HYDROGEN STORAGE AS METAL HYDRIDES – A REVIEW OF CONCEPTS NEEDED IN UNDERSTANDING H2 SORPTION – DESORPTION PROCESSES

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Abstract

The production, purification, storage and transportation of hydrogen play an important role in the development of the green hydrogen-based economy. The hydrogen storage in the form of metallic or intermetallic hydrides requires suitable materials that could absorb a large amount of hydrogen and, on demand, release it. Significant efforts are currently being made worldwide in the field of hydrogen storage research and development, and despite these efforts and advances in solid-state hydrogen storage, no material simultaneously satisfying all the necessary requirements of an ideal material used for this purpose has been discovered. All advantages of using hydrogen as a form of energy and the growing international interest in finding feasible materials for use as hydrogen storage media were taken into consideration. The paper presents the theoretical concepts needed to understand the metal hydrides formation to allow future attempts to obtain performance materials for hydrogen isotopes storage. The research studies carried out at the RATEN ICN Pitesti in this direction are also presented.

Keywords: *Hydrogen storage, Metal hydrides, Hydrogen sorption, Hydrogen desorption, Hydrogen isotopes storage*

Introduction

Hydrogen use as energy form and the need for developing storage methods

Hydrogen is considered a strong candidate to replace conventional fuels. Since it is an energy carrier rather than an energy source, additional sources must be used to produce hydrogen. Electrolysis of water is one of the most used methods for producing hydrogen; if power generated from renewable sources is used in the process, hydrogen can be produced entirely from renewable sources. Once hydrogen is produced, it must be transported to end consumers or distribution facilities before being stored for later use. The hydrogen economy consists of these three stages: production, transportation and storage [1, 2].

The development of advanced hydrogen storage technologies is a topic of great actuality, interest and, at the same time, a necessity for the transition to a sustainable society with low carbon emissions [3].

Significant efforts are currently being made worldwide in the field of hydrogen storage research and development. Despite these efforts and advances in the field of solid-state hydrogen storage, no material simultaneously satisfying all necessary requirements of an ideal material used for this purpose has been found [4]. Some of the requirements for efficient hydrogen storage are shown in Fig. 1, [5].

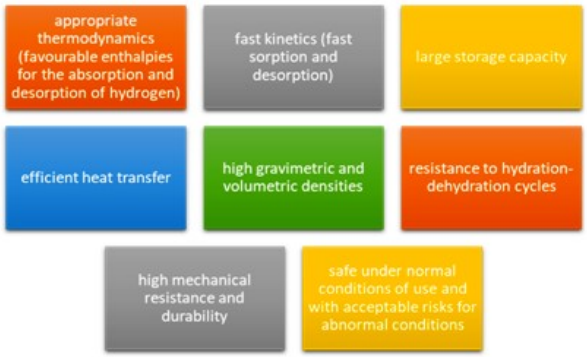


Fig. 1. Requirements for efficient hydrogen storage, [5]

Hydrogen storage methods

Hydrogen storage methods can be classified into three main categories, shown schematically in Fig. 2, [6].

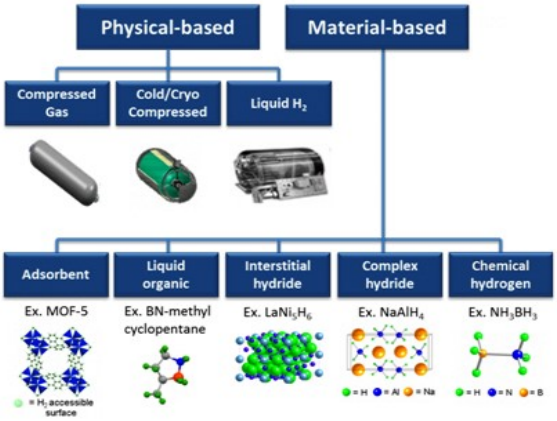


Fig. 2. Hydrogen storage methods, [6]

In physical storage methods, hydrogen does not interact with the storage medium; in chemical methods it interacts with the storage media through strong covalent/ionic bonds or weak van der Waals forces (i.e. hydrogen is chemically bound to a storage material). Chemical methods always include a hydrogen storage material, [1].

Hydrogen storage in solid state hydrides

Metal hydrides are composed of metal atoms, which bond with hydrogen atoms, occupying the free spaces of the lattice. Hydrogen and the metal usually produce two hydride phases: the α phase, in which small amounts of hydrogen are absorbed, and the β phase, in which the hydride is completely formed.

