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Ph.D. Thesis (abstract)

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Ph.D. Thesis
(abstract)

Tritium storage by absorption in metals and alloys

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Key words: hydrogen isotopes, tritium, storage, isotherms

1. INTRODUCTION

Tritium (^3H sau T) is the only radioactive isotope of hydrogen, the other two isotopes protium (^1H) and deuterium (^2H or D) are stable, [1]. The nucleus of tritium contains one proton and two neutrons and atomic mass is 3.016049. It has a half-life of 12.26 years. In nature, tritium is founded in small amounts as result of cosmic radiation action on gas reactions in the stratosphere; the global quantity was estimated at 7.3 kilograms. Tritium is also produced in nuclear weapon test or in nuclear reactors, [1,2]

By desintegration tritium emits low energy radiation:



The maximum distance that β particle can cross the air is 4,5 – 6 mm, [3-5].

The presence of tritium in heavy water used in CANDU nuclear reactors is a major source of radiation for operations personnel and radioactive contamination of plants, [2,6,7]. To eliminate these negative effects it is investigating the possibility of extraction of tritium from tritiated heavy water.

At I.C.S.I. Ramnicu Valcea was realized an experimental pilot plant for separation of tritium from tritiated heavy water. The technology of tritium separation from heavy water will be applied at industrial scale at Cernavoda Nuclear Power Plant.

An important problem which appears is the storage of tritium, resulting at the end of the separation process, safely to the environment and personnel [3,6,7]. Materials used for storage has to have the ability to "bond" strong tritium, at normal temperature and pressure; the formed tritide must be easy to obtain and to allow, if necessary, recovery of tritium. In this regard, the following items are essential for tritium storage: choosing the most suitable material for the storage operation, the design and building of the storage device. Many of the experimental data required, can be obtained using stable isotopes of hydrogen (protium or deuterium) without using tritium, [5,9].

Metals and intermetallic compounds are advantageous as storage materials for hydrogen isotopes (as metal hydrides) considering the following reasons [15,16]:

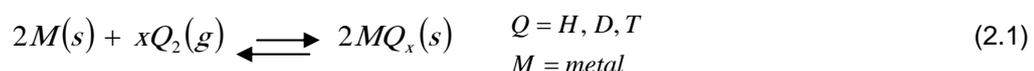
- High storage capacity;
- Gas is easily released by heating of hydride;
- Transport and handling of gas is safely.

Intermetallic compounds are defined as solid phase, consisting of two or more metallic elements, and optionally, one or more non-metallic elements, whose crystal structure differs from that of constituent elements.

Hydride forming reaction is exothermic and usually spontaneous at room temperature, especially when the metal is finely divided. Since the reaction is reversible, immobilized hydrogen can be recovered by heating of hydride at the temperature characteristic of each material, [11-15].

2. METAL-HYDROGEN INTERACTION

The reaction of formation of metal hydrides is, [11-15]:



Hydrides for tritium storing are those that are obtained by an exothermic process. By increasing the hydrogen pressure in contact with metal it will be formed metallic hydrides, the process being reversible, [13-15,17].

3. OBTAINING OF THE METALLIC HYDRIDES; FACTORS INFLUENCING THE PROCESS

3.1 Metal – hydrogen systems

Depending on the type of metal-hydrogen bond, metal hydrides are divided into three main categories, [27,28]:

- ionic hydrides;
- metallic hydrides;
- covalent hydrides.

4. THE EXPERIMENTAL STAND FOR HYDROGEN ISOTOPES SORPTION IN METALS AND INTERMETALLIC COMPOUNDS

4.1 Experimental stand

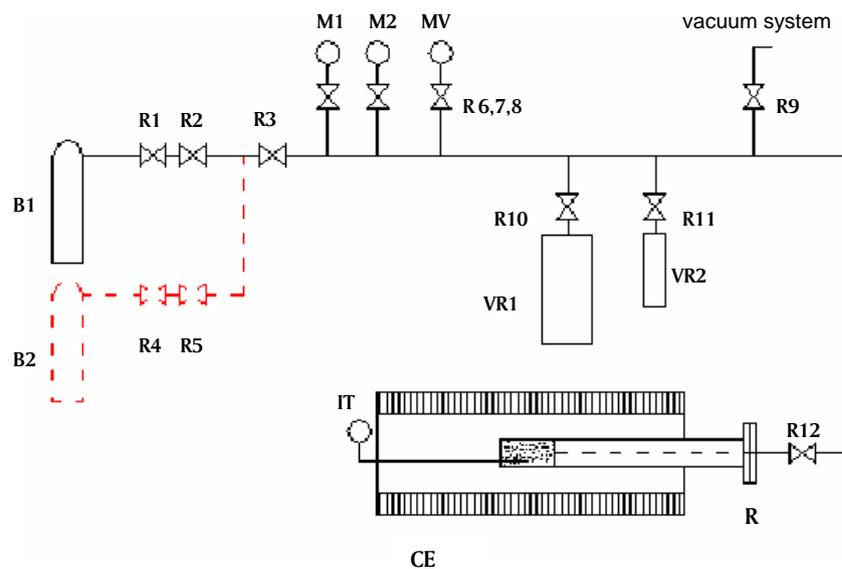


Fig. 4.1 Experimental stand for hydrogen isotopes sorption
R1- R12 - valves; B1 – hydrogen cylinder; B2 – isotopic mixture cylinder; M1, M2 -
manometers; MV- manovacuummeter; IT – temperature measurement;
CE – electric oven; VR1, VR2 – reference vessel
R - reactor

4.2 Experimental methods

Testing method has the following steps:

Sample activation. Activation was done by heating in vacuum (10^{-3} Torr) the metallic samples. The activation temperature is the range 200-700°C and remained constant during a certain time, depending on sample and experimental conditions.

Cooling the sample. The initiation temperature of the reaction depends of the sample but, generally, is ambient temperature (20 - 25°C). Reactor cooling, from the activation temperature to the initiation one, can be done by air jet blowing of the outside of the reactor, where the sample was inserted; the sample may be allowed to cool gradually over time.

Sorption. The procedure of obtaining hydrides depends on the type of the hydride, the desired composition and its final form, [8]. Dry hydrogen is introduced at the required pressure in the vessel with known volume and then over the sample, in the reactor.

Desorption. The process takes place in vacuum by heating at required temperature as a function of the metal hydride type.

5. EXPERIMENTAL STUDY ABOUT HYDROGEN ISOTOPES SORPTION IN METALLIC SAMPLES

To carry out experiments of hydrogen isotopes absorption it has been chosen materials that have highest storage capacity.

5.1 Protium and deuterium sorption in metallic materials

Preparation of metal surfaces by removing layers of impurities in order to obtain a clean metal surfaces is important because the metallic samples, exposed to air, are generally covered with a layer of compounds naturally formed on the surface. The activation produces evacuation of the adsorbed species or of dissolved oxygen from material and reconstruction of reactive surface, [55-56].

The factors that could influence the absorption and were experimentally investigated are: activation temperature of metal sample, time of activation, the initial pressure of hydrogen, etc, [93,96,99,100].

5.1.1 Reaction with hydrogen of powder and sponge titanium samples

The reaction between titanium and hydrogen is spontaneous at room temperature, [106]:



5.1.1.1 Determination of the storage properties for sponge titanium

The sponge titanium was in the form of granules of 2 – 12 mm diameter. The absorption gases were: hydrogen 99.999% purity and a mixture of deuterium (5%) in hydrogen.

5.1.1.1.1 Factors influencing reaction of the sponge titanium with hydrogen; experimental determination

One of the significant factors that can influence the reaction between of powder titanium and tritium is activation temperature.

