen concentration region for 5 consecutive absorption cycles [9]

5. Conclusion

However, the thermodynamic and kinetic properties of most of these systems are complicated by hysteresis, and for practical applications it is necessary to develop activation procedures to optimize sorption capacities and kinetics. The thermodynamic and kinetic characterization of metal hydride systems is complicated by the presence of important hysteresis: the equilibrium pressure during absorption is significantly higher than the equilibrium pressure during desorption, indicating that irreversible transformations are occurring. For an unactivated sample of LaNi5 powder, the difference between the two equilibrium pressures is significantly greater (about 1400 mbar at 298 K). During the first hydration cycles, the equilibrium absorption pressure decreases and the difference can be reduced to approx. 400 mbar for 10 cycles. This process is known as decrepitation: the precipitation of the hydride phase produces significantly high internal stresses and tensions, which in turn crush metal samples. In the literature for activated samples, average particle diameters of several microns were reported.

The development of new materials for hydrogen storage requires overcoming many thermodynamic and kinetic constraints. In a new generation of modern materials, proper engineering of alloy composition, surface properties, microstructure, grain size, etc., we can design and control material properties according to the requirements of a particular application. A number of metastable phases and microstructures offer tremendous possibilities for modifying the p-c-T characteristics for better performance [7].

6. Acknowledgement

This paper was written with the financial support of the granting agency VEGA within the project solution No. 1/0108/19 and of the granting agency KEGA within the project solution No. 005TUKE-4/2019.

7. References

[1] Z. Wu et. all, „Microstructure and improved hydrogenstorage properties of Mg based alloy powdersprepared by modified milling method“, In: Powder Metallurgy, February 2014; 57(1):45-53.

[2] D. Vyas, P. Jain, G. Agarwal, A. Jain and I. P. Jain: „Hydrogenstorage properties of Mg2Ni affected by Cr catalyst“, Int. J.Hydrogen Energy, 2012,37, 16013–16017.

[3] H. H. Cheng: „Special hydrogen storage materials and themeasurement apparatus“, PhD thesis, Institute of Metal Research, Chinese Academic of Sciences, Shenyang, China, 2007,20–25.

[4] E.D. Koultoukis et. all, „High-Temperature Activated AB2 Nanopowders for Metal Hydride Hydrogen Compression“, online in: https://arxiv.org/ftp/arxiv/papers/1311/1311.4465.pdf.

[5] Sakintuna B, Lamari-Darkrim F, Hirscher M.: „Metal hydride materials for solid hydrogen storage“, A review. International Journal of Hydrogen Energy 2007; 32,1121-1140.

[6] L. Zaluski, A. Zaluska, P. Tessier, J.O. Ström-Olsen and R. Schulz, J. Alloys Comp., 217 (1995) 295.

[7] L. Zaluski, A. Zaluska, P. Tessier, J.O. Ström-Olsen and R. Schulz, Mater. Sci. Forum, 225–227 (1996) 853.

[8] L. Zaluski, A. Zaluska, J. OStröm-Olsen, „Nanocrystalline metal hydrides“, Journal of Alloys and Compounds, Volumes 253–254, 20 May 1997, Pages 70-79.

[9] Pierre Millet, Michel Guymont, „METAL HYDRIDES : ACTIVATION PROCEDURES, THERMODYNAMICS AND KINETIC ANALYSIS“, 2IWH 2007, 27-29 October 2007, Ghardaïa – Algeria.

[10] T. Jacobsen and K. West,” Diffusion impedance in planar, cylindrical and spherical symmetry”, Electrochim. Acta, 40, 255-262, (1995).

[11] Michael E. Badding, „PROCESS FOR ACTIVATION OF METAL HYDRDES“, Lucent Technologies Inc., Murray Hill, N.J., No.: 292,556, Aug. 18, 1994.

Copyright Disclaimer