The ability to dissociate hydrogen varies from one metal to another, depending on morphology, concentration and surface structure. An optimal hydrogen storage material should have the following characteristics: low heat of formation, low dissociation temperature to reduce the energy required to release hydrogen, moderate dissociation pressure, limited energy loss during hydrogen absorption and desorption, high stability, resistance to recycling, low costs and a high level of safety, [7].

Various metals in the periodic system are able to store hydrogen in the form of hydrides (see Fig. 3, [8]), through the direct dissociative chemisorption of H_2 gas, according to the equation:

$$M + \frac{x}{2} H_2 \leftrightarrow MH_x(s) \pm \Delta H^{\theta}$$

where M is the metal or alloy, x is hydrogen concentration and ΔH^{θ} is the enthalpy of hydride formation. The reaction is exothermic and the metal hydride formation does not occur in the one-step reaction, [9].

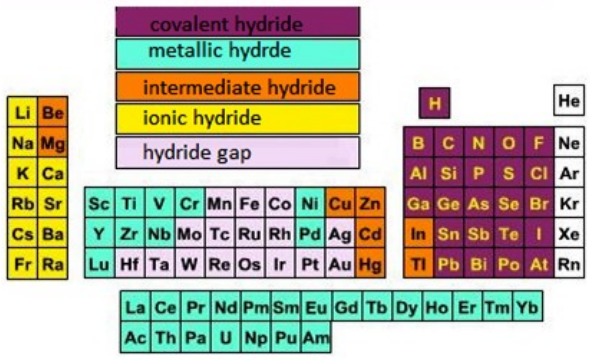


Fig. 3. Hydride forming elements, [8]

Solid state materials used to store hydrogen can be broadly divided into two categories, depending on the strength of the interaction between hydrogen and the storage material:
- reversible hydrides (based on strong interactions), further divided into: metallic hydrides and complex hydrides, the main difference being the transition to an ionic or covalent compound after hydrogen absorption.
- physisorption materials (based on weak interactions), [1].

The network structure is typical of a metal with hydrogen atoms in the interstitial positions (Fig. 4, [10]), and for this reason they are also called "interstitial hydrides". This type of structures is limited to compositions in the form: MH, MH_2 and MH_3, where M represents the metal.

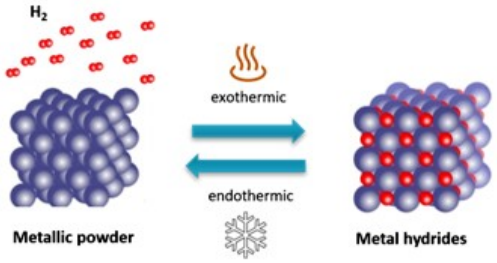


Fig. 4. Metal hydride structure, [10]

Ternary systems are in the form AB_xH_n, where A is usually a rare earth element (Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) or an alkaline earth metal (Be, Mg, Ca, Sr, Ba, Ra), and element B is often a transition metal and forms only unstable hydrides, [5]. Different categories of materials used for hydrogen storage are briefly presented in Fig. 5, [3, 11].

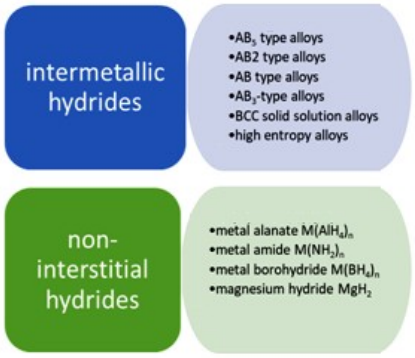


Fig. 5. Categories of materials used for hydrogen storage as metal hydrides

Theoretical aspects in understanding hydrogen storage as metal hydrides

For characterizing the hydrogen storage performance of a material, two principal types of measurements can be used: kinetics measurements and pressure-composition-temperature (PCT) measurements. Kinetics measurements can be considered the fundamental measurement of hydrogen storage because other types of measurement, including PCTs, are collections of several individual kinetics measurements, [12].

Kinetics of the metal – hydrogen system

The steps involved in the metal hydrides formation as well as those characterizing the dehydrogenation process [13] are schematically shown in Fig. 6.

The maximum amount of hydrogen in the hydride phase is given by the number of interstitial sites. As a general rule, it can be said that all elements with electronegativity between 1.35 - 1.82 do not form stable hydrides ("hydride gap"). More general is the Miedema model: the more stable an intermetallic compound is, the less stable its hydride is, and vice versa [5].

For dehydrogenation, the process is reversed, i.e. hydrate phase breaks down and the hydrogen atoms diffuse to the sub-surface and subsequently to the surface, where the hydrogen atoms recombine and are desorbed as H_2 [14].

