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PhD THESIS

Contributions to the study of hydrogen interactions with uranium compounds for nuclear energy

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UNIVERSITY POLITEHNICA OF BUCHAREST
Materials Science and Engineering Faculty
Doctoral School of Materials Science and Engineering

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Summary of the thesis

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CONTENT

(pagination is the one in the thesis)

Keywords: hydrogen storage, metal hydrides, intermetallic compounds, hydriding kinetics, reaction mechanism, hydrogen diffusion, activation energy, reaction rate.

Note The summary of the thesis retains the numbering of chapters and paragraphs, as well as of figures, tables and bibliographical indications.

INTRODUCTION

Energy and environment are two of the major concerns of our modern society. Today, more than 85% [1] of the energy needed worldwide is covered by fossil fuels. The production, processing and transportation of fossil fuels [2] had a considerable impact on the environment. Thus, humanity currently [3] faces two major problems: the depletion of hydrocarbon resources, exacerbated by the continuous demand for energy and the dusky prospects of global climate change caused by the huge quantities of carbon dioxide (CO2) emissions emerged by burning fossil fuels [4].

Currently, there are several options for future energy [6-8]: nuclear fission, tidal, wind, water, solar and nuclear fusion. Nuclear fusion has many advantages particularly important in the context of global warming. However the most important aspect remains the efficiency of the fusion nuclear reactions, which is superior to all other types of reaction implemented so far by human civilization [8].

The hydrogen is a common element of all future energy options [10-12]. Called "the main energy carrier of the future", the hydrogen is involved more or less in all these new technologies and the use of hydrogen as an energy source [12] has the advantage of eliminating harmful emissions and as a result, the use of hydrogen as energy carrier could solve, in principle, the problem of global greenhouse effect [11].

While there is a vision on the hydrogen economy [17], the development of a way for production, storage and use of hydrogen is not a simple task to be solved. Solving it covers large areas and the side effects that hydrogen economy might have on society for long-term are still unpredictable today. We can say that the first steps towards a future economy of hydrogen were performed, but research and development activity is just in the starting point.

Storing hydrogen is a key element in ensuring an economy based on hydrogen. Research on hydrogen storage are focused now on the technologies needed to improve the volume, weight and cost of the storage systems and to develop new technologies. In addition to the traditional storage systems (storage in liquid and gaseous state), there is currently a great interest for other types of storage, such as using solid materials [14-17].

The doctoral thesis „*Contributions to the study of hydrogen interactions with uranium compounds for nuclear energy*" had as objective to conduct studies and experimental research on obtaining new materials for hydrogen storage. Of the many compounds that may act as a storage material, depleted uranium metal alloys (materials with remarkable properties in storing hydrogen isotopes) were used in the experimental studies. Depleted uranium metal, widely studied as a storage material for tritium resulted from detritiation of heavy water from CANDU reactors is characterized by excellent absorption / desorption properties. However, the uranium hydride (UH_3) is in powder form and is pyrophoric and radioactive. With these limitations, it has been shown that the properties of storing hydrogen in depleted uranium can be improved by alloying it with other elements and the alloys based on metalic depleted uranium have the ability to eliminate, totally or partially, the difficulties raised by using uranium as storage material.

The thesis comprises two parts and is organized into six chapters that present the research activity performed and the results, an introductory section and a section of conclusions.

Part I of the thesis contains Chapters 1 and 2. These chapters present a summary of the significant studies published in the literature on the fundamentals of storing hydrogen isotopes and in particular, on the metal hydride storage, presenting the current state of research in obtaining hydrides of the intermetallic compounds of depleted metalic uranium, as well as the objectives of the thesis.

Part II of the theis contains Chapters 3, 4, 5 and 6. They consist of original contributions that are found in thesis and resulted from the experimental research related to the application of original methods for synthesis of depleted metalic uranium alloys, followed by characterization of the materials obtained and the study of their interaction with hydrogen. Through theoretical documentation presented in the first two chapters, this part of the thesis presents the materials, equipment and analytical techniques used in the experimental research performed. The description of the experimental program and the presentation of experimental results are organized into chapters as follows:

Chapter III - EXPERIMENTAL AND MATERIALS TECHNIQUES presents the experimental program established to achieve the objectives of the thesis. At this stage, the research plan was based on the testing of materials with remarkable properties in absorbing hydrogen. Also in this section there are presented, in the light of the theoretical documentation in the first two chapters, the materials, equipment and analytical techniques used in the experimental research performed.

Chapter IV - EXPERIMENTAL RESEARCH ON OBTAINING, CHARACTERIZATION AND HYDROGEN ABSORBTION IN COMPOUNDS OF THE U-Zr SYSTEM presents original experimental research, results, and conclusions on the techniques addressed for obtaining and hydriding of alloys in the U-Zr system with various Zr content. The influence of temperature, Zr content and test duration on the kinetics of hydriding process, morphology and phase composition of the ternary alloy, U-Zr-H, resulted from hydriding, were assessed. The chapter ends with the main conclusions drawn from the analysis of experimental data.

Chapter V - EXPERIMENTAL RESEARCH ON OBTAINING, CHARACTERIZATION AND HYDROGEN ABSORBTION IN COMPOUNDS OF THE U-Ti SYSTEM, presents original experimental research, results and conclusions on the techniques addressed for obtaining and hydriding of alloys in the U-Ti system. The influence of temperature and test duration on the hidrurare kinetics, kinetics of hydriding process, morphology and phase composition of the ternary alloy, U-Zr-H, resulted from hydriding, were assessed. The chapter concludes with key findings arising from analysis of experimental data.

Chapter VI - CONCLUSIONS. ORIGINAL CONTRIBUTIONS AND PROSPECTS presents general conclusions of research results highlighting the innovative aspects. There are also synthesized the author's original contributions to the development and implementation of the experimental program which was the basis of the PhD thesis and the possibilities for further research in this area.

The thesis concludes with references which include the titles of literature papers, papers presented at scientific meetings or published in scientific journals.

The theme of the thesis is framed in an area of great interest today: storing of hydrogen isotopes, a field that is in line with national and international research priorities. This statement is based on an extensive research program that involved countries and international bodies that support research in this area.

The research activities performed in the thesis have followed two directions of study: obtaining the alloys of U-Zr and U-Ti systems and determination of the hydrogen absorption in the alloys of the U-Zr and U-Ti systems, so that the derived objectives of the thesis are: to obtain U-xZr alloys by powder metallurgy method and their characterization by diffraction of X-ray, scanning electron microscopy, energy-dispersive X-ray spectroscopy, differential scanning calorimetry; obtain U-Ti alloys by melting in an inert gaseous atmosphere and their characterization by diffraction of X-ray, scanning electron microscopy, energy-dispersive X-ray spectroscopy, differential scanning calorimetry; the interaction of hydrogen with synthesized alloys in order to determine the influence of the alloying element concentration and temperature on the kinetics of the hydriding process, morphology and phase composition; validation of results by comparison with results reported in the literature.

1. CHAPTER I - Fundamentals of storing hydrogen isotopes

This chapter provides an overview of the main methods for storing hydrogen (constant pressure compression, storage in liquid form and storage in solid form) highlighting the advantages and limitations in applications or functionality. Of the three main methods of hydrogen storage, storage in the solid form (metal hydrides, in particular) attracted the most attention at the moment, based on the fact that many metal and intermetallic systems reversibly absorb large amounts of hydrogen.

The metal hydrides were discovered in 1866 [31] and after almost 100 years after their discovery, the interaction of hydrogen with intermetallic compounds was studied by Libowitz [32] using ZrNi alloys and opening the possibility of using metal hydrides to store hydrogen.

The mechanism of formation of metal hydrides involves many processes and has a high degree of complexity. The metals or intermetallic compounds can absorb hydrogen based on the energy and according to the bond type of the metal-hydrogen system, and the formation reaction of metal hydrides can be expressed by the following equation:

$$M(s)+\frac{x}{2}H_2(g)\rightarrow MH_x(s)+Q \tag{1.2}$$

where: M is the metal or intermetallic compound as a solid solution, MH_X is a metal hydride, x is the atomic ratio H / M, and Q is the amount of heat released during the hydriding reaction.

The kinetics of the formation reaction of metal hydrides is different from other gas-solid reactions and there are specific features of the hydriding reaction such as the diffusivity of hydrogen in the crystal lattice of the material storage and physical disintegration of the material at each stage of the reaction. Thus, the formation of metal hydrides can be divided into the following elementary reactions [6] or hydriding steps as follows:

- Physical adsorption of hydrogen molecules to the metal surface
- Chemisorption and dissociation of hydrogen molecules
- Penetration of metal surface by the H atoms and forming the α solid solution;
- The diffusion of hydrogen atoms through the layer of solid solution;
- Hydride formation.

A large number of metals and intermetallic compounds were studied as storage materials. However, the evolution of these materials in a fully functional storage system still require many years of research and development. The existence of storage materials with high capacity to absorb hydrogen, coupled with a good absorption / desorption kinetics facilitate using this method.

This chapter ends by drawing conclusions based on which the research directions for the experimental program were established.

2. CHAPTER II - ASPECTS RELATED TO RESEARCH FOR CHARACTERIZATION OF HYDROGEN ABSORPTION PROPERTIES IN U-Zr AND U-Ti ALLOYS

This chapter presents a study of the the current state of global research on hydrogen absorption properties in alloys of the U-Zr and U-Ti systems, materials investigated in this thesis. The theoretical studies on the current state of research on storage materials reported that depleted metalic uranium alloys have the ability to remove all or part of the difficulties encountered by the use of uranium as a storage material. Alloying elements have numerous facilities for modifying the structure and properties of uranium. These are possible due to the transformations in solid phase, present in the phase diagrams and address two major issues: allotropic modifications and variations in solubility of alloying elements with temperature.

The experimental studies performed by various authors [58, 61, 62, 76, 77] have demonstrated that during the process of hydrogen absorption, the alloys of U-Zr and U-Ti systems are decomposing into UH_3 and ZrH_x ($x < 2$), or UH_3 and UTi_2H_x ($x < 5$). Since the equilibrium pressure of ZrH_x phase is low, the ability of hydriding of U-Zr alloy is dependent upon the U amount of alloy and the temperature at which the hydriding reaction is happening. In case of the U-Ti system, the formation of the ternary phase UTi_2H_x reduces less the hydriding capacity after a number of absorption / desorption cycles. With respect to the spraying phenomenon, which occurs during hydriding process of the depleted metalic uranium, it has been found that it is reduced with the increase in content of alloying element. **Table 2.3** [78] presents the absorption capacity of the U-Zr and U-Ti systems, after a certain number of cycles of chemical processes of hydrogen absorption / desorption.