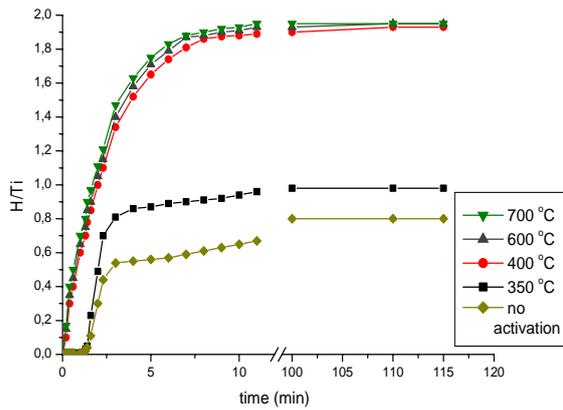


Fig. 5.2 Effect of the activation temperature on the reaction of sponge titanium with hydrogen

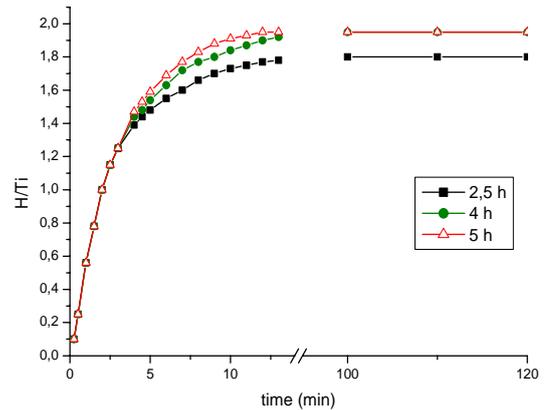


Fig. 5.3 The activation time on the reaction of sponge titanium with hydrogen

A temperature higher than 400°C is sufficient to remove the compounds formed on the surface of sponge titanium.

Another factor that can affect hydrogen absorption is time of the activation process. If the time of keeping the sample in vacuum at high temperature is too short it would lead to incomplete activation and the storage capacity of metallic material is diminished.

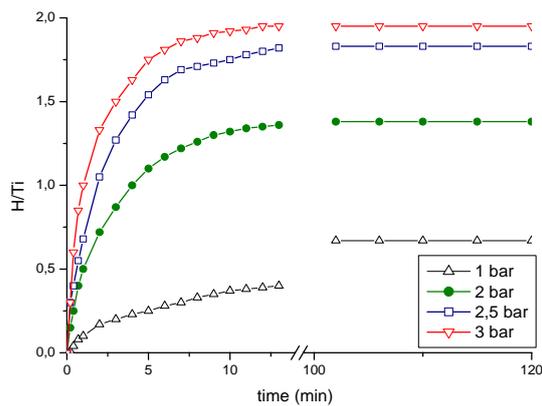


Fig. 5.4 Dependence of the hydrogen concentration in sponge titanium vs. the initial pressure of hydrogen

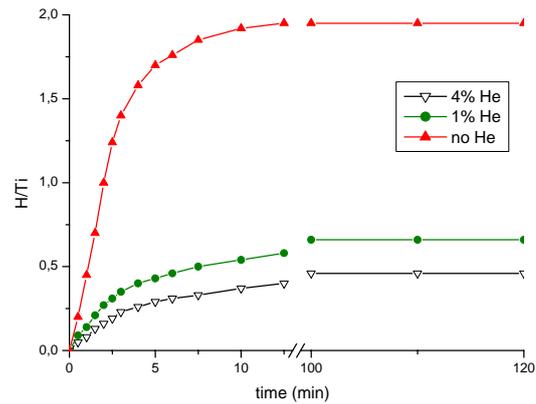


Fig. 5.5 Influence of the of helium content in the initial mixture of hydrogen in the hydriding reaction of sponge titanium

The dependence of the hydriding capacity of sponge titanium versus the initial pressure of hydrogen introduced into the reactor is shown in Figure 5.4. A higher initial pressure in the reactor increases the number of moles of hydrogen absorbed in metal in a certain time interval.

To simulate the presence of tritium, in absorption gas was introduced various amounts of helium. A higher concentration of helium has a negative influence on the sorption process.

The number of absorption/desorption cycles do not influence the storage capacity of sponge titanium and atomic ratio H/Ti of 1.95 ± 0.03 remained constant.

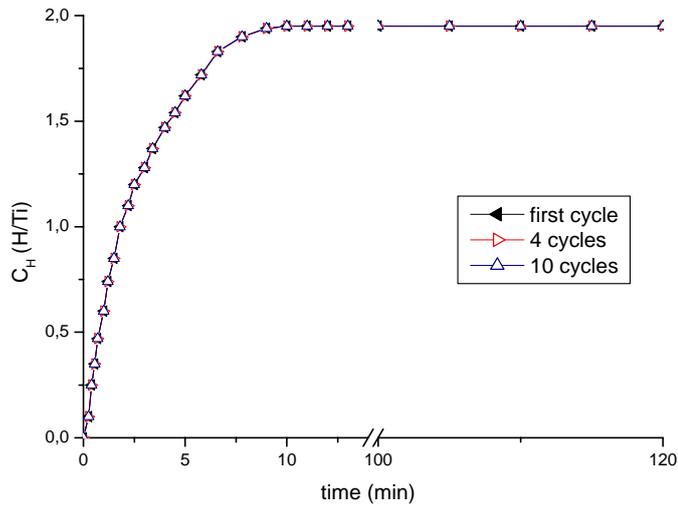


Fig. 5.6 Influence of absorption/desorption cycle on sponge titanium storage capacity.

5.1.1.2 Determination of the storage properties for powder titanium

Due to large storage capacity of titanium, both sponge and powder forms can be used to store tritium, [103].

5.1.1.2.1 Factors influencing reaction of the powder titanium with hydrogen; experimental determinations

Activation temperature. From figure 5.12 results that a temperature of at least 400°C is enough to obtain a high concentration of hydrogen in metal.

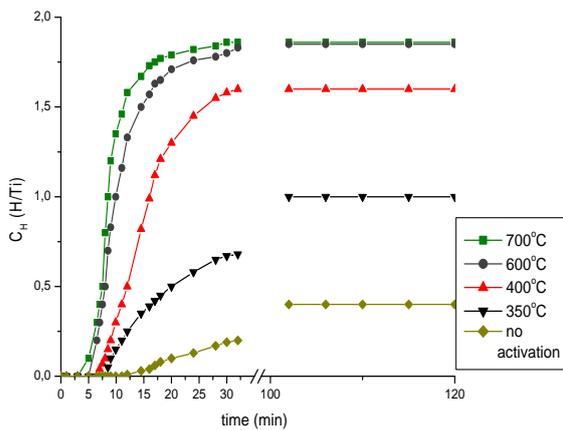


Fig. 5.12 Effect of activation temperature on the reaction of powder titanium with hydrogen

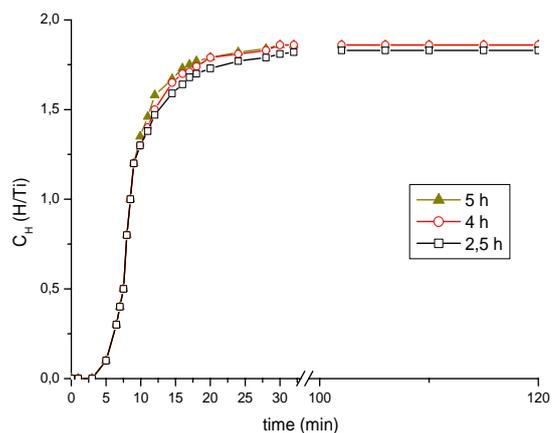


Fig. 5.13 Effect of the activation time on reaction of powder titanium with hydrogen

The influence of the activation time in the case of powder titanium sample is shown in Figure 5.13.

Figure 5.14 presents the evolution of H/Ti in time, depending on the pressure of hydrogen initially introduced into the reactor.

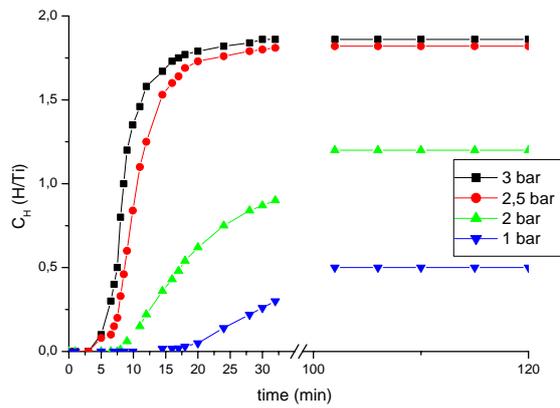


Fig. 5.14 Dependence of the hydrogen concentration in powder titanium vs. initial hydrogen pressure

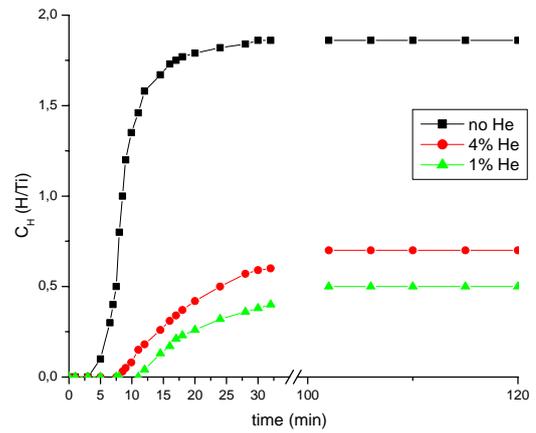


Fig. 5.15 Influence of the helium content on the hydriding reaction of powder titanium