Hydrogenation process
a - Physisorption
b - Chemisorption
c - Penetration of the metal surface
d - Formation of the hydride phase
e - Diffusion through the hydride phase
f - Nucleation and growth of the hydride phase with α/β interface movement

Dehydrogenation process
a - Decomposition of the hydride phase with α/β interface movement
b - Diffusion through the metal
c - Release from the metal surface
d - Recombination of the hydrogen atoms ($H + H \rightarrow H_2$)
e - Release of the hydrogen molecule (H_2)

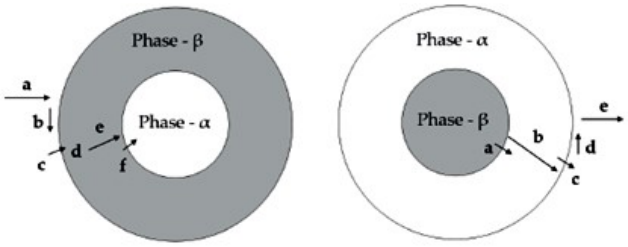


Fig. 6. Steps of hydrogenation /dehydrogenation process [14]

Kinetics is generally used to express the rates of hydrogen sorption and desorption from a storage material.

The difference between capacity and kinetics, in reversible systems, is that capacity measurements are theoretically taken at thermodynamic equilibrium, independent of the time required to reach the equilibrium, while kinetics investigates how the material approaches equilibrium and the factors influencing this approach. The equilibrium is perturbated by changing the thermodynamic state of the sample's environment, which causes the sample to sorb or desorb hydrogen, in the attempt to restore equilibrium.

Generally, kinetics experiments provide a useful measure of the rate of hydrogen uptake or release from a storage material. For the gravimetric and volumetric methods, kinetics measurements are generally conducted under isothermal conditions, with changes in pressure used to perturb equilibrium (Fig. 7).

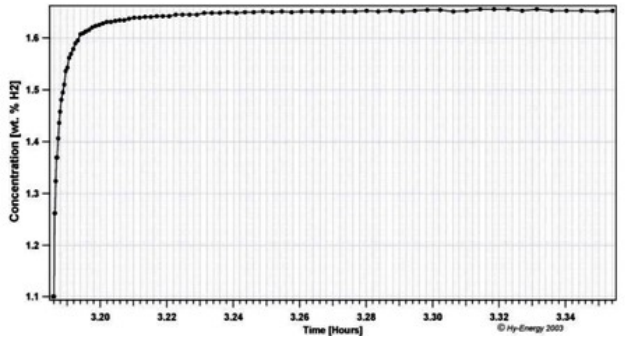


Fig. 7. Example of kinetics measurement experiment for hydrogen absorption, [12]

At the beginning of an experiment, the concentration varies quickly because the sample is the farthest from equilibrium and, with time, the rate of change of concentration reduces until it becomes effectively zero [12].

Fundamental Mechanisms of Reactions

To improve the kinetics characteristics and performance of potential hydrogen storage materials, it is important to understand the rate-controlling steps of the process. The sorption and desorption of hydrogen by a material involves a number of important steps that occur both in series and in parallel; these steps vary from process to process, and are dependent on the storage material.

The kinetics mechanisms are generally classified into three broad categories: surface interactions, mass (hydrogen, potentially the host elements) and energy transport (heat transfer), and bond breaking and forming mechanisms. Surface interactions, mass and energy transport, and binding mechanisms are considered intrinsic processes. Mass and energy transport also depend on a number of extrinsic factors including particle size, packing density, sample and sample holder shape, thermal contact between sample and sample holder, and gas mobility and pressure. Any one of these parameters may be rate controlling [12].

Binding mechanisms

Hydrogen storage mechanisms differ between physisorption and storage media, with the former involving bond breaking and the latter involving bond formation between hydrogen and the host. The relative strength of the bonding situations between these two types of storage greatly influences the kinetics and thermodynamics.

- *Storage of H_2 on surfaces by physisorption*

For physisorption, molecular hydrogen interacts with the surface via weak van der Waals forces and remains in molecular form (H_2). Storage via physisorption is generally limited to porous and nano-structured materials. For hydrides, this step is followed by the chemisorption of H_2.

- *Storage of H_2 by forming hydrides*

The dissociation of hydrogen and subsequent bond formation to produce bulk hydrides or interstitial metal hydrides provides the basis for a large number of hydrogen storage materials. Depending on the type of hydride bond formed, hydrides can be classified as ionic, metallic (interstitial) or covalent, [12].

Mass transport

The kinetics of hydrogen storage in reversible systems is strongly influenced by the mobility of hydrogen and, possibly, the storage material itself, as well as the transport of energy through the storage media (material and gas). The mobility of hydrogen, reactants, and energy inside the storage media requires a wide range of transport properties.