Table 2.3: *The hydrogen absorbtion capacity in alloys of the U-Zr and U-Ti systems [78]*

Alloy	Capacity $[H]/[UM_x]$		Spraying	
	Maximum	Recharging	ϕ particles (μm)	Number of cycles
U	3.0	3.0	20-30	2-3
$UZr_{1/2}$	4.0	3.0	-[b]	19.5
UZr	5.0	2.7	100	11.0
UZr_2	6.5	1-3	1-400	12.5
$UTi_{1/2}$	3.7	2.7-3.7[a]	-[b]	13.0
UTi	5.0	2.3-4.5[a]	-[b]	14.5
UTi_2	7.0	1.2-5.5	1-10	12.0

a - High storage capacity;
b - Fine powder, except for a small amount of particles

The prospect of using these alloys for storage materials is motivated by significant research on these systems. The results suggest that this approach has an important role in increasing the number of materials used in hydrogen storage. It is also important to note that the absorption properties depend largely on the concentration of the alloying element, the experimental parameters used and the method used.

Also depleted uranium metalic alloys have been extensively studied in terms of structural, morphological and compositional behavior before and after hydriding process. The current state of research presented in this chapter, points out that with increasing concentration of alloying element the phenomon of spraying and pyrophorus behavior are reduced.

Moreover, it has been observed that the alloys of the U-Ti system contain ternary hydride, compared with the alloys of U-Zr system in which the ternary hydride is considered to be the mixture of uranium hydride and zirconium hydride. It is also important to note that the absorption properties are influenced by the methods used in obtaining and hydriding of these materials.

3. Chapter III - EXPERIMENTAL MATERIALS AND TECHNIQUES

This chapter provides a complete description of materials, equipment and characterization techniques used in this study.

3.2. Studied materials

The materials investigated in this thesis are alloys of depleted metalic uranium: alloys of the U-Zr system with different concentrations of Zr and alloys of the U-Ti system. For the preparation of U-Zr and U-Ti alloys, the following raw materials were used:

- Zirconium, purity 99.679%;
- Depleted metalic uranium U^{238}(<0.72%U^{235}), purity 99.956%;
- Titanium powder provided by Alfa Aesar GmbH&Co KG, Karlsruhe, purity 99.9%.

3.3. The experimental programme

The experimental program was focused on two directions of study: an experimental study for obtaining / characterization of alloys and an experimental study to determine the hydrogen absorbing properties of the alloys of the U-Zr and U-Ti systems. The experimental program on the study of the hydrogen absorption properties was performed using the SETRAM thermo analyzer by thermogravimetric analysis (TG), at constant pressure and as shown in **Table 3.9.** It aimed primarily to evaluate the kinetics of isothermal hydriding reactions and the influence of certain testing parameters on them.

To determine the kinetics of the hydriding reactions instead of mass gain, the use of the conversion degree of the reaction was preferable. Thus, the influence of temperature, influence the content of alloying elements and the duration of exposure on the kinetic curves were assessed. In addition, particularly important data have been obtained regarding the morphological appearance and the phase composition of the resulting compounds. These data were used to assess the influence of test parameters. By research activities performed, I have sought to bring new and original contributions on hydrogen absorbtion in alloys of depleted metalic uranium.

Table 3.9: *Hydriding tests performed on the studied alloys*

Hydriding of alloys of the U-Zr and U-Ti systems					
Alloy system	No	Sampling code	Hydriding method	Testing temperature, [°C]	Duration (h)
U-Zr	1	U-11Zr	TGA	350	24
	2	U-25Zr			24
	3	U-35Zr			24
	4	U-55Zr			24
	5	U-70Zr			3
U-Zr	1	U-55Zr-1	TGA	350	22
	2	U-55Zr-2		400	22
	3	U-55Zr-3		500	22
	4	U-55Zr-4		600	22
U-Ti-(1)	1	U-Ti-1-(1)	TGA	350	24
	2	U-Ti-2-(1)		400	21
	3	U-Ti-3-(1)		500	96
	4	U-Ti-4-(1)		600	48
U-Ti-(2)	1	U-Ti-1-(2)	TGA	300	2
	2	U-Ti-2-(2)		400	2
	3	U-Ti-3-(2)		400	18
	4	U-Ti-4-(2)		500	1
	5	U-Ti-5-(2)		600	20
	6	U-Ti-6-(2)		650	72
Heating / cooling thermal cycles					
U-Zr-H	1	U-55Zr-H	DTA-TGA	500÷750	100 cycles

3.4. Synthesis of materials used

__The powder metallurgy method__ has been used in the synthesis of U-xZr alloys with various concentrations of Zr. The main stages of the process flow are presented in **Figure 3.14**.

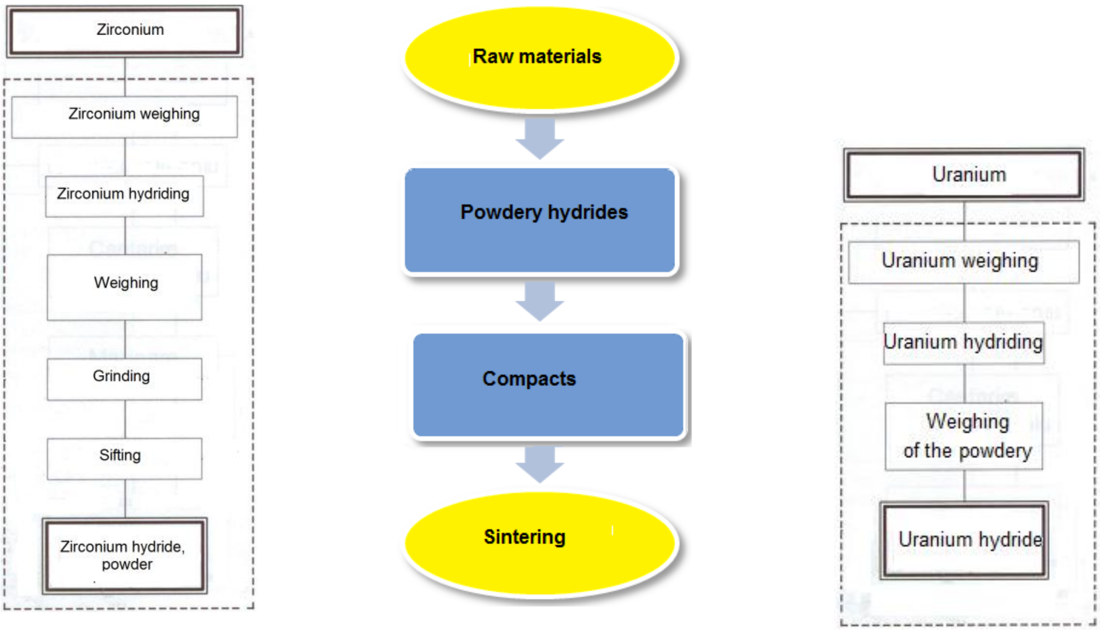


Figure 3.14: *The flow diagram for obtaining U-Zr alloys by powder metallurgy*

The method of melting in an inert gas atmosphere was used in the synthesis of U-Ti alloys. Melting of raw materials in order to obtain U-Ti alloys was done in two ways: using the furnace with induction, Degussa VSL 10/18 type and using the SETSYS EVOLUTION 24 (SETRAM) thermo analyzer, in the variant of coupling the thermo-gravimetric analyzes with the thermal differential analysis (TG-DTA).

The alloys obtained by these methods are shown in Table 3.8.

Table 3.8: The *U-Zr and U-Ti alloys studied*

<table>
<tr><td colspan="5">Method for obtaining: powder metallurgy</td></tr>
<tr><td colspan="2">U-Zr Alloys</td><td>$m_{U,}$[g]</td><td>U content, [wt.%]</td><td>Zr content, [wt.%]</td></tr>
<tr><td rowspan="5">U-xZr</td><td>U-11Zr</td><td>148.452</td><td>89</td><td>11</td></tr>
<tr><td>U-25Zr</td><td>124.875</td><td>75</td><td>25</td></tr>
<tr><td>U-35Zr</td><td>107.315</td><td>65</td><td>35</td></tr>
<tr><td>U-55Zr</td><td>80.428</td><td>45</td><td>55</td></tr>
<tr><td>U-70Zr</td><td>48.690</td><td>30</td><td>70</td></tr>
<tr><td colspan="5">Method for obtaining: melting in an inert gas atmosphere</td></tr>
<tr><td colspan="2">U-Ti Alloys</td><td>$m_{U,}$ [g]</td><td>U content, [wt.%]</td><td>Ti content, [wt.%]</td></tr>
<tr><td rowspan="2">U-Ti</td><td>U-Ti-(1)*</td><td>15.0854</td><td>86.50</td><td>12.50</td></tr>
<tr><td>U-Ti-(2)*</td><td>8.85765</td><td>83.34</td><td>16.66</td></tr>
</table>

(1)*- furnace with induction

(2)*- Simultaneous analysis TG and DTA, in SETARAM thermo analyzer

3.5. Equipment used

In order to achieve the experimental part, the following equipments were used:

1. Chain of niches, needed for preparation of the U-Zr system alloys
2. Furnace with induction, Degussa VSL 10/18 type, needed for preparation of U-Ti -(1) alloys;
3. SETSYS EVOLUTION-24 (SETARAM, France) thermo analyzer, needed for preparation of the U-Ti-(2) alloys and performing hydrogen absorbtion tests.

3.7. Characterization techniques

The analysis techniques and equipments used for materials characterization performed in the experimental research were:

1. X-ray Diffraction (XRD) for the crystal structure, using the diffractometer X’PERT PRO MPD-PANALYTICAL;
2. Thermal analysis (ATD, ATG, DSC) for the physico-chemical transformations that occur during heating and for the hydrogen absorption tests carried out with the thermo analyzer SETSYS EVOLUTION-24 (SETARAM, France);
3. Scanning Electron Microscopy (SEM) for morphology and chemical composition, using a scanning electron microscope, TESCAN VEGA II LMU type

4. Chapter IV. EXPERIMENTAL RESEARCH ON OBTAINING, CHARACTERIZATION AND HYDROGEN ABSORBTION IN COMPOUNDS OF THE U-Zr SYSTEM

In this chapter there are presented and discussed the differences in the structure and morphology of U-xZr alloys, followed by determination of their influence on the hydrogen absorption properties in these alloys.