Helium has a negative influence on final ratio H/Ti (powder), as is presented in Figure 5.15

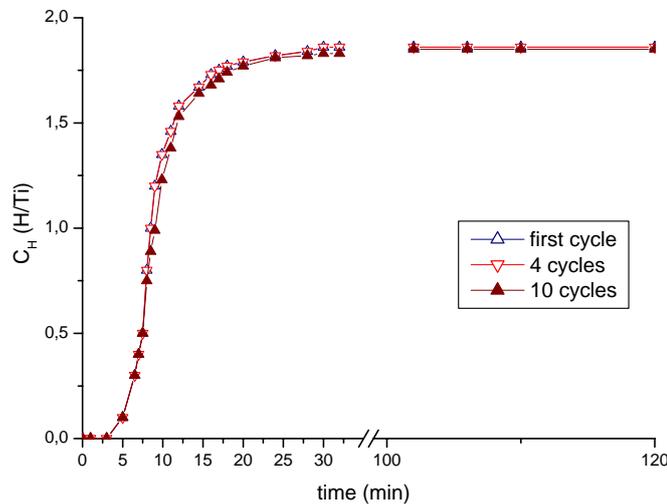


Fig. 5.16 Influence of absorption/desorption cycle on powder titanium storage capacity.

From Figure 5.16, presenting the influence of absorption/desorption cycles on storage capacity, is seen that powder titanium presents a slight decrease of storage capacity by comparison with sponge titanium.

5.1.2 Reaction of ZrCo intermetallic compound with hydrogen

The alloy ZrCo of 98.5% purity, used in our experiments, was provided by the National Research and Development Institute for Electrical Engineering ICPE-CA Bucharest.

If the metal surface is clean, the reaction between hydrogen and ZrCo is spontaneous at room temperature, [116]:



where Q = H,D,T

A disadvantage of intermetallic compound is due to the tendency of ZrCo to disproportionation, if it is used in the successive absorption/desorption cycles. The disproportionation reaction can take place thereby, [53,117]:



The zirconium hydride formed is more stable than the hydrides formed from intermetallic compound ZrCo, requiring high temperatures for a complete desorption of hydrogen, [80,117,118].

5.1.2.1 Factors influencing reaction of the ZrCo with hydrogen; experimental determinations

When using an activation temperature lower than 300°C, retained hydrogen concentration in the form of metal hydrides is very low.

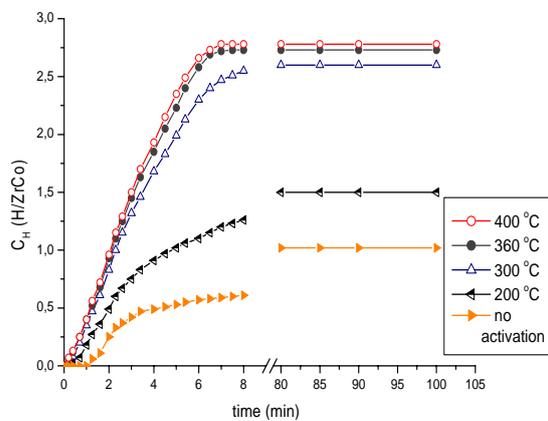


Fig. 5.21 Effect of activation temperature on the hydriding reaction of ZrCo

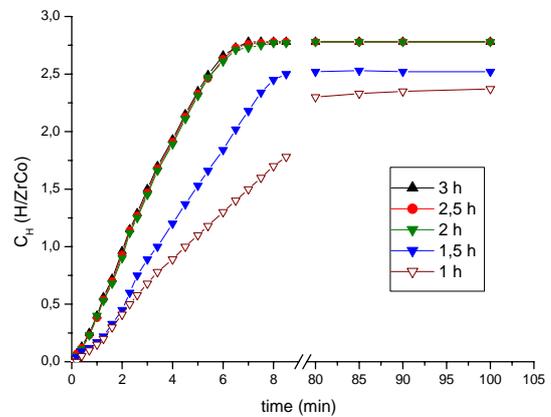


Fig. 5.22 Effect of the activation time on the hydriding reaction of ZrCo

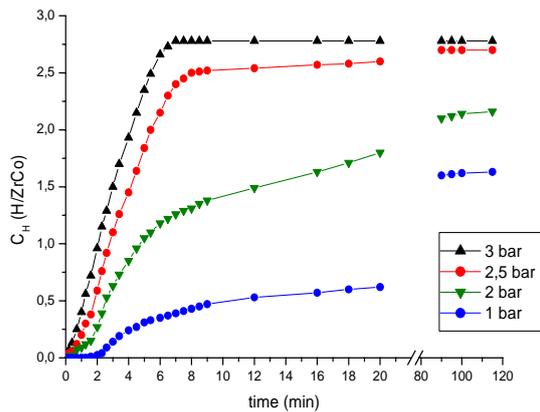


Fig. 5.23 Dependence of the hydrogen concentration in ZrCo vs. initial hydrogen pressure

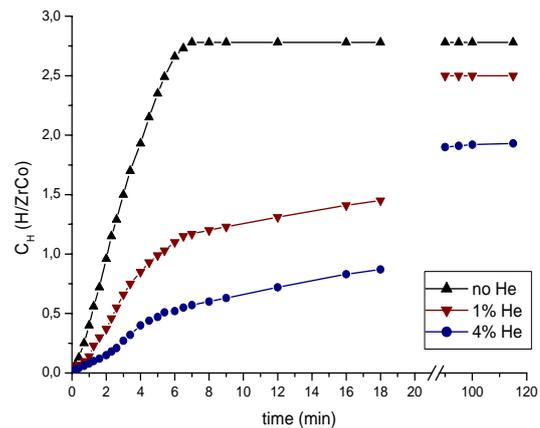


Fig. 5.24 Influence of the helium content on the hydriding reaction of ZrCo

From experimental determination of the influence that activation time has on hydriding reaction, is observed that the activation at 400°C for at least 2 hours is enough to achieve maximum storage capacity of the intermetallic compound ZrCo. After this time the impurities from the metal surface were removed.

Figure 5.23 shows the effect of the initial hydrogen pressure on storage capacity of intermetallic compound ZrCo. It is seen that a low pressure leads to a low atomic ratio H/ZrCo.

In Figure 5.24 is seen that a low concentration of helium in the gas affects the storage capacity of intermetallic compound. Helium forms an envelope on the metal surface braking the hydrogen absorption in ZrCo.

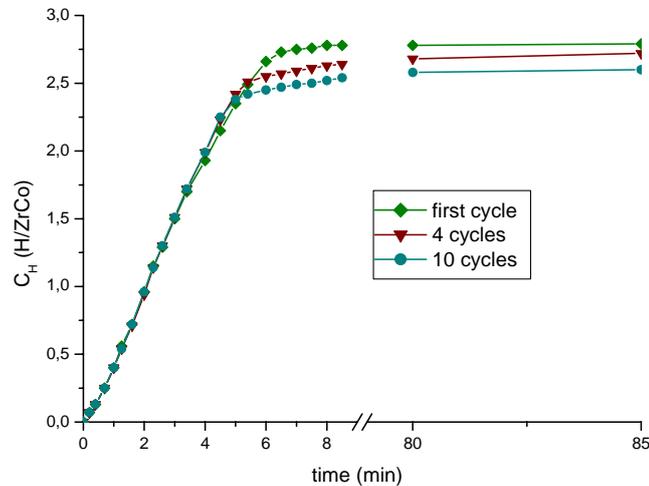


Fig. 5.25 Influence of absorption/desorption cycle on ZrCo storage capacity

Influence of number of absorption/desorption cycles on hydriding process is shown in Figure 5.25. After several cycles of absorption/desorption, the amount of retained in metal hydrogen decreases.

5.1.3 Reaction of ZrNi intermetallic compound with hydrogen

In experiments we used the intermetallic compound ZrNi prepared at INCDIE ICPE-CA Bucharest. The reaction between the intermetallic compound and hydrogen takes place according to the equation, [119]:



where Q = H,D,T

Hydrogen storage on ZrNi is of interest because the reaction is spontaneous at ambient temperature and does not require high temperatures to recover hydrogen, [121].

At high temperatures, intermetallic compound ZrNi disproportionates.