- *Physisorption*

For porous materials, molecular hydrogen easily passes through macroscopic boundaries and is transported through the network of pores to the internal surfaces of the material. Transport through the internal networks is governed by porous media-specific transport laws, Darcy's Law being the most used transport constitutive equation.

- *Hydrogen Diffusion in Metal Hydrides*

Hydrogen mobility in metal hydrides is achieved via atomic diffusion through the host metal structure's interstitial sites. The mechanisms controlling local diffusion in metal hydride materials are highly temperature dependent.

Impact of Surface Interactions on Kinetics

As described above, hydrogen can be stored on the surface (adsorption) and in the bulk (absorption) of metal hydride materials. Hydrogen is weakly bound to the host's surface. For bulk metal hydride formation, only atomic hydrogen can pass through the surface layers and be transported into and out of the bulk. To store molecular hydrogen, the surfaces of metal hydride storage materials must dissociate it into atomic hydrogen. This is performed through the dissociation of H_2 via the transfer of electrons into the sample material. Hydrogen dissociation on the surface of a metal hydride is shown in Fig. 8.

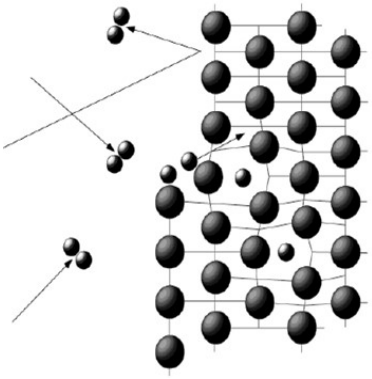


Fig. 8. Representation of the H – M interaction, [12]

Generally, hydrogen exists as a diatomic molecule before interacting with the material surface (left side of the figure), it dissociates at the surface into two atomic hydrogen atoms, and then diffuses into the bulk of the material (small molecules in the lattice).

Doping with metal catalysts is a common technique for increasing the efficiency of hydrogen dissociation at the surface of chemisorbing materials, [12].

Heat transfer

Due to the exothermic nature of most hydrogen storage materials, heat transfer often plays the most critical role in the kinetics of hydrogen sorption and desorption. Heat transfer in porous media occurs through the internal pore network and the material itself. With few exceptions, hydrogen storage materials are often powders with limited particle-to-particle interaction. As a result, heat transfer is governed by many of the principles as porous media, [12].

Thermodynamics of the metal – hydrogen system

In academic literature, the most common type of hydrogen storage measurement is pressure-composition-temperature (PCT), composition being used for the concentration of hydrogen in a sample. A PCT measurement is a collection of data points indicating the pressure, concentration and temperature of a sample in equilibrium and it relates the thermodynamic variables influence on concentration.

PCTs are also referred to as PCIs (Pressure-Composition Isotherms) since they are performed under isothermal conditions. This reduces the number of free variables and allows representing the relationship between concentration and pressure using two-dimensional graphics. Temperature effect on hydrogen storage properties can be determined by comparing PCT isotherms at various temperatures. PCTs, which represent a sample in equilibrium, can also be used to determine the thermodynamic properties of a hydrogen storage material, [12].

The procedure for determining PCIs consists of placing the metal/material to be hydrided in a closed vessel connected to a hydrogen source, and gradually increasing hydrogen pressure at a constant temperature (see PCI curves in Fig.9).

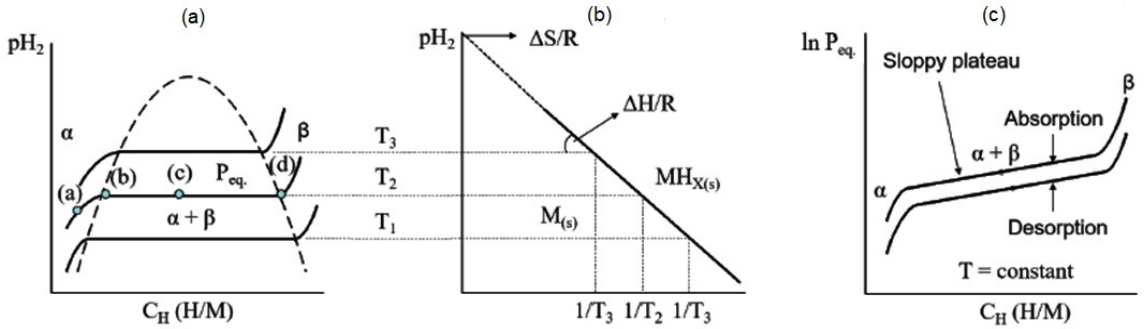


Fig. 9. (a) Ideal PCI curve describing hydrogen absorption /desorption process; (b) van't Hoff plotting; (c) PCI curve for real behaviour.