4.2. Characterization of U-Zr alloys

The U-xZr alloys produced by the powder metallurgy method were characterized through:

- density measurements;
- calorimetry measurements for the determination of phase transformations
- X-ray diffraction for crystal structure;
- Electron microscopy coupled with X-ray spectroscopy.

From the variation of density with the Zr content, it is observed that the density of U-Zr alloys decreases with increasing the Zr content. Also, it has been found that the presence of Zr acts as modifier in the crystalline lattice. The density dependence on Zr content is not linear, which is indicative of the occurrence of structural changes in the host metal matrix.

Qualitative phase analysis of U-xZr alloys was evaluated by X-ray diffraction. This allowed the determination of the compositional evolution of the U and Zr powders, during the process of forming the alloy. In **Figure 4.9,** a comparison of the diffraction spectra of the alloys investigated is presented and from the qualitative phase analysis the presence of the δ-UZr_2, a compound of uranium and zirconium with hexagonal lattice, can be observed.

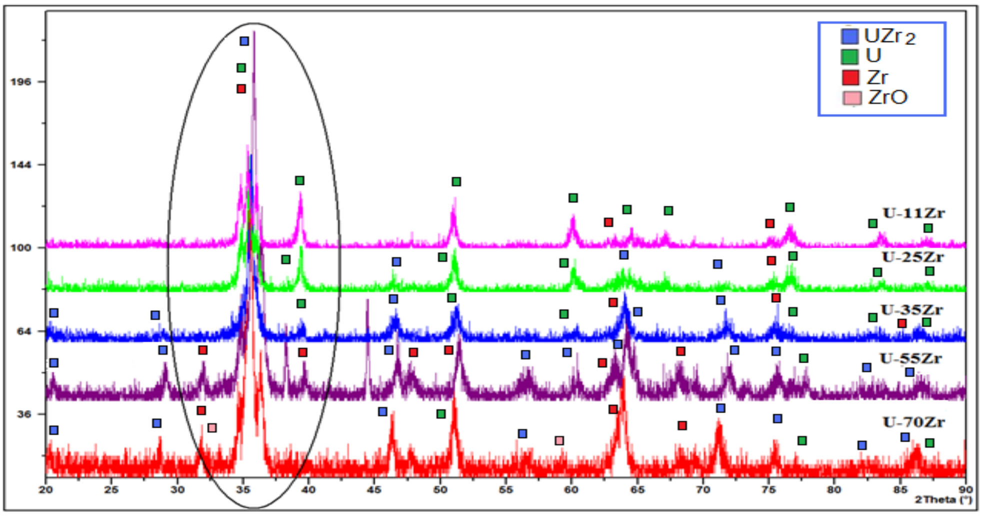


Figure 4.9: *Comparative presentation of the X-ray diffraction spectrums*

The spectra are characterized by diffraction peaks that highlight the phase composition. The δ-UZr_2 phase is dominant in the alloys U-25Zr, U-35Zr and U-55Zr. The differences in the abundance of different phase are related to the concentrations of Zr, the atomic number of alloy elements, and the difference in the atomic radii of the two elements, U and Zr. It can also be observed diffraction peaks at the same angle, different in intensity, which confirms a quantitative difference of the formed phases.

The morphological aspects of the U-xZr alloy samples obtained by powder metallurgy, have been determined by scanning electron microscopy and presented in **Figure 4.10**. From the analysis of the images presented, it can be noticed the structure (matrix) of samples after sintering. All alloys show a heterogeneous structure with inter diffusion between the two constituents, and it can be also noticed the presence of secondary phases that emphasize U and Zr, as confirmed by X-ray diffraction spectra.

The light gray regions have been associated with the δ-UZr_2 phase, the dark gray regions were associated with the Zr rich phases, and the white regions were associated with the U-rich phase. Also regions containing pores have been detected. Their emergence was associated with the conditions of powder pressing or with the presence of small amounts of H which has not been totally removed during sintering [121].

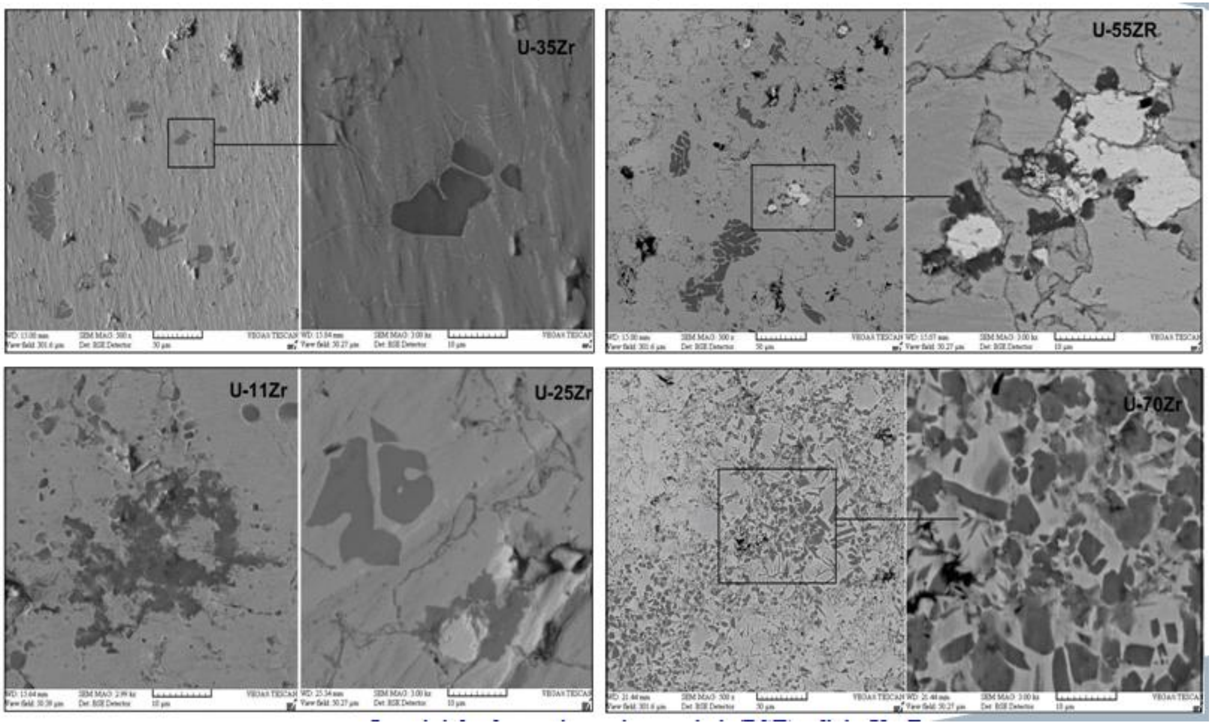


Figure 4.10: *Comparative presentation of backscatter electron images for U-xZr alloys*

The microstructural difference of U-xZr alloys was highlighted by backscatter electron images. By comparing these images it was found that U-11Zr and U-70Zr alloys contain two microstructural phases, identified in variable quantities. In the U-25Zr, U-35Zr and U-55Zr alloys there were identified three microstructural phases. The difference is given by the presence of δ-UZr_2 phase that in the U-11Zr and U-70Zr alloys is found as UZr compound with different stoichiometry. The different compositions are given by the different concentrations of alloying element.

4.3. Interaction of hydrogen with alloys of the U-xZr system

This subchapter presents the results obtained from the hydriding tests of the U-Zr alloys, using the thermogravimetric method at constant pressure. The thermo analyzer SETSYS EVOLUTION 24, TG version, was used aiming to control as rigorous as possible the concentration of absorbed hydrogen by continuously monitoring the mass increases.

The measurement program sought to determine the hydriding mechanism, the absorption capacity and the activation energy for the hydriding reaction of the U-xZr alloys in the following conditions:

- hydrogen absorption kinetics in alloys with different concentrations of Zr under isothermal conditions, with the same treatment duration, and the temperature of 350°C;
- hydrogen absorption kinetics in the U-55Zr alloy under isothermal conditions, the same treatment duration, temperatures in the range 350÷600°C.

4.3.2 Interaction of hydrogen with U-xZr alloys, with different Zr content

Figure 4.42 presents the evolution of hydrogen absorption for all alloys investigated. TG curves show mass changes and highlight the increasing of samples’ mass. The distinct changes that occur during the hydrogen absorption process are visible using the thermogravimetric derivative (dm / dt).