Intermetallic compounds used in the experiments were prepared in two compositions, 50% Zr; 50% Ni (Zr₅₀Ni₅₀) and Zr 70%; Ni 30% (Zr₇₀Ni₃₀), (mass %).

5.1.3.1 Factors influencing reaction of the Zr₅₀Ni₅₀ with hydrogen; experimental determinations

To determine the influence of activation temperature on the reaction of hydrogen, the intermetallic compound was activated in vacuum at temperatures of 200 - 400°C, figure 5.30. From the experiments results that a lower activation temperature, or the use of the sample without activation by

heat treatment, leads to much lower concentrations of hydrogen in intermetallic compound by comparison with stoichiometric ratio of $H/ZrCo = 3$.

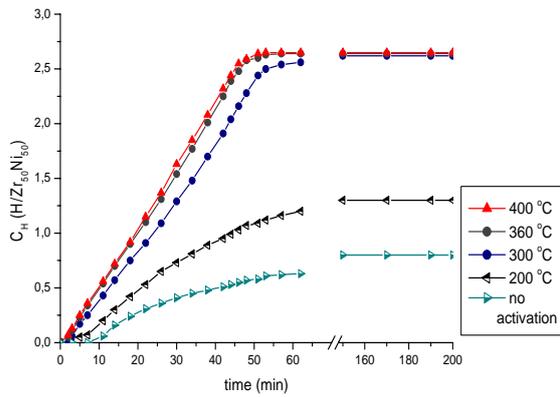


Fig. 5.31 Effect of activation temperature on the hydriding reaction of $Zr_{50}Ni_{50}$

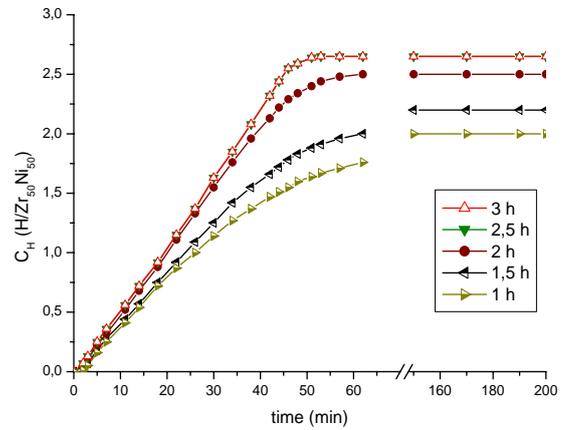


Fig. 5.32 Effect of the activation time on hydriding reaction of $Zr_{50}Ni_{50}$

Influence of activation time on the reaction between hydrogen and $Zr_{50}Ni_{50}$ compound is shown in figure 5.32. Heating the alloy for at least 2.5 hours at high temperature is enough to obtain a concentration of $2,65 \pm 0,03 H/Zr_{50}Ni_{50}$.

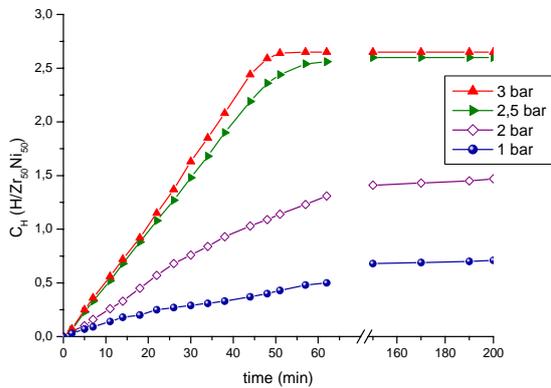


Fig. 5.33 Dependence of the hydrogen concentration in $Zr_{50}Ni_{50}$ vs. initial hydrogen pressure

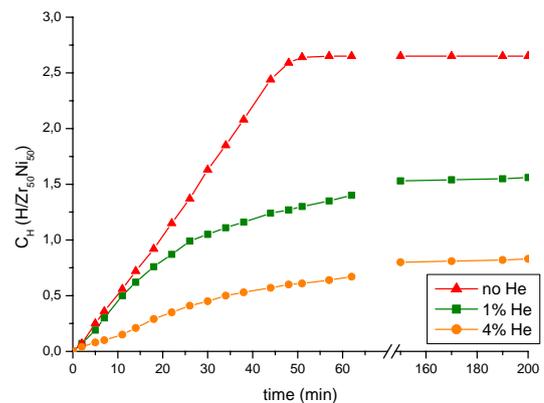


Fig. 5.34 Influence of the helium content on the hydriding reaction of $Zr_{50}Ni_{50}$

Influence of initial hydrogen pressure on the concentration of hydrogen stored in $Zr_{50}Ni_{50}$ is shown in figure 5.33. When initial pressure is greater, the concentration of hydrogen in intermetallic compound is higher in a certain period of time.

The helium from sorption gas has a negative effect on the hydrogen absorption in intermetallic compound. Figure 5.34 presents the effect of the helium concentration on sorption reaction.

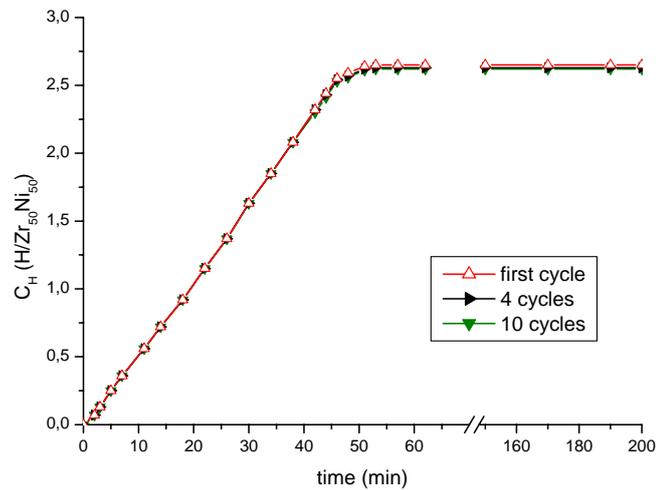


Fig. 5.35 Influence of absorption/desorption cycle on $Zr_{50}Ni_{50}$ storage capacity

Number of cycles of absorption/desorption does not affect the storage capacity; after 10 cycles the absorption capacity is constant and maximum ratio $H/Zr_{50}Ni_{50}$ of $2,65 \pm 0,03$ is maintained.

5.1.3.3 Factors influencing reaction of the $Zr_{70}Ni_{30}$ with hydrogen; experimental determinations

The activation temperature has an important influence on the hydrogen absorption, as shown in figure 5.39.

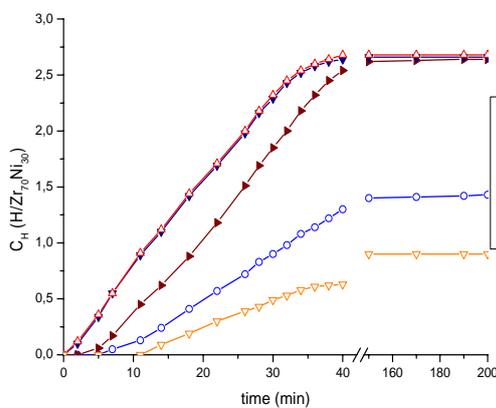


Fig. 5.39 Effect of activation temperature on the hydriding reaction of $Zr_{70}Ni_{30}$

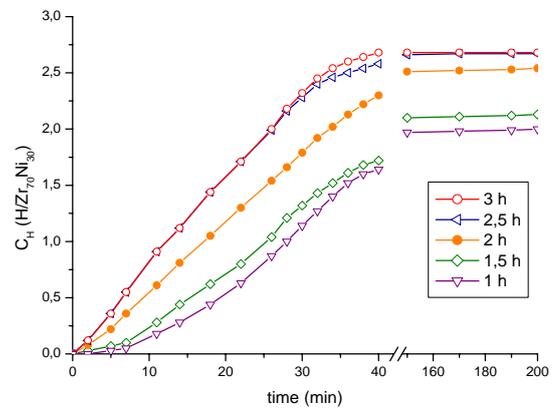


Fig. 5.40 Effect of the activation time on hydriding reaction of $Zr_{70}Ni_{30}$

Activation time is other important factor that has influence on the hydriding process of intermetallic compound $Zr_{70}Ni_{30}$. If the metal sample was activated for at least 2.5 hours, hydrogen concentration is $2,68 \pm 0,03 H/Zr_{70}Ni_{30}$.