During hydrogen absorption in a metal under equilibrium conditions, several steps are involved. In Fig.9 (a), the PCI at temperature T_2 can be described in detail as follows:

1) At the beginning of the process, molecular hydrogen (H_2) near the metal surface undergoes van der Waals interactions, H_2–M interaction being called physisorption.

2) Molecular hydrogen dissociates at the metal surface ($H_2 \rightarrow H+H$) and forms M–H bonds, process called chemisorption.

3) Chemosorbed hydrogen diffuses into the interstitial locations of the metal lattice and dissolves exothermically to form a solid solution (α phase). This process takes place in the area with low hydrogen concentration (H/M < 0.1) – point a in Fig. 9 (a), and is described by the reaction:

$$M_s + (Y/2)H_{2(g)} \leftrightarrow MH_{Y(s)} \quad (\alpha \text{ phase})$$

4) By increasing the hydrogen pressure, the solid solution (α phase) reaches a hydrogen concentration saturation at H/M = 0.1. From this hydrogen concentration, the hydride phase (β phase) begins to form – point b in Fig. 9 (a).

The significant expansion of the metal lattice causes strong H-H interactions, leading to nucleation and further growth of the hydride phase.

In the ideal case, the entire hydride phase formation process takes place at a constant pressure, called "plateau region" on the PCI curve – from point b to point d in Fig. 9(a). In this region, the solid solution (α phase) and the hydride phase (β phase) coexist in equilibrium conditions – point c in Fig. 9 (a). The pressure associated with the plateau region is called "equilibrium pressure" (P_{eq}), the process being described by the equation below [13]:

$$MH_{Y(s)}\ (\alpha \text{ phase}) + [(X\text{-}Y)/2]H_{2(g)} \leftrightarrow MH_{x(s)}\ \ (\beta \text{ phase})$$

Plateau pressure provides valuable information regarding the reversibility of storage capacity; the width of the plateau and its position at a given temperature can provide insight on the hydride's stability. Stable hydrides require higher temperatures than less stable hydrides to reach a certain plateau pressure, [14].

5) Once hydride phase formation is complete, hydrogen pressure rises again – from point d in Fig. 9. This phenomenon is attributed to the dissolution of atomic hydrogen in the hydride phase.

Under experimental conditions, the equilibrium pressure for the plateau region is not perfectly constant, as shown in Fig. 9 (c). The neglected plateau is attributed to the expansion of the hydride network and relaxation of the metal matrix, which causes a slight increase in the equilibrium pressure during the chemical reaction to form the hydride phase (β phase).

Further, it is also observed that equilibrium pressure for the hydrogenation process is lower than the one for the dehydrogenation process. This phenomenon is called hysteresis and is attributed to localized defects in the metal lattice and metal surface inhomogeneity. As a result, different equilibrium pressure values are usually reported for hydrogenation and dehydrogenation processes.

Equilibrium pressure (P_{eq}) dependence on temperature (T) is given by the van't Hoff equation:

$$ln(P_{eq}) = [\Delta H/RT] - [\Delta S/R]$$

where ΔH and ΔS are the enthalpy and entropy changes for the chemical reaction to form the hydride phase, and R is the ideal gas constant. Values for ΔH and ΔS can be obtained from the slope and intercept of the linear correlation between $ln(P_{eq})$ and $1/T$, as shown in Fig. 9 (b). This linear correlation is constructed from the equilibrium pressure determined by PCI measurements.

ΔS indicates the entropy change for hydrogen, i.e. from hydrogen as a molecular gas to hydrogen in the hydride phase. For metal–hydrogen systems, the standard entropy change is 130 kJ/Kmol, but may have a different value for other hydride systems, as the hydrides composed of boron, aluminium or nitrogen, alkali and alkaline earth metals.

ΔH of a hydride compound or system characterizes the stability of the metal – hydrogen bond (M – H) and takes a negative value for exothermic hydration and a positive value for endothermic dehydration.

The parameters ΔH and ΔS play a significant role in designing of hydrate material formation and their practical applications. They allow calculation of the temperature for hydrogen release from the hydride phase at atmospheric pressure (~1 bar), which refers to the minimal temperature for the dehydrogenation process without any kinetic constraint. Furthermore, the thermodynamic properties of the hydride phase provide information regarding the pressure and temperature range within which the hydride system operates, [13].