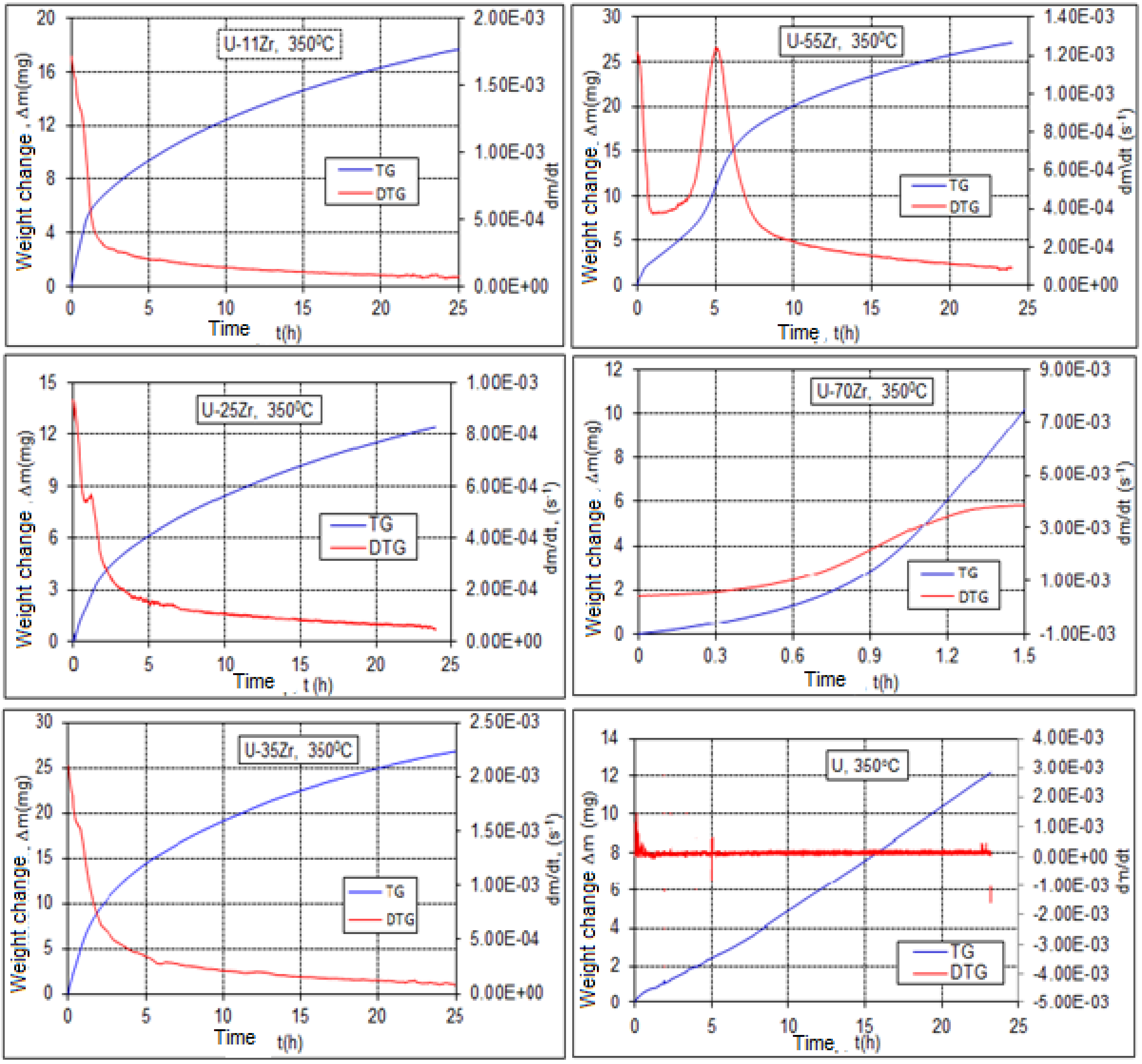


Figure 4.42: *Hydrogen absorbtion in U-xZr alloys and in U, at 350 °C*

Analyzing the thermogravimetric curves, it is noted that U-rich samples (U-11Zr, 25Zr and U-U-35Zr) have two separate areas on the mass variation curves. The first area is an initialization of the hydriding process based on a linear law followed by a hydriding process that follows a parabolic law. The U-55Zr sample, enriched in U, presents three areas of hydriding: initialization of the hydriding with a linear law, followed by a sigmoidal hydriding and then a parabolic hydriding.

The hydriding capacity, represented by the ratio x = H / (U + Zr), was determined by weighing the mass of the analyzed samples before and after hydriding. According to literature data [78], the U-Zr alloys contain, after absorbing hydrogen, UH_3 and ZrH_x ($x < 2$) and can reach a capacity of hydriding x = 6.5. Based on the mass variation, the hydriding capacity of each alloy was determined. The values obtained are presented in **Table 4.24**.

Table 4.24: *Hydriding capacity and the maximum value of the conversion factor, U-xZr alloys*

Alloys	$m_{i,}$ [g]	α_{max}	H/(U+Zr)
U-11Zr	1.1443	0.8609	5.13
U-25Zr	0.32318	0.9713	5.89
U-35Zr	0.72406	0.9374	6.32
U-55Zr	0.70960	0.9619	6.14
U-70Zr	0.85394	0.8174	1.59

To study the effect of hydrogen absorption on the morphology of samples, the U-xZr alloys hydrided at 350°C for 24 hours, were investigated by scanning electron microscopy, SE mode. The evolution of the morphology of the samples is shown in **Figures 4.49 ÷ 4.52**. The images obtained show significant differences. This is possible because of the Zr concentration which produces different interactions with hydrogen resulting in different levels of internal stress.

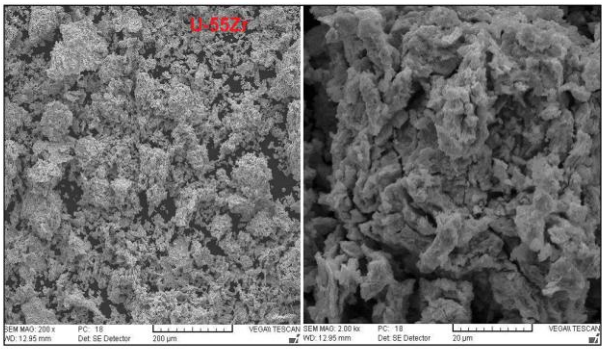


Figure 4.49: *Morphological aspects of the U-11Zr alloy hydrided at 350℃, 24 h*

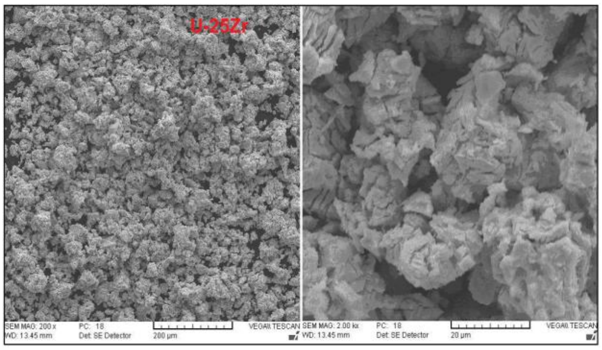


Figure 4.50: *Morphological aspects of the U-25Zr alloy hydrided at 350℃, 24 h*

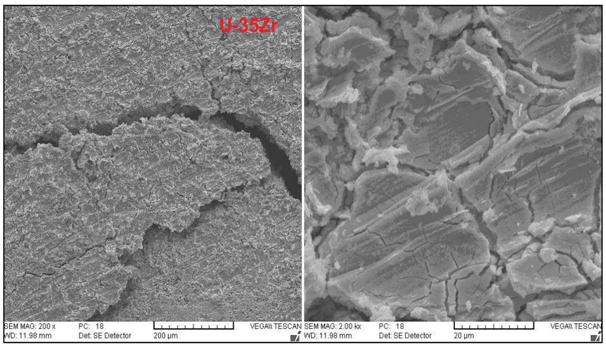


Figure 4.51: *Morphological aspects of the U-35Z alloy hydrided at 350℃, 24 h*

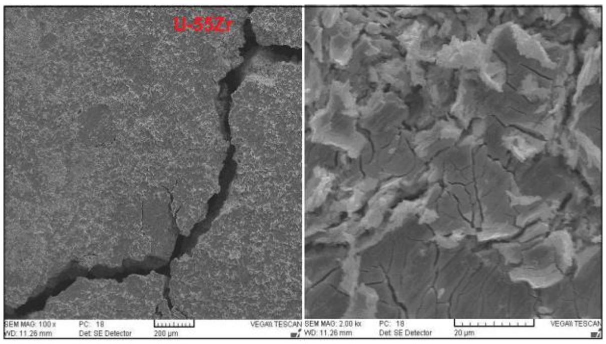


***Figure 4.52**: Morphological aspects of the U-55Zr alloy hydrided at 350℃, 24 h*

The U-35Zr, U-55Zr and U-70Zr alloys did not disintegrate after hydrogen absorbtion, but show secondary crackings in all directions. The crackings suggest tensions in the crystalline lattice. These are wider inside the closed regions, which represent a compound of the U with Zr, with an atomic number lower than the rest of the matrix. By morphological analysis of the hydriding samples, it was highlighted that the disintegration decreases with increasing in Zr content, also demonstrated in the literature [78].

4.3.3 The interaction of hydrogen with U-55Zr alloy at different temperatures

The progress of hydrogen absorption in the U-55Zr alloy was continuously recorded for all test temperatures, and significant gains in mass were observed for each sample. TG curves, shown in **Figure 4.56**, highlight the increasing of sample mass. Distinct changes that occur during the process of hydrogen absorption become visible using thermogravimetric derivative (dm / dt).

From the analysis of the thermogravimetric curves, it is noted that the sample mass increases linearly with the time, in domains with different slopes, and in the end the samples tend to reach the steady state when the speed of hydrogen absorption is slower. Several stages of hydriding can be clearly observed, in which the hydrogen absorption process takes place following a linear law. The numer of the hydriding stages is different for each test temperature, and the occurrence of the hydriding stages is linked to several factors starting with the surface condition and the experimental parameters. The choice of domains for each hydriding stage is based on the best linearization analysis of these domains. The appropriate intervals are selected so that the determination coefficient R^2 is as high as possible [6].

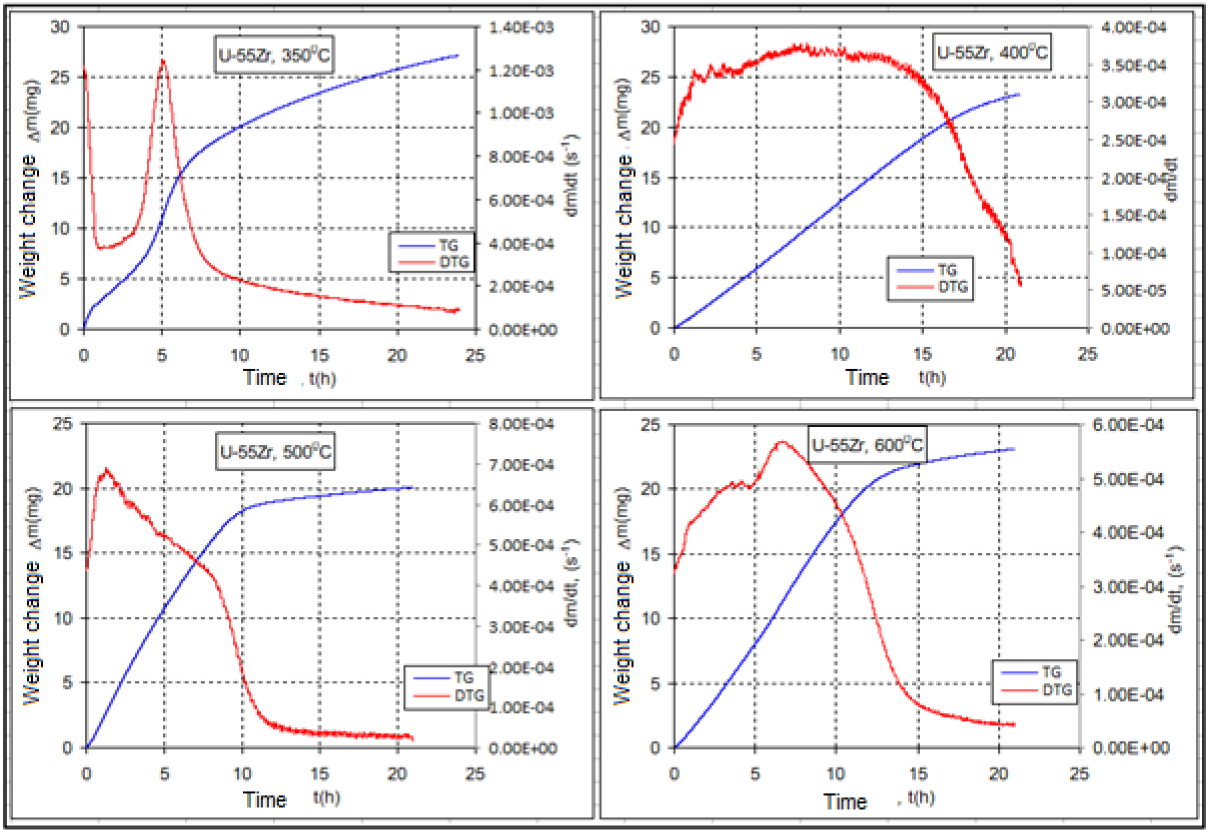


Figure 4.56: *The hydrogen absorbtion curves in U-55Zr, at different temperatures*

Table 4.27 shows the hydrogen absorption capacity in the U-55Zr alloy, tested at four different temperatures. The hydriding capacity, given by the atomic ratio x = H / (U + Zr) was determined by weighing the mass of the samples before and after the absorption of hydrogen. To determine the hydriding capacity, the original structure of the alloy and the fact that above 400°C uranium does not absorb hydrogen were taken into account.