To determine the influence of initial pressure on the concentration of hydrogen stored in $Zr_{70}Ni_{30}$, the pressure was in the range of 1-3 bar, figure 5.41. In order to obtain high concentrations of hydrogen in metal powders in a short time, hydrogen pressure must be high enough.

Figure 5.42 presents the effect of helium on sorption reaction: a high concentration of helium in gas produces a decrease of hydrogen retained in $Zr_{70}Ni_{30}$.

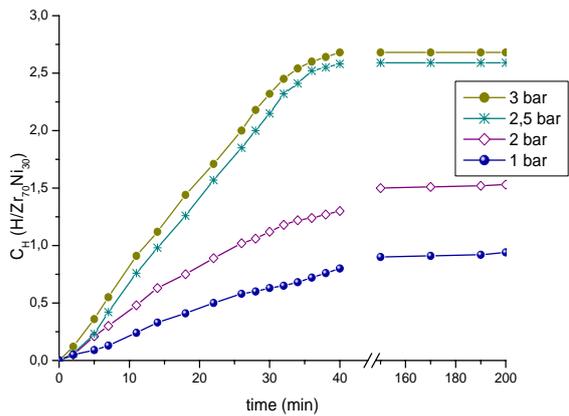


Fig. 5.41 Dependence of the hydrogen concentration in $Zr_{70}Ni_{30}$ vs. initial hydrogen pressure

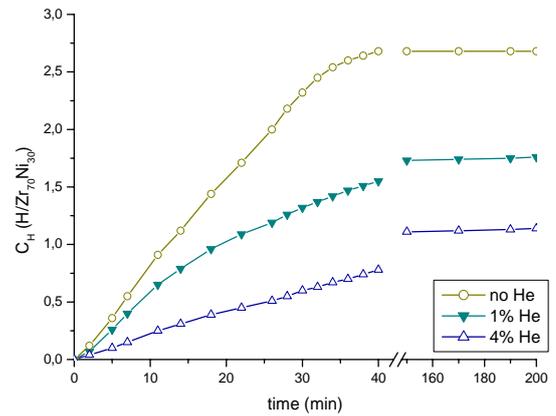


Fig. 5.42 Influence of the helium content on the hydriding reaction of $Zr_{70}Ni_{30}$

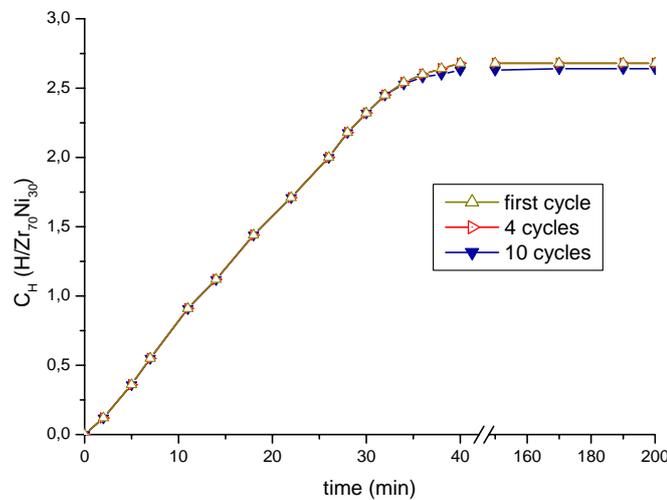


Fig. 5.43 Influence of absorption/desorption cycle in $Zr_{70}Ni_{30}$ storage capacity

Storage capacity of intermetallic compound could be influenced by the number of cycles of absorption/desorption, due to disproportionation. After 10 cycles, the absorption capacity does not decrease significantly

6. TRITIUM STORAGE IN METALLIC MATERIALS

The experiments were performed at the National Institute of Research - Development for Cryogenics and Isotopic Technologies Rm Valcea ICSI, using a mixture of hydrogen-tritium. Properties of metal samples before and after the absorption of hydrogen-tritium mixture were investigated by X ray diffraction.

6.1 Reaction between titanium and hydrogen-tritium mixture

Analyzing the data obtained on hydrogen storage, both on powder and sponge titanium, it was determined that the sponge titanium absorbs a larger amount of gas. An atomic reports H/Ti close to 2, according to reaction stoichiometry, was obtained.

6.1.1 Sorption of the hydrogen-tritium mixture in sponge titanium

Activation of sponge titanium was performed in vacuum at a temperature of 600°C for 5 hours. The sample was cooled to a temperature of 25 °C and then was tested for absorption.

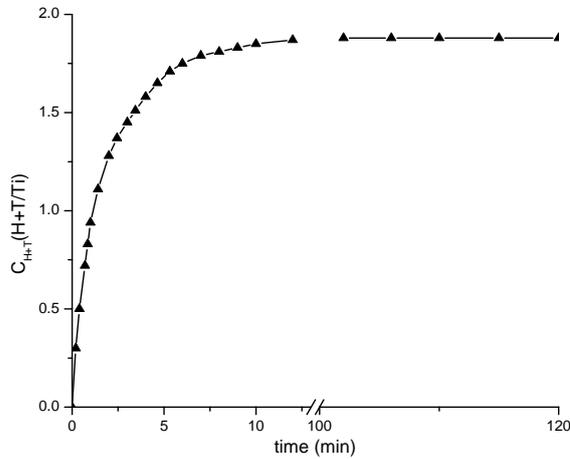


Fig. 6.2 Atomic ratio (H+T)/Ti in time in sorption of hydrogen-tritium mixture in sponge titanium

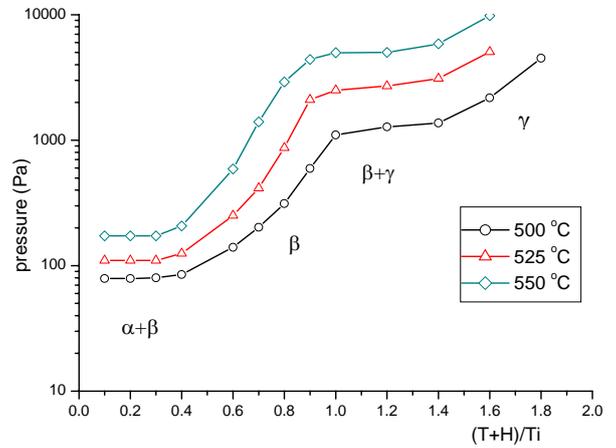


Fig. 6.5 Pressure-composition isotherms in hydrogen-tritium mixture sorption in sponge titanium

The evolution of hydrogen concentration in the metal mass, expressed as atomic ratio (H+T)/Ti, during absorption in the sponge titanium is shown in Figure 6.2. Sponge metal is Ti- α 100%, with a compact hexagonal crystalline structure. After sorption of the mixture hydrogen-tritium, it was formed titanium hydride with cubic volume centered crystalline structure.

The plot of the logarithm of pressure versus 1/T presents two lines, corresponding to two horizontal levels of pressure-composition isotherms, figure 6.6.

Table 6.1 Thermodynamic parameters for the sorption of hydrogen-tritium mixture in sponge titanium

	ΔH° (kJ/ mol)		ΔS° (J/molxK)		Phases in equilibrium
	Own data	[127]	Own data	[127]	
First plateau	- 97,7	-101,5	- 161,5	-165,3	$\alpha+\beta$
Second pleteau	- 173,6	-179,6	- 281,6	- 290,3	$\beta+\gamma$

The parameter values, obtained from our experimental data, are in good agreement with the literature data, [127].

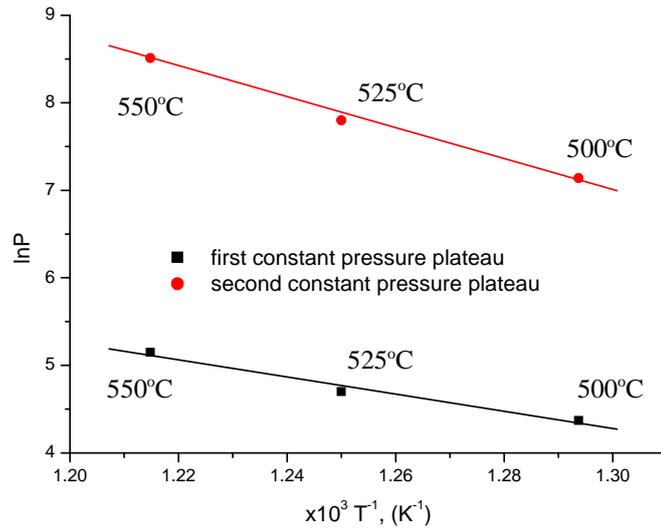


Fig. 6.6 Van't Hoff plot for hydrogen-tritium mixture sorption in sponge titanium

6.1.2 Sorption of the hydrogen-tritium mixture in powder titanium

The determinations of absorption by hydrogen-tritium mixture were done in the same conditions as in the case of sponge titanium, the samples were activated prior to absorption by high temperature vacuum for 5 hours.