Kinetics study equations

Based on experimental data of hydrogen absorption curve, depending on the technique used, the reacted fraction can be calculated for:

- constant pressure and variable mass, $\alpha = \dfrac{m_t - m_0}{m_{eq} - m_0}$

- constant volume and variable pressure, $\alpha = \dfrac{p_0 - p_t}{p_0 - p_{eq}}$

where m_0/ p_0 is the initial mass/ pressure, m_t/ p_t is the mass/ pressure at time t, and m_{eq}/ p_{eq} is the mass/ pressure at equilibrium.

The commonly used experimental technique employed to study the thermal reaction is the thermo-gravimetric (TG) technique under isothermal condition. Kinetics study of thermal absorption of gas is one of the most important applications of thermal analysis.

Hydrogen concentration can be calculated by means of gravimetric technique using a highly sensitive microbalance to determine the change in weight. For this, the following formula can be used:

$$H_{ppm} = \frac{(\Delta m_{mass\ gain})\,in\ mg}{(m_{sample})\,in\ mg} \times 10^6$$

In all the kinetic methods, reacted fraction $\dfrac{d\alpha}{dt}$ is linearly related to reaction mechanism function $f(\alpha)$, whose slope is the temperature - dependent rate constant, $k(T)$. The mechanism function $f(\alpha)$ is independent of temperature. Mathematically, relation could be expressed as follows, where α is the fraction reacted at time t, $k(T)$ temperature dependent rate constant.

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \qquad (1)$$

Here, $k(T)$ is Arrhenius type rate constant which depends on temperature. Under isothermal conditions, the integral of the above equation could be expressed as:

$$g(\alpha) = \frac{d\alpha}{f(\alpha)} = k(T)t + C \qquad (2)$$

The mechanism of the function depends on *g(α)*. The mechanism of gas absorption reactions can be described by using various kinetics models available in the literature. Usually, it is ascertained by fitting the isothermal TG data into these kinetic equations and selecting the model which fit linearly.

The slope of the linearly fitted line has given the rate constant *k(T)*. The kinetic parameters are evaluated by plotting *ln[k]* versus reciprocal of temperature expressed in Kelvin.

The *α–t* kinetic curve gives the data for *α* and *t* for hydrogen absorption, which can be linearly fitted to all the possible mechanism functions controlling the reaction based on Eq. (1) or (2).

The mechanism of hydrogen absorption reaction in the metal is decided by the function *g(α)* giving the best linearity. The rate function of hydrogen absorption and the kinetic parameter *k(T)* can be obtained from the linear regression fitting.

Based on the Arrhenius equation, the apparent activation energy of hydrogen absorption can be subsequently calculated.

The rate constant *k(T)* and the activation energy *(E)* are related by Arrhenius equation. Mathematically, it could be expressed as:

$$k(T) = Ae^{-\frac{E}{RT}}$$

where *A* is pre-exponential or frequency factor, *R* is the molar gas constant, *T* is temperature in absolute scale, and *E* is activation energy in $Jmol^{-1}$. Applying natural logarithms on both sides, the above expression reduces to:

$$\ln k(T) = \ln A - \frac{E}{RT}$$

The constant *k(T)* was calculated from the slope of isothermal hydrogen absorption kinetics curve [*g(*α) vs. time]. Slope of *ln k(T)* versus $\frac{1}{T}$ gives the value of $-\frac{E}{RT}$ which is eventually converted into the activation energy *E*.

INR Pitesti experience in hydrogen storage – a brief overview of performed hydrogen storage studies

The main activity objective of the Institute for Nuclear Research Pitesti is the scientific research and support for Romania's nuclear energy sector. One of the 18 research and development programs is "Heavy water and tritium" program, which includes theoretical and experimental activities regarding hydrogen storage and contributes to: developing applications based on hydrogen generation and storage using nuclear energy and developing new methods for energy storage.

Intermetallic compounds have long been known to be useful for reversible hydrogen storage. According to theoretical studies on the current state of research on storage materials, depleted metallic uranium alloys have the potential to remove all or some of the difficulties associated with the use of uranium as a storage material. Alloying elements provide several options for modifying the structure and characteristics of uranium. These are made possible by the solid phase transformations shown in phase diagrams and address two major issues: allotropic modifications and temperature-dependent variations in solubility of alloying elements.

Significant research on these systems has led to the possibility of using these alloys as storage materials. The findings suggest that this approach has a significant impact on expanding the number of materials used in hydrogen storage. It is also important to note that the alloying element concentration, experimental conditions and methodology have a great impact on the absorption properties.