Table 4.27: *Hydrogen asorbtion capacity in U-55Zr alloy at all test temperatures*

Sample	m (g)	Δm(mg)	T(^{0}C)	Hydriding capacity [H/U+Zr]		
				[H/U+Zr]	[H/Zr]	[H/U+Zr] - Stage II
UZr-55Zr-1	0.70960	27.170	350	6.14	-	5.79
UZr-55Zr-2	1.69640	23.266	400	4.17	2.24?	4.03
UZr-55Zr-3	1.59177	20.082	500	4.11	2.10?	3.65
UZr-55Zr-4	2.09979	23.182	600	3.60	1.84	3.10

The hydriding capacity for hydriding samples at 400, 500 and 600°C was determined, considering that only Zr is hydrided. The maximum quantity of hydrogen absorbed for each sample was: H/M = 2.24 at 400°C, H/M = 2.10 at 500°C and H/M = 1.84 at 600°C. According to the phase diagram of Zr-H system [73], the Zr hydride has the maximum hydriding ration of 2, which is not in accordance with the data obtained.

The results from the qualitative phase analysis by X-ray diffraction for the samples tested are shown in **Figures 4.63** and **4.64**. The analysis of the diffraction spectra was performed using X'Pert Plus High Score software, and the compounds were identified with the ICDD PDF 4+ database. They are characterized by wide diffraction peaks highlighting the phase composition and show the existence of significant deviations in the structural lattice of the alloy, deviations caused by different concentrations of hydrogen absorbed. From the analysis of diffraction spectra, it can be noted that all hydrided samples have several phases in composition and the hydriding temperature influences both the type and the amount of phase compounds that are formed.

The hydride phases highlighted by the diffraction analyzes are UH_x and ZrH_x, with different stoichiometries. They appear together only at 350°C. Above this temperature, only ZrH_x appears. It should be noted that at all hydriding temperatures unknown diffraction peaks were identified, which is attributed to the formation of a ternary hydride. Yet a ternary hydride was not identified. The appearance of a ternary hydride is justified by the amount of absorbed hydrogen, which is larger than the amount of hydrogen absorbed by any element of the alloy composition.

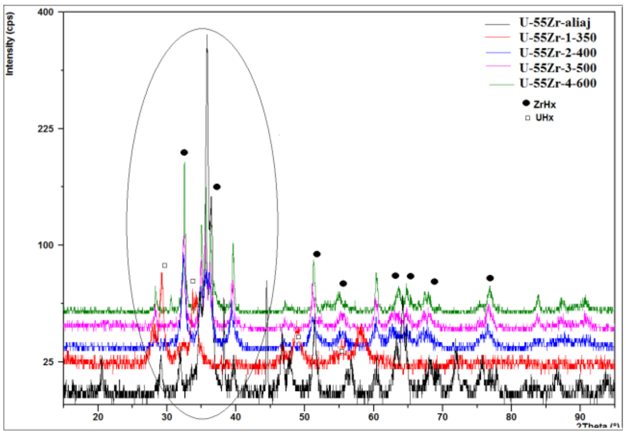


Figure 4.63: *The overlapping of the diffraction spectra for the U-55Zr alloy after hydrogen absorption*

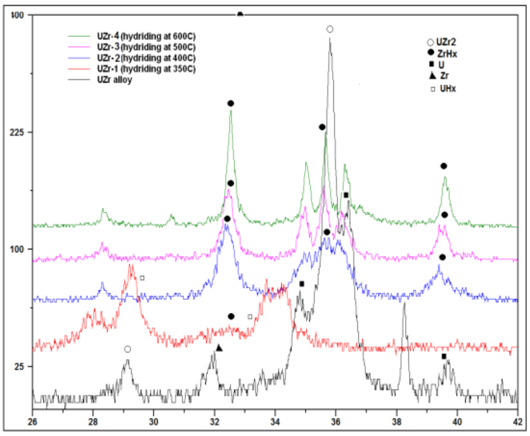


Figure 4.64: *The overlapping of the diffraction spectra for the U-55Zr alloy, in the interval 2θ=30÷40°*

4.4. Determination of thermal stability of the compound U-55Zr-H

The U-55Zr-H compound has a great importance for nuclear energy, being an integral part of the nuclear fuel element used in experimental reactors of the TRIGA type [132, 133] and the complexity of the phenomena associated with the operation of the fuel elements in reactor derives firstly from the specific physical properties of the fuel material.

The tests performed consisted in subjecting the U-55Zr-H samples to 100 thermal heating / cooling cycles in the temperature range of 500-750°C. The experiment sought to determine the capacity of the $ZrH_{1.6}$ matrix to accommodate to the volume changes due to anisotropic expansion of uranium. 100 heating / cooling cycles were performed, as shown in Figure 4.66. The mass decreases shown in Figure 4.67 are small. These variations in the sample mass are associated with the release of hydrogen during the heating process.

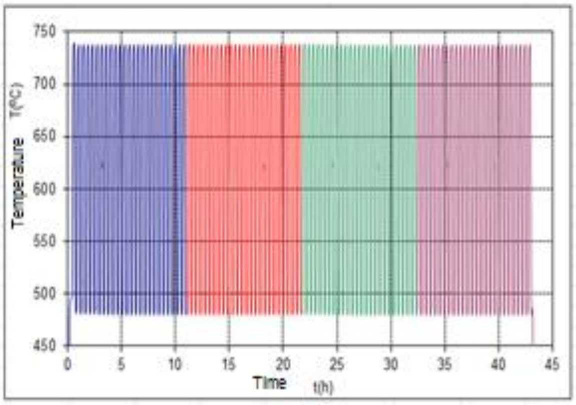


Figure 4.66: *The temperature variation for 100 heating / cooling cycles on the U-$ZrH_{1.6}$ compound*

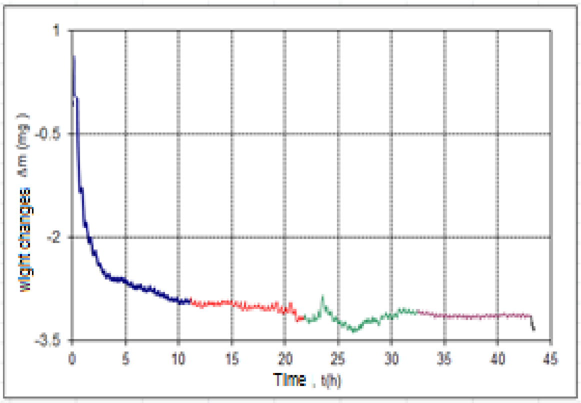


Figure 4.67: *Mass variation after 100 heating / cooling cycles in the interval 500÷750°C on the U-$ZrH_{1.6}$ compound*

The morphology evolution of the U-55Zr-H compound can be traced in **Figures 4.69** and **4.70**, figures in which aspects of the U-55Zr-H compound are presented before and after the heating / cooling testing. From the results obtained, it was found that the structure of the samples before and after the heating / cooling cycles consists of a U-α phase dispersed in a matrix of zirconium hydride (δ-$ZrH_{1.6}$). This fact confirms the ability of the $ZrH_{1.6}$ matrix to accommodate the volume changes due to anisotropic expansions of uranium.

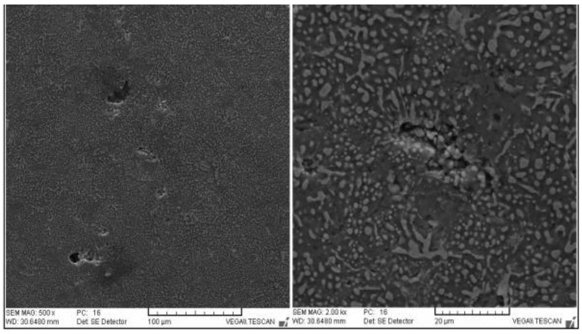


Figure 4.69: *The morphology of the U-55Zr-H compound, before the thermal cycles*

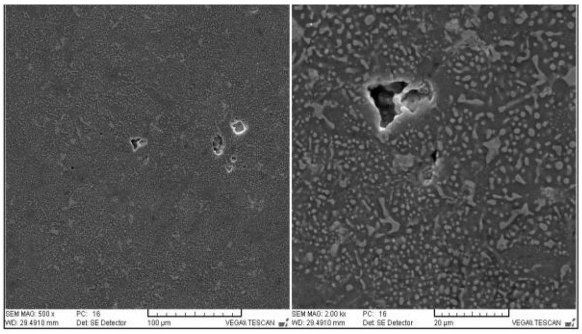


Figure 4.70: *The morphology of the U-55Zr-H compound, after 100 thermal cycles*

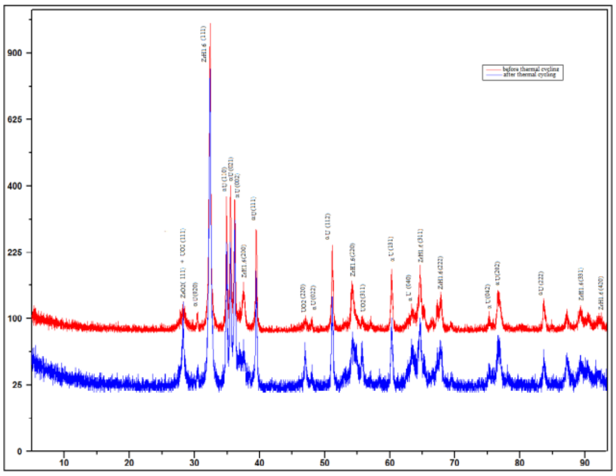


Figure 4.71: *The diffraction spectra before and after 100 thermal cycles*

By analyzing the spectra obtained, the following phases were identified: α-U with orthorhombic structure, β-U with tetragonal structure, as well as $ZrH_{1.63}$ and $ZrH_{1.5}$. This observation allows us to say that following the heating / cooling testing no significant changes in the structure of the U-55Zr-H system are encountered. Also from the analysis of the spectra obtained, it has been found that small amounts of oxide, such as ZrO_2 and UO_2, are formed. This undesirable process of oxygen contamination can affect the quality of the final product, leading to the stabilization of the hydride α phase [107].