In Figure 6.8 is presented the evolution of atomic ratio (H + T)/Ti powder in time, during the absorption of hydrogen-tritium mixture. The value obtained is $1,82 \pm 0,02$; being in good agreement with literature data for hydrogen sorption on powder titanium, [72]. X ray diffraction spectrum of powder titanium indicates a hexagonal crystal type phase.

In figure 6.11 are shown pressure-composition isotherms and two horizontal levels which are characteristic of the two forms of crystallization of titanium hydride.

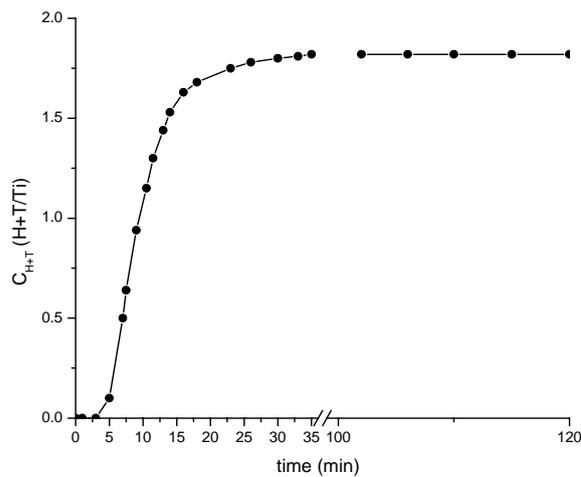


Fig. 6.8 Atomic ratio (H+T)/Ti in time at sorption of hydrogen-tritium mixture in powder titanium

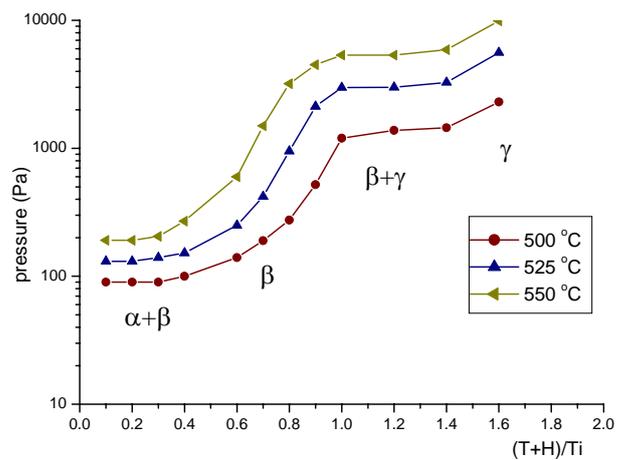


Fig. 6.11 Pressure-composition isotherms at hydrogen-tritium mixture sorption in powder titanium

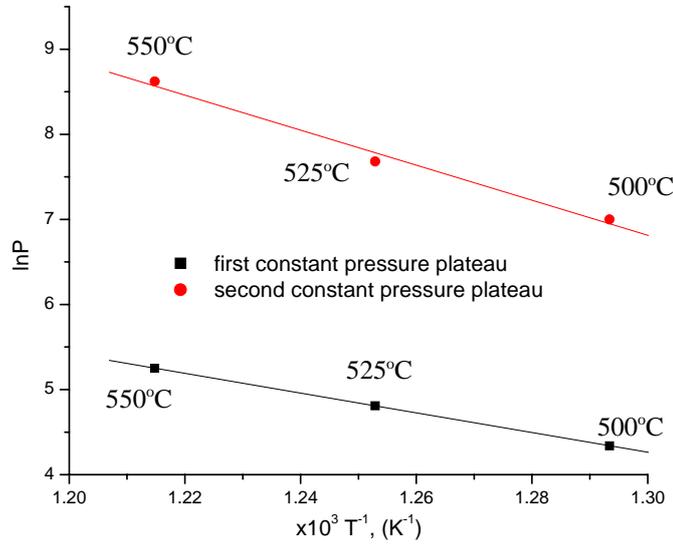


Fig. 6.12 Van't Hoff plot for hydrogen-tritium mixture sorption in powder titanium

Standard reaction enthalpy and standard entropy of reaction values, calculated from the van't Hoff equation, are given in Table 6.2.

Table 6.2 Thermodynamic parameters for the sorption of hydrogen-tritium mixture in sponge titanium

	ΔH° (kJ/ mol)		ΔS° (J/molxK)		Phases in equilibrium
	Own data	[72]	Own data	-	
First plateau	- 96,3	- 99,75	- 160,6	-	$\alpha+\beta$
Second plateau	- 171,1	-	- 279,2	-	$\beta+\gamma$

6.2. Sorption of the hydrogen-tritium mixture in ZrCo

The samples were heated at 400°C in vacuum, for activation. Figure 6.14 shown the evolution of atomic ratio (H + T)/ZrCo in time, during the sorption reaction of hydrogen-tritium mixture with ZrCo. The maximum concentration obtained, expressed as atomic ratio, is $2,71 \pm 0,02$, [120] .

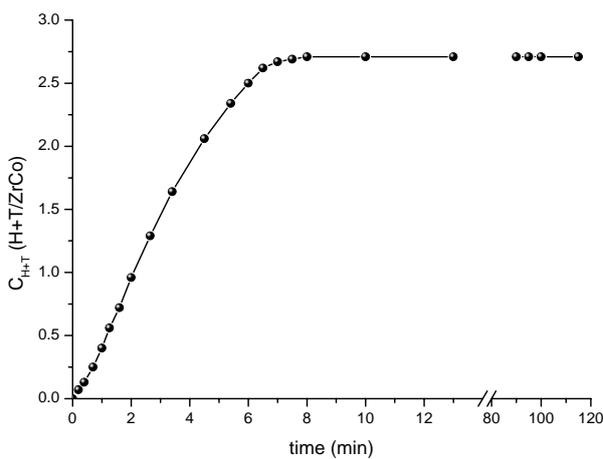


Fig.6.14 Atomic ratio (H+T)/Ti in time at sorption of hydrogen-tritium mixture in ZrCo

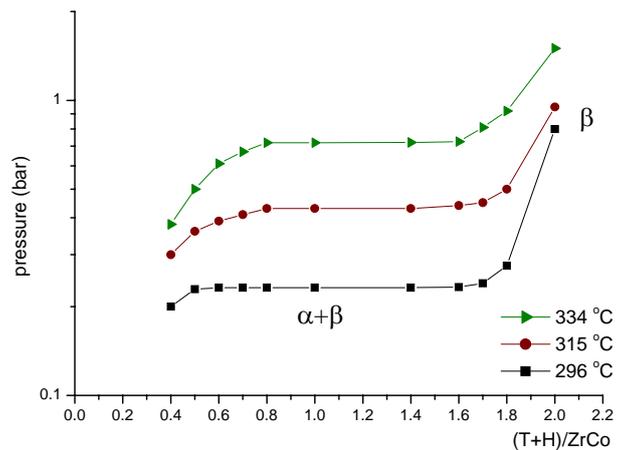


Fig. 6.17 Pressure-composition isotherms at hydrogen-tritium mixture sorption in ZrCo

Figure 6.17 presents the pressure-composition isotherms where it is observed the constant pressure horizontal plateau. The plot of the logarithm of pressure versus $1/T$ is presented in figure 6.18, [120].

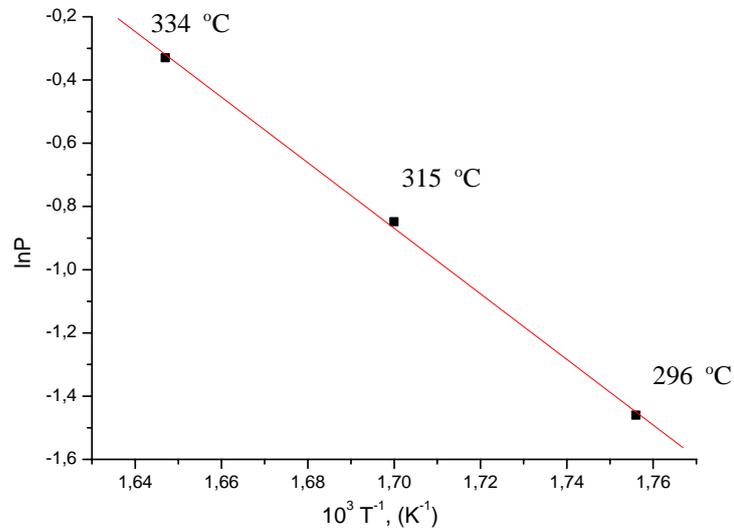


Fig. 6.18 Van't Hoff graph for hydrogen-tritium mixture sorption in ZrCo

The thermodynamic properties characteristic for $\alpha \rightleftharpoons \beta$ equilibrium obtained from van't Hoff plot, are presented in Table 6.3; the data are in good agreement with the literature, where the hydride with atomic ratio H/ZrCo of 1.2, [68,69] is presented.