In this context, using SETARAM SETSYS EVOLUTION 24 experimental installation available at INR Pitesti and various data processing methods, several studies on hydrogen storage as metal hydrides on different compounds of the U-Zr and Zr-Co systems were performed, focusing on thermal stability, hydrogen absorption, as well as other structural properties of the materials.

Study on hydrogen absorption properties of U-55Zr alloy

In the context of hydrogen storage materials development, possibility of using U-55Zr alloy was studied [16]. Hydrogen absorption properties of Zr alloy with 55 wt% Zr (U-55Zr) were examined in the following conditions: temperature in (350 – 600) °C range, hydrogen pressure slightly lower than one atmosphere.

Hydrogen absorption isotherms were measured at 350 °C, 400 °C, 500 °C and 600°C, respectively, on four alloy specimens, using SETARAM SETSYS EVOLUTION 24 installation and the thermo-gravimetric (TG) analysis.

By using powder metallurgy, U-55Zr alloy was prepared from the constituent elements, which included depleted uranium and sponge zirconium. The alloy was then tested, as a hydrogen storage material, in cast form. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to investigate the microstructure of the initial alloy specimens as well as the hydrogenated ones. The specimens' crystal structures were also examined using X-ray diffraction technique. The hydrogen storage capacity of U-55Zr alloy was evaluated by weighing the samples before and after the hydrogenation. The kinetics of hydrogen absorption related to the hydride composition was analysed and discussed (see Fig. 10).

For all of the specimens, it was observed that hydrogen capacities were comparable to or greater than those of UHx or ZrHx hydrides. The samples were divided into two main phases before hydrogenation and a few hydride phases after hydrogenation. A clear ternary hydride was not identified. It is possible that the ternary hydride is a mixture of UHx and ZrHx.

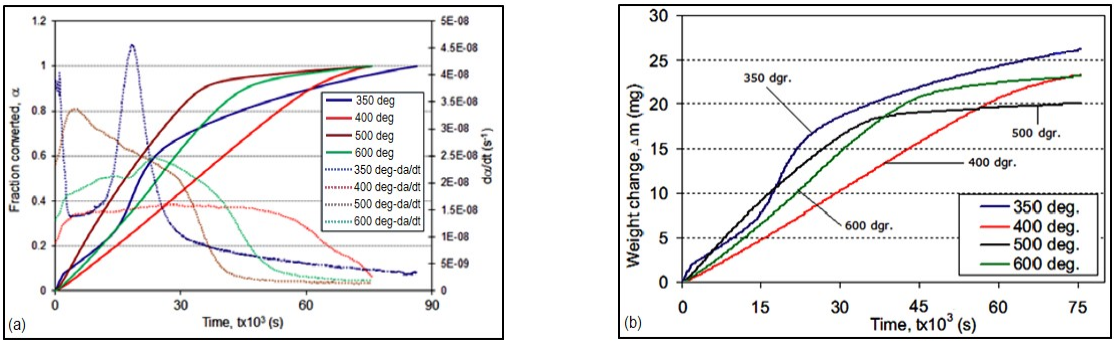


Fig. 10. (a) Reacted fraction curves of hydrogen absorption in U-55Zr alloy at different temperatures (b) Hydrogen absorption rate curve of U-55Zr vs. time, at different temperatures, [16].

Hydrogen storage in the U-Zr compounds prepared by powder metallurgy

Hydrogen absorption properties of several uranium-rich alloys with varying compositions, U-xZr (x=11, 25 and 35 wt%Zr), were investigated to determine their hydrogen absorption capability [17]. Powder metallurgy was used to prepare the alloys, which were then analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM), and Differential Scanning Calorimetry (DSC) methods. The hydrogen absorption properties of all specimens were determined by TG analysis under a hydrogen pressure of one atmosphere, and as cast form.

The samples were heated up to 350°C (test temperature), and isothermal measurements were performed as a function of time**.** The isothermal thermo gravimetric curves are shown in Fig. 11. The obtained results reveal that U-Zr alloys react slowly with hydrogen. Since the sample masses in each experiment differed, the results were normalized based on mass. The rate of hydrogen alloy absorption was measured as a function of time at a given temperature. The weight variations over time were used to calculate the fraction reacted (α) at time t. When comparing the three compositions, U-35Zr appears to be the most active for hydrogen absorption.