5. Chapter V. EXPERIMENTAL RESEARCH ON OBTAINING, CHARACTERIZATION AND HYDROGEN ABSORBTION IN COMPOUNDS OF THE U-Ti SYSTEM

This chapter presents and discusses the results of the experimental tests for obtaining, characterization and hydriding of U-Ti alloys. The influence of the testing temperature on the hydrogen absorption properties of the U-Ti alloys was assessed.

5.1. Obtaining of the U-Ti alloys

Two types of alloys were obtained, coded such as: U-Ti-(1) and U-Ti-(2). The U-Ti-(1) alloy was obtained by melting in He atmosphere in the DEGUSSA furnace and the U-Ti-(2) alloy was obtained by melting in Ar atmosphere by differential thermal analysis (ATD). The composition and the coding of the alloys is shown in **Table 5.1.**

Tabel 5.1: *U-Ti alloys, nominal composition*

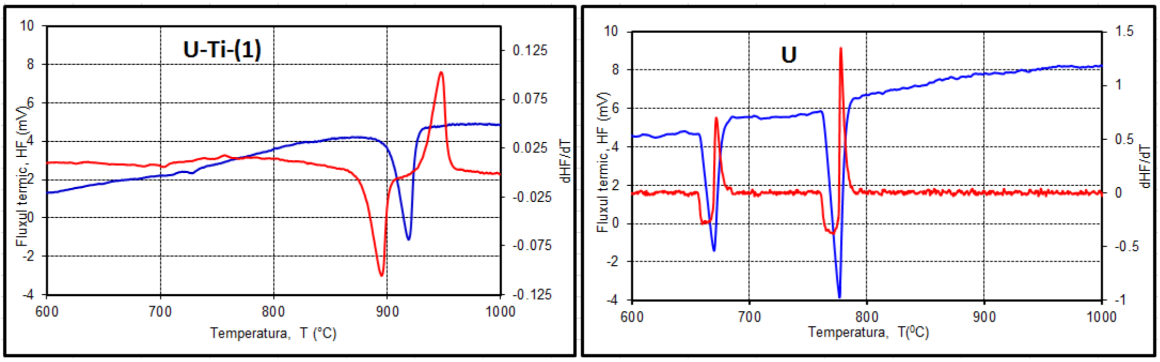
Alloy	m_U [g]	U content		Ti content	
		[wt.%]	[at.%]	[wt.%]	[at.%]
U-Ti-(1)*	15.0834	86.50	53.7	12.50	46.3
U-Ti-(2)**	8.85761	83.34	49.8	16.66	51.2

5.2. The characterization of the U-Ti alloys obtained by melting in an inert gas atmosphere

The U-Ti alloys were characterized in the following manner:

- calorimetry measurements for the determination of phase transformations
- X-ray diffraction for crystal structure;
- Electron microscopy coupled with X-ray spectroscopy

Figure 5.4-a shows the phase transformations in the U-Ti-(1) alloy, during heating. As it can be noticed, the U-Ti-(1) alloy has a single phase transformation at around 900°C. It can be also observed the occurrence of an exothermic maximum at around 200°C associated with the appearance of an uranium compound with oxygen. It should be noted that this maximum is also present in the U sample, shown in **Figure 5.4-b**.



a) b)

Figure 5.4: *The phase transformations : a) U-Ti-(1) alloy; b) uranium*

Figures 5.5 and **5.6** present the diffraction spectra of the investigated alloys and from the qualitative phase analysis the presence of U_2Ti phase with a peak at 2θ = 37.24 can be noticed. In the case of the U-Ti-(2) alloy, the diffraction peaks of the U_2Ti compound are much weaker.

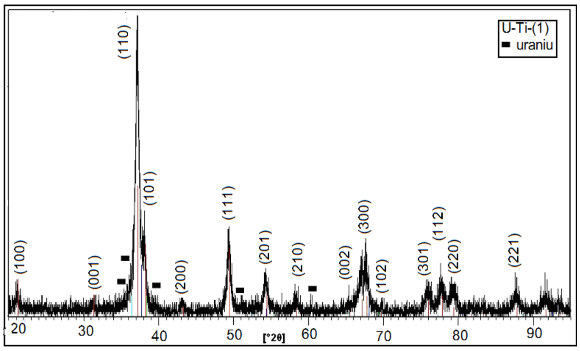


Figure 5.5: *The X-ray diffraction spectra of the U-Ti-(1) alloy - crystallographic planes for the peaks of the U_2Ti compound*

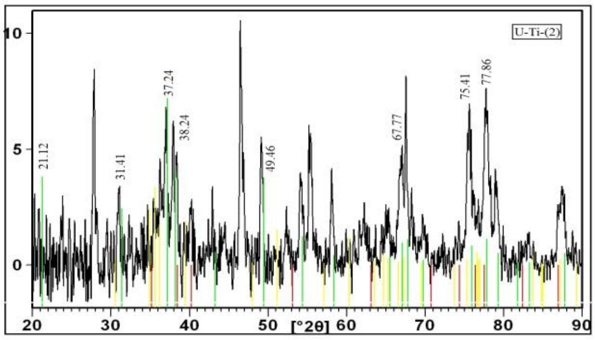


Figure 5.6: *The X-ray diffraction spectra of the U-Ti-(2) alloy with 2θ for the maxima of the U_2Ti compound*

The U-Ti-(1) alloys were investigated by scanning electron microscopy. The SEM images obtained by the detector of secondary electrons with scintillation (SE) in a cross section of the alloy are shown in **Figure 5.8**.

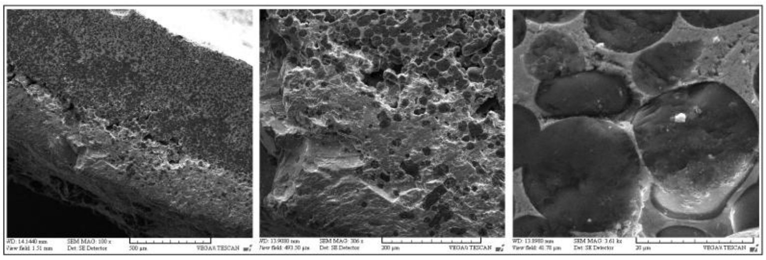


Figure 5.8: *Morphological aspects of the U-Ti-(1)*

The existence of a fragile compound with a heterogeneous structure formed by the incomplete interdiffusion of the constituent elements can be clearly noticed. This fact is justified by the lack of a homogenization treatment. The representative area of the U-Ti-(1) alloy indicates the presence of two distinct phases.

Figure 5.12 shows an image in the BSE mode for the microstructure of the U-Ti-(1) alloy, in which the fluorescence spectrum was processed in the points marked on the image. **Table 5.5** summarizes the results obtained for the chemical composition in each point analyzed. The spectrum shown in **Figure 5.13**, was processed with the QUANTAX Esprit 400 software with an automatic method, without standards (PB / ZAF standardless). The homogeneity degree of the alloy was confirmed by the element map shown in **Figure 5.14**. From the analysis of the results it can be established the existence of a heterogeneous alloy composed of U, Ti and U_2Ti compound.

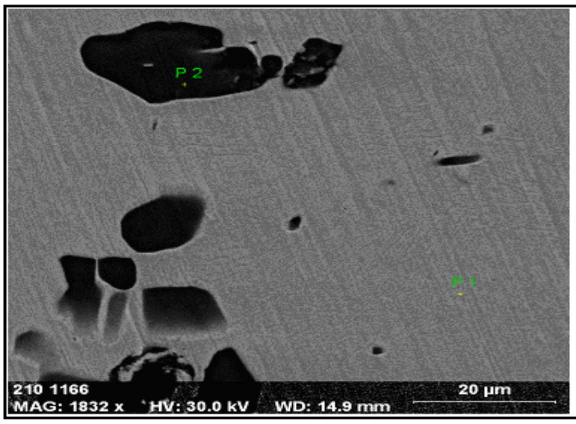


Figure 5.12: *Backscattered electron image; points where was determined the elemental composition by EDS*

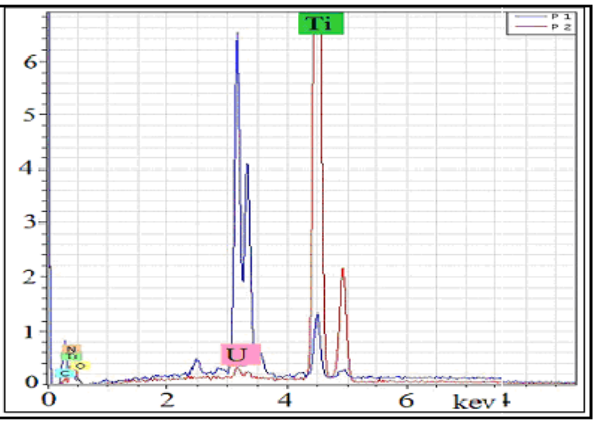


Figure 5.13: *EDS spectrum; the points where was determined the elemental composite*

Table 5.5: *Chemical compozition in each point analyzed (Figure 5.12)*

Puncte analizate	P_1, wt.%	P_2, wt.%	Media, wt.%
Ti	**9.36**	**95.12**	**73.71**
U	**90.58**	**4.81**	**47.96**
O	**0.00**	**0.07**	**0.035**
N	**0.04**	**0.00**	**0.02**
C	**0.02**	**0.00**	**0.01**
Total	**100**	**100.00**	**100**

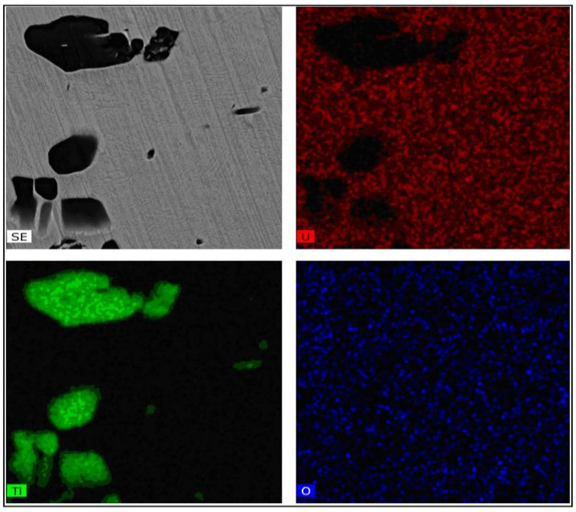


Figura 5.14: *SEM and elemental mapping images, U-Ti-(1) alloy*

According to **Table 5.5**, the open regions contain a large amount of uranium and the closed regions contain a large amount of Ti. Given the fact that the alloy was obtained using a graphite crucible, the impurities O, C, N, etc can be observed.