Table 6.3 Thermodynamic parameters for the sorption of hydrogen-tritium mixture in ZrCo

ΔH° (kJ/ mol)		ΔS° (J/molxK)		Phases in equilibrium
Own data	[53]	Own data	[53]	
- 86,2	- 87,5	- 139,3	- 146,4	$\alpha+\beta$

6.3 Reaction between ZrNi and hydrogen-tritium mixture

6.3.1 Sorption of the hydrogen-tritium mixture in $Zr_{50}Ni_{50}$

Figure 6.20 presents the variation of concentration $(H+T)/Zr_{50}Ni_{50}$ in time at the absorption of hydrogen-tritium mixture in ZrNi. At the end of reaction, the maximum concentration was $2,61 \pm 0,03$ $(H+T)/Zr_{50}Ni_{50}$, [120].

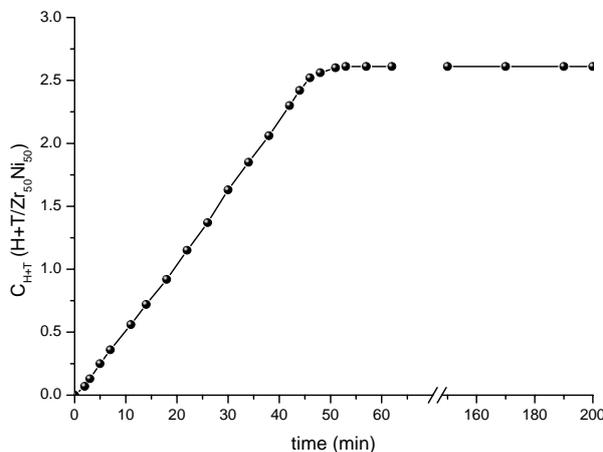


Fig.6.20 Atomic ratio $(H+T)/Ti$ in time at sorption of hydrogen-tritium mixture in $Zr_{50}Ni_{50}$

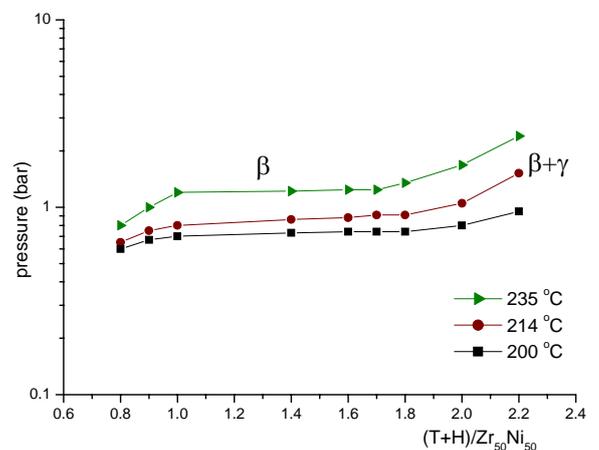


Fig. 6.23 Pressure-composition isotherms at hydrogen-tritium mixture sorption in $Zr_{50}Ni_{50}$

Figure 6.23 presents the pressure-composition isotherms, with pressure plateau formed at sorption of hydrogen-tritium mixture in $Zr_{50}Ni_{50}$.

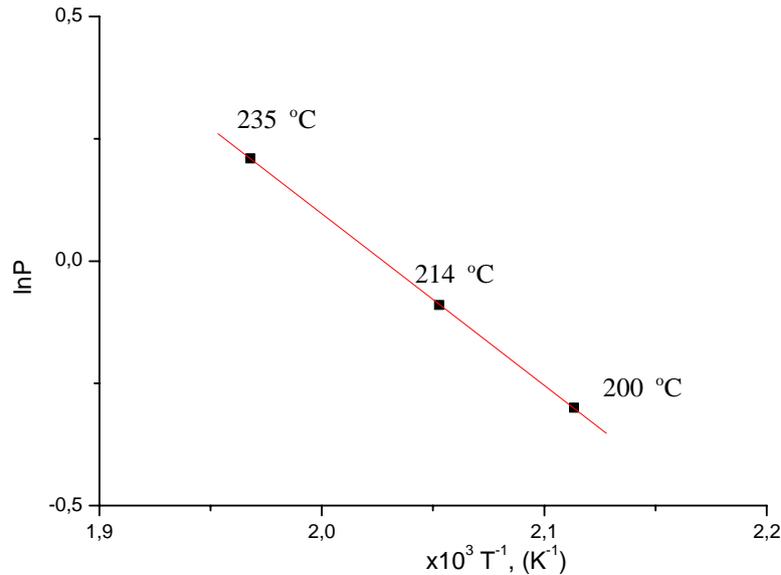


Fig. 6.24 Van't Hoff plot for hydrogen-tritium mixture sorption in $Zr_{50}Ni_{50}$

From the plot of the logarithm of pressure vs. $1/T$ (Figure 6.24) was calculated the entropy and the enthalpy corresponding to absorption of hydrogen-tritium mixture in $Zr_{50}Ni_{50}$, [120,128].

Table 6.4 Thermodynamic parameters for the sorption of hydrogen-tritium mixture in $Zr_{50}Ni_{50}$

ΔH° (kJ/ mol)		ΔS° (J/molxK)		Phases in equilibrium
Own data	[119]	Own data	-	
- 35,06	- 34,3	- 71,4	-	$\beta+\gamma$

6.3.2 Sorption of the hydrogen-tritium mixture in $Zr_{70}Ni_{30}$

For the experiments we used hydrogen-tritium mixture, metal samples were activated for 3 hours by heating at $400^{\circ}C$. After activation, the samples were cooled to ambient temperature, [128].

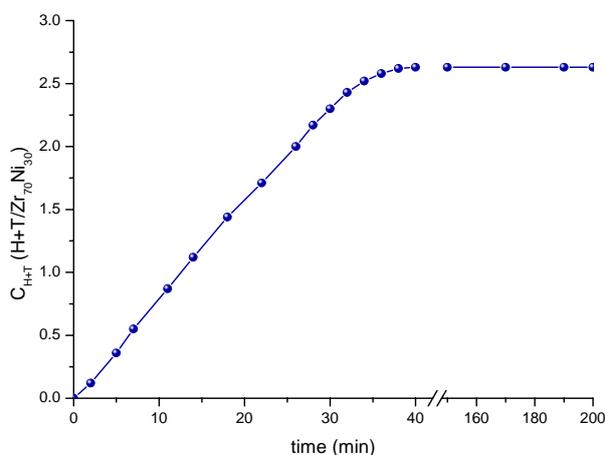


Fig.6.26 Atomic ratio (H+T)/Ti in time at sorption of hydrogen-tritium mixture in $Zr_{70}Ni_{30}$

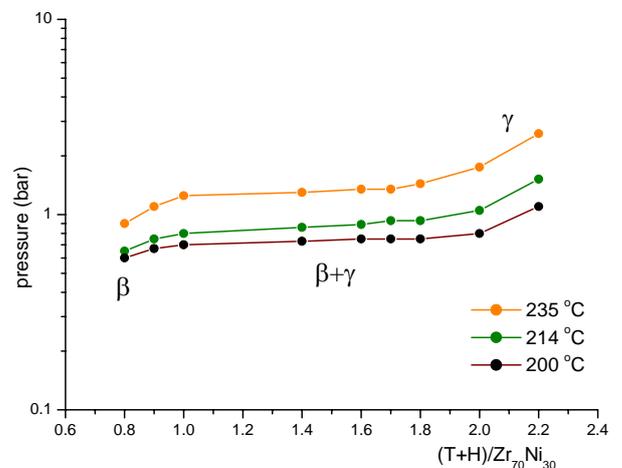


Fig. 6.29 Pressure-composition isotherms at hydrogen-tritium mixture sorption in $Zr_{70}Ni_{30}$

During the sorption reaction of hydrogen-tritium mixture and $Zr_{70}Ni_{30}$ intermetallic compound, maximum ratio obtained in the powder metal is $2,63 \pm 0,03 (H+T)/Zr_{70}Ni_{30}$. Figure 6.26 presents the variation of concentration of hydrogen-tritium at sorption process in $Zr_{70}Ni_{30}$, [128].