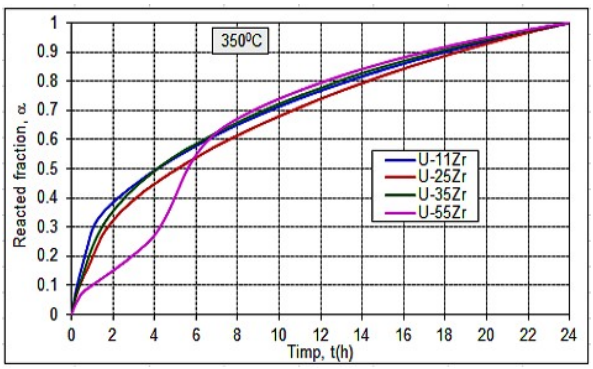


Fig. 11. Thermo gravimetric curve for hydrogen absorption in U-xZr alloys, [17]

Evaluation of physical stability of the U-ZrH system

The main objective of the study [18] was to demonstrate the stability for thermal cycling. Thermal cycling tests on U-ZrH1.6 alloy were performed, the samples having the following elemental analysis: 45 wt% uranium content, 1.6 H/Zr ratio, 3140 ppm level oxygen content. The tests were carried out at temperatures varying in the range from 500°C to 750°C, which includes the transformation from orthorhombic to tetragonal phase at 653°C. Each sample was thermally cycled over 100 times, in the before mentioned temperatures range and at 1100 mbar, the heating rate for TGA-DTA analysis being 90 °C/min, under argon static atmosphere (Fig. 12).

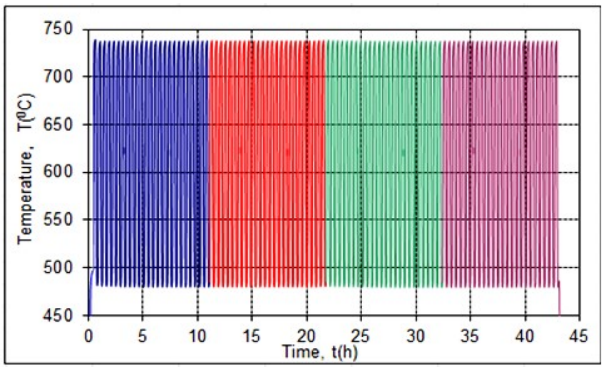


Fig. 12. Temperature variation for 100 heating/cooling cycles on U-ZrH1.6 alloy, [18]

The results of TGA-DTA analysis on U-ZrH1.6 alloy are shown in Fig. 13. The temperatures range is associated with a loss of weight and strong evolution of hydrogen, after 25 cycles. Then, the release of hydrogen levels off quickly and tends to zero or has small increase. A weight loss of 6.07 wt% was observed under the endothermic process, thus indicating that the sample released hydrogen. TG curves show that both endothermic peaks have an associated mass loss and can only be related to hydrogen desorption. Differential thermal analysis showed that mass loss is endothermic. During heating, endothermic peaks of H_2 release accompanies desorption in the DTA curves.

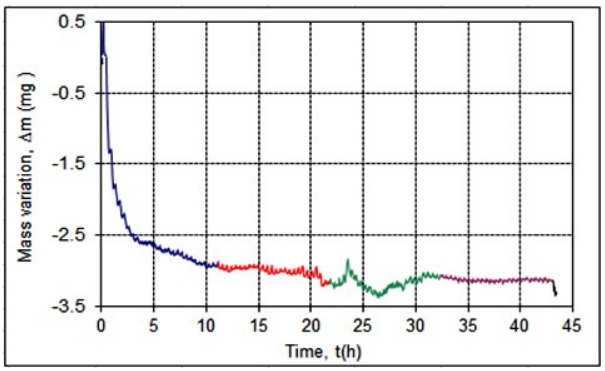


Fig. 13. Mass variation after 100 heating/cooling cycles in the interval 500-750°C, on U-ZrH1.6 alloy, [18]

Conclusions

To meet the growing demand for energy, current and future systems must be cost effective, reliable, and sustainable, as well as having a low environment impact. In this context, scientists and researchers are working to develop energy sistems from renewable sources, with a particular focus on hydrogen as an energy carrier.

Worldwide researches are focused on synthetizing and finding metal hydrides with low thermodynamics, fast kinetics, and big gravimetric hydrogen storage capacity; hence, at the present, is still looking for materials that meet the requirements imposed worldwide for hydrogen storage systems.

To conduct studies on hydrogen storage in metal hydrides, it is necessary to know and understand the main features of the systems and materials:

- capacity → refers to the maximum steady-state hydrogen content of a storage material;
- kinetics → refers to the rate of hydrogen sorption or desorption of a material;
- thermodynamics → refers to how the hydrogen storage materials' intrinsic thermodynamic properties affect a number of other parameters, most notably the hydrogen capacity based on temperature and pressure;
- cycle-life → cycle-life measurements are typically used to assess the effect of cycling on capacity, including activation effects, grain growth, structural deterioration, or chemical degradation due to gas impurities.

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