5.3. Interaction of hydrogen with alloys of the U-Ti system

This chapter presents the results obtained from the hydriding treatments of the U-Ti alloys, using the thermogravimetric method, at constant pressure. The Setsys Evolution 24, TG version thermo analyzer was used, aiming to control rigorously the concentration of the absorbed hydrogen by continuously monitoring the mass increases.The measurement program was developed to determine the hydriding mechanism, the absorption capacity and the activation energy required for the hydriding of the U-Ti alloys in the following conditions:

- hydrogen absorbing in the U-Ti-(1) alloy, the isothermal method, at different temperatures;
- hydrogen absorbing in the U-Ti-(2) alloy, the isothermal method, at different temperatures.

5.3.2. Interaction of hydrogen with the U-Ti-(1) alloy

In order to analyze the effect of temperature on the hydriding mechanism for the U-Ti-1(1) alloy, hydriding isothermal tests were performed at different temperatures. The temperatures selected were 350, 400, 500 and 600°C. The samples were heated in argon (20 mL / min) up to the test temperature, by 20°C / min, and after hydriding they were cooled to the room temperature under similar conditions to heating. The data related to the test conditions and samples are shown in **Table 5.8**.

Table 5.8: The parameters and results of hydriging process, U-Ti-(1) alloy

Sample	Initial weight, m (g)	Temperature, T (^{0}C)	Reaction time, (h)	Weight difference, Δm (mg)
UTi-1-(1)	1.37884	350	24	11.961
UTi-2-(1)	1.44949	400	21	8.2560
UTi-3-(1)	1.92120	500	96	10.435
UTi-4-(1)	1.27315	600	48	6.6170

The evolution of hydrogen absorption in the U-Ti-(1) alloy is shown in **Figure 5.19**. From the analysis of the TG curves, mass increases throughout the hydriding process, as well as a different sample behavior can be noticed, clearly showing that the htdriding process is influenced by temperature. The progress of the hydrogen absorption was continuously recorded for all test temperatures. The TG curves present the mass changes and highlight the increasing of sample mass, and distinct changes that occur during the hydrogen absorption are visible using the thermogravimetric derivative (dm / dt).

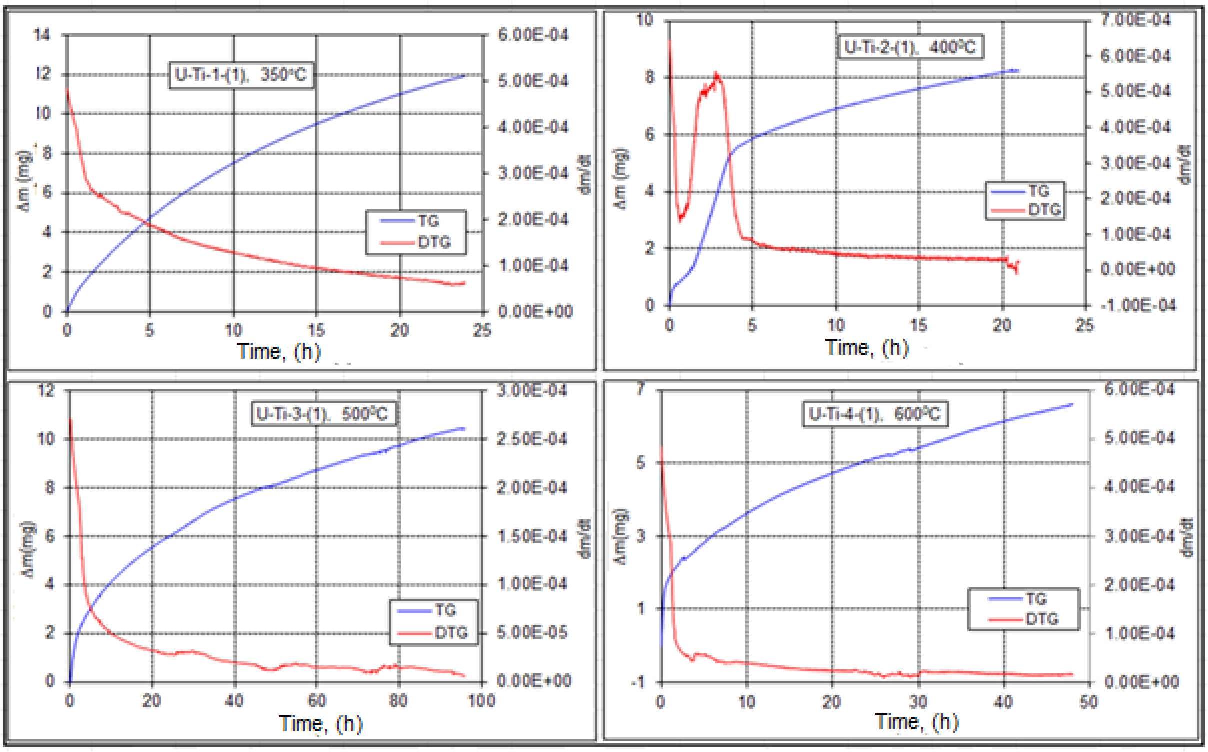


Figure 5.19: *Thermogravimetric curve for hydrogen absorption in UTi-(1) alloy*

Since the samples investigated have different initial mass, the conversion degree was used for a better comparison of the absorption curves. The basis for determining the conversion factor was data obtained on mass increases. The variation of the conversion factor (α) and the reaction rate ($d\alpha/dt$) are shown in **Figures 5.21** and **5.22**.

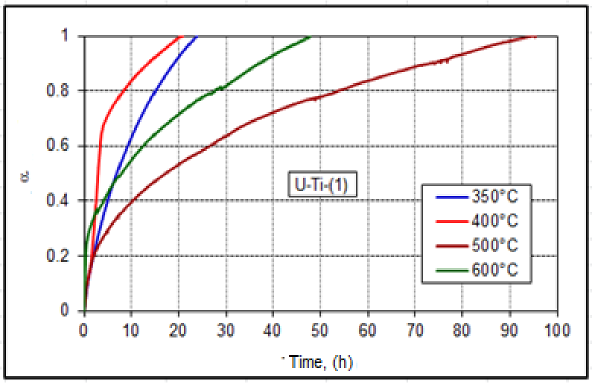


Figure 5.21: *Reacted fraction curves of hydrogen absorption at different temperatures*

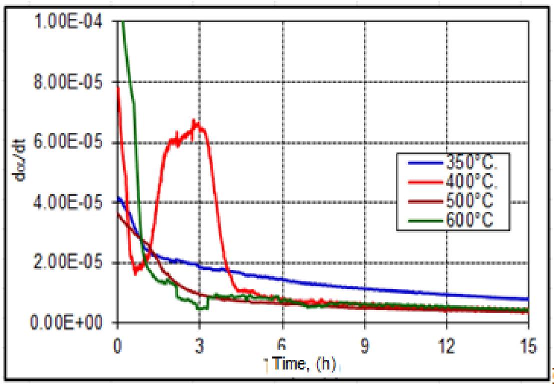


Figure 5.22: *Hydrogen absorption rate curve with respect to time and temperature*

The kinetics and the mechanism of the hydriding reaction are determined by the linearization of the variation in the conversion factor or the reactant fraction, α (t), with different variation laws from which the reaction rate-limiting steps are obtained. From the analysis of the results in **Figure 5.23**, it can be noticed that the initial reaction rate decreases for all test temperatures, with the lowest value at 500°C and the highest value at 600°C. Following the evolution of the reaction rate in time, it can be observed that the samples hydrided at 350, 500 and 600°C have only two hydriding stages. The sample hydrided at 400°C indicates the presence of all hydriding stages.

The activation energy necessary to carry out the hydrogen absorption has been calculated by identifying the rate constant or kinetic coefficients at the temperatures at which the absorption tests were carried out. To assess the rate constants or kinetic coefficients k the experimental curves obtained were linearized. Thus, the value of the kinetic coefficients for each temperature of the hydriding process were inferred. The results are presented in **Figure 5.25** and the values of the rate constants are shown in **Table 5.9**.

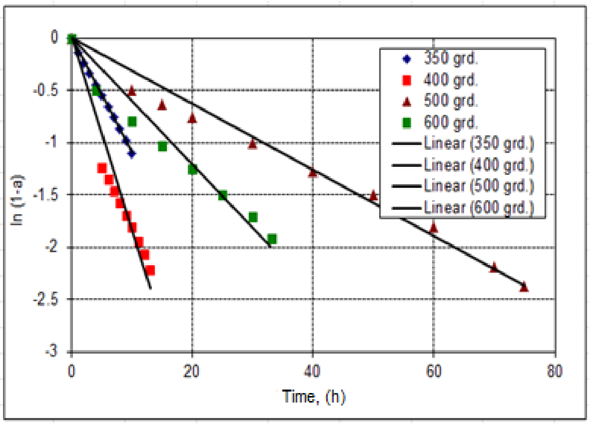


Figure 5.25: *Reaction mechanism function curves for hydrogen absorption in U-TI alloys, stage II*

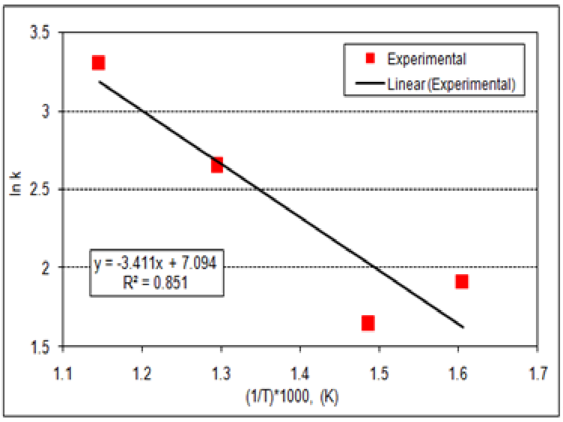


Figure 5.26: *Arrhenius plot for activation energy calculation, stage II*

The dependence of the rate constants on the temperature is given by the Arrhenius equation showing the exponential dependence of the rate constant k on the temperature. For a reaction with kinetics accordingly to this equation, the representation *ln k vs. 1 / T* gives a straight line and the slope of the line can be used to determine the activation energy. The Arrhenius equation representations of the kinetics coefficients obtained from the upward portions of the variation curves of the conversion degree for the hydriding reactions performed are presented in **Figure 5.26**, and the value of the the activation energy obtained is of 28 kJ / mol.