The plot of the logarithm of pressure vs. $1/T$ is presented in figure 6.30. Calculated thermodynamic parameters are presented in table 6.5 [69].

As in the case of $Zr_{50}Ni_{50}$, thermodynamic parameters show that hydrogen-tritium mixture can be stored in $Zr_{70}Ni_{30}$, the temperature required for desorption process is lower than for ZrCo or Ti tritides.

Table 6.4 Thermodynamic parameters for the sorption of hydrogen-tritium mixture in $Zr_{70}Ni_{30}$

ΔH° (kJ/ mol)		ΔS° (J/molxK)		Phases in equilibrium
Own data	[122]	Own data	-	
- 42,03	- 39	- 85,67	-	$\beta+\gamma$

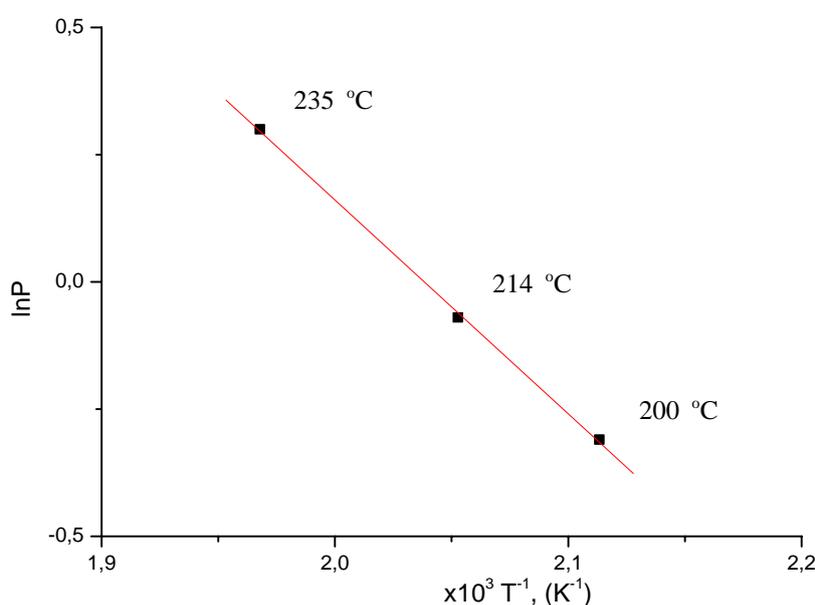


Fig. 6.30 Van't Hoff plot for hydrogen-tritium mixture sorption in $Zr_{70}Ni_{30}$

7. CONCLUSIONS

The thesis presents experimental results regarding the reaction between metal and intermetallic compounds with hydrogen isotopes performed on an experimental stand, [90].

Materials used in this work are: titanium sponge (Sigma-Aldrich) and powder (Merck) and intermetallic compounds: ZrCo, ZrNi ($Zr_{70}Ni_{30}$, $Zr_{50}Ni_{50}$) provided by the National Research and Development Institute for Electrical Engineering ICPE-CA Bucharest. In experimental determinations it was also used hydrogen (Messer) and a mixture of deuterium (5%) in hydrogen (Linde).

- ❖ If the samples are activated using an insufficient temperature, formed hydride will have a small concentration of hydrogen. If compounds are usually adsorbed on metallic surface will not be cleared, they will not allow the dissociation of hydrogen molecule and starting of the absorption process. Activation temperatures determined experimentally and used to obtain high concentrations of hydrogen in metal are: $600^\circ C$ for titanium powder and sponge and $400^\circ C$ for ZrCo intermetallic compounds, $Zr_{70}Ni_{30}$, and $Zr_{50}Ni_{50}$, [108].

- ❖ The time required for activation process is different, depending on the material used for absorption. If the samples not are sufficiently time heated, the impurities from the surface will not allow the absorption of hydrogen in metallic samples. Powder and sponge titanium must be heated in vacuum for 5 hours to obtain maximum concentration of hydrogen in metal, [108,109]. In case of ZrCo, Zr₇₀Ni₃₀, and Zr₅₀Ni₅₀, it is enough to heat the samples for 3 hours to obtain high hydrogen concentration.
- ❖ The hydrogen pressure in the reactor was between 1 and 3 bar, for all metallic materials, [108].
- ❖ Helium content of gas has a negative effect on the reaction between metal and hydrogen. A concentration higher than 1% helium in hydrogen, decreases ratios obtained as follows: in case of sponge titanium atomic ratio is 0.66 ± 0.03 in comparison with maximum ratio obtained: 1.95 ± 0.03 ; for titanium powder: 0.5 ± 0.02 in comparison with: 1.86 ± 0.02 ; for ZrCo: 1.93 ± 0.02 in comparison with: 2.78 ± 0.02 ; for Zr₅₀Ni₅₀: 0.83 ± 0.03 compared to 2.65 ± 0.03 , and if Zr₇₀Ni₃₀ was obtained 1.76 ± 0.03 compared to 2.68 ± 0.03 . Also, the absorption rate decreases due to formation of helium envelope on metallic surface, which brakes access of hydrogen to metallic network, [108].
- ❖ Number of absorption/desorption cycles determines the diminution of the hydrogen absorption in titanium powder because of powder agglomeration. In the case of ZrCo, repeated cycles lead to decrease of hydrogen concentration because of disproportionation of ZrCoH₃, forming ZrH₂. Hydrogen retained as ZrH₂ can be released only at high temperatures. Titanium sponge and ZrNi maintain the storage capacity even after 10 absorption/desorption cycles.

Titanium powder, in presence of hydrogen, starts reaction after 3 minutes from the contact of the solid with the gas. Reaction is finished after 35 minutes. The alloys Zr₅₀Ni₅₀ and Zr₇₀Ni₃₀ react completely with hydrogen after 42 and 50 minutes, respectively. All materials presented suitable properties for hydrogen storage if samples are adequate activated. In the case of hydrogen-tritium mixture absorption in the same materials the conclusions are:

- ❖ Titanium powder and sponge react in the same way with hydrogen-tritium mixture at room temperature. The concentrations of hydrogen-tritium mixture in metal, expressed as atomic ratios, are: 1.88 ± 0.03 for sponge titanium, and 1.82 ± 0.02 for powder titanium, the values of the atomic ratios are near to stoichiometric values. Negative values of enthalpy demonstrate the exothermic characteristic of the process. At temperatures used for obtaining the isotherms, the values of pressure are small. Results that, at room temperature, the equilibrium pressures are much lower and titanium tritides are thermodynamically stable. For desorption process it is necessary a large amount of heat, to recover the stored gas.
- ❖ Maximum concentration obtained in the reaction between ZrCo and hydrogen-tritium mixture was 2.71 ± 0.02 (H+T)/ZrCo. From the van't Hoff plot was determined the enthalpy of reaction, - 86.2 kJ/mol, [120].
- ❖ Zr₅₀Ni₅₀ reacts spontaneously with hydrogen-tritium mixture, the maximum concentration in the metal is 2.61 ± 0.03 (H+T)/Zr₅₀Ni₅₀ and the enthalpy of reaction is -35.06 kJ/mol, [120].
- ❖ In case of reaction between hydrogen-tritium mixture and Zr₇₀Ni₃₀, maximum atomic ratio obtained after 42 minutes of reaction is 2.63 ± 0.03 (H+T)/Zr₇₀Ni₃₀. Enthalpy of reaction of -42.03 kJ/mol, is lower than in case of Zr₅₀Ni₅₀.

All materials utilized in this work are suitable for hydrogen-tritium mixture storage. If it is not necessary to recover stored tritium, titanium sponge is recommended. In case of titanium hydride, the equilibrium pressure is low at ambient temperature and for desorption is necessary a high temperature.

For a temporary storage of tritium, ZrCo can be used. An inconvenience of this material is that forming zirconium hydride with the increasing number of absorption/desorption cycles. Zirconium hydride needs high temperature for tritium desorption. In addition, ZrNi ($Zr_{50}Ni_{50}$, $Zr_{70}Ni_{30}$) presents properties for storage in order to recover tritium, because it is not necessary a high temperature for desorption. Due to high equilibrium pressure at ambient temperature, it is possible to produce gas leakage, which is dangerous for operating personnel and environment.

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