Table 5.9: Temperature depended kinetics parameters

Samples	Temp. (°C)	Δm_{max} (mg)	Reaction stage	Rate constant $kx10^{-4}(s^{-1})$	Correlation constant, R^2
UTi-1-(1)	350	11.9264	II	0.1475	0.999
UTi-2-(1)	400	8.2563	I	0.3597	0.980
			II	0.1941	0.993
UTi-3-(1)	500	10.4351	II	0.0707	0.997
UTi-4-(1)	600	6.6169	II	0.0366	0.996

In order to study the effect of hydrogen absorption on the sample morphology, the U-Ti-(1) alloys were investigated by scanning electron microscopy, SE mode. The images obtained show significant differences. This fact is possible due to the temperature at which the process took place, leading to different levels of internal stress. The evolution of morphology for the U-Ti-(1) samples with the test temperature, after different exposure in hydrogen atmosphere, is presented in **Figure 5.27**.

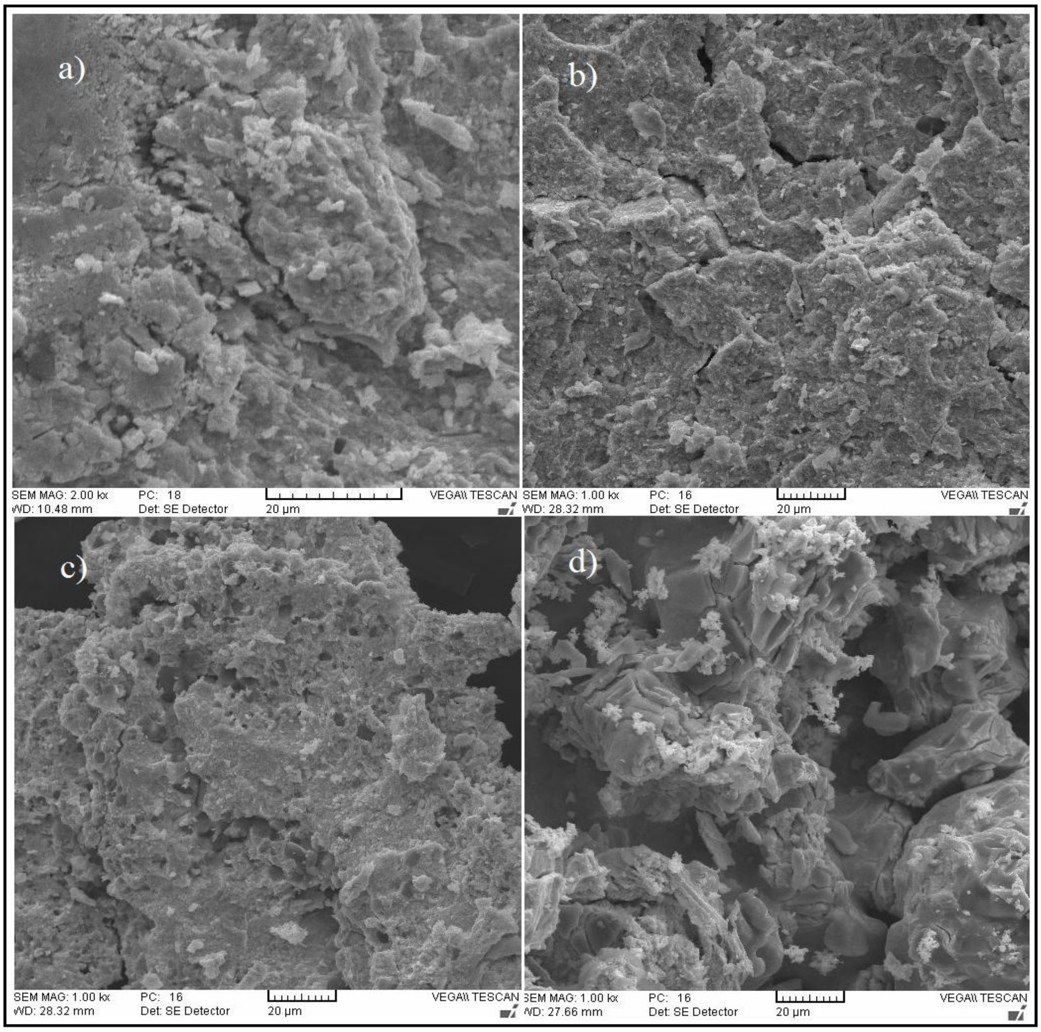


Figure 5.27: *Morphological aspects, U-Ti-(1): a) 350℃, b) 400℃, c)500℃, d) 600℃*

From the analysis of the results, it can be observed the existence of secondary crackings in all directions, suggesting the presence of internal tensions in the crystalline lattice. Regarding the resistance to spraying, the sample hydrided at 350°C was the most resistant. All the specimens consist of several associated phases, which is noticed from the different tones that can be assigned in the following manner [76]: white - U, gray - ternary hydride and black - TiH_x. The resistance to spraying for hydrided samples is considered to be related to the crystal structure of the ternary hydride formed UTi_nH_m. The ternary hydride has a structure of $MgCu_2$ type.

The phase composition was determined by X-ray diffraction, and the spectra were recorded in the range of 20-90 degrees in 2θ, with a step of 0.02 degrees, the recording time per step being 5s.The results obtained from the qualitative phase analysis by X-ray diffraction technique for the samples tested are presented in **Figures 5.28**.

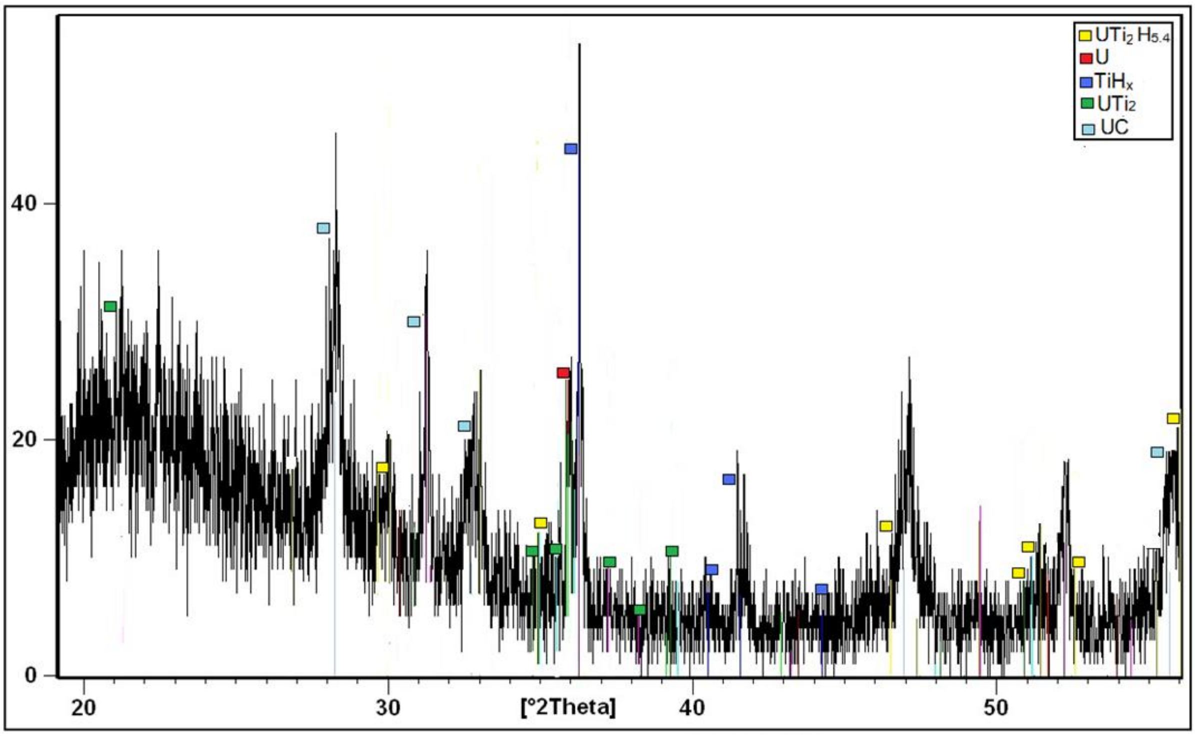


Figure 5.28: *The X-ray diffraction spectra of hydrogenated samples, 600°C*

The diffraction spectra analysed shows no peaks attributable to the uranium hydride, but there are major peaks indicating the presence of titanium hydride. In addition, there are unknown peaks, probably attributable to the formation of a ternary hydride, which may be formed as a single phase. The $UTi_2H_{4.5}$ compound was clearly revealed in the isothermal hydriding process, at 600°C.

5.3.3. Interaction of hydrogen with the U-Ti-(2) alloy

This section presents the data that show the influence of temperature and treatment duration on the hydriding behavior of the U-Ti-(2) alloy. The selected temperatures are in the range 300÷650°C, and the experimental data and test conditions are given in **Table 5.13**. The samples were heated in argon (20 mL / min) at a heating rate of 30 ° C / min up to the test temperature. After hydriding reaction, they were cooled to room temperature under similar conditions to heating.

The thermogravimetric curves are shown in **Figure 5.30**. From the analysis of the thermogravimetric curves, corresponding to the hydriding isotherms, it can be noticed that sample hydrided at 500°C for 1 h had the best absorption. For all six investigated temperatures, the reaction rate decreases throughout the test. These results indicate the absence of the induction period and the first stage of the hydriding process for all the samples and the time to reach steady state decreases with temperature increasing. Also in the case of these samples, it is noted that the hydriding process is slow, the amount of absorbed hydrogen being quite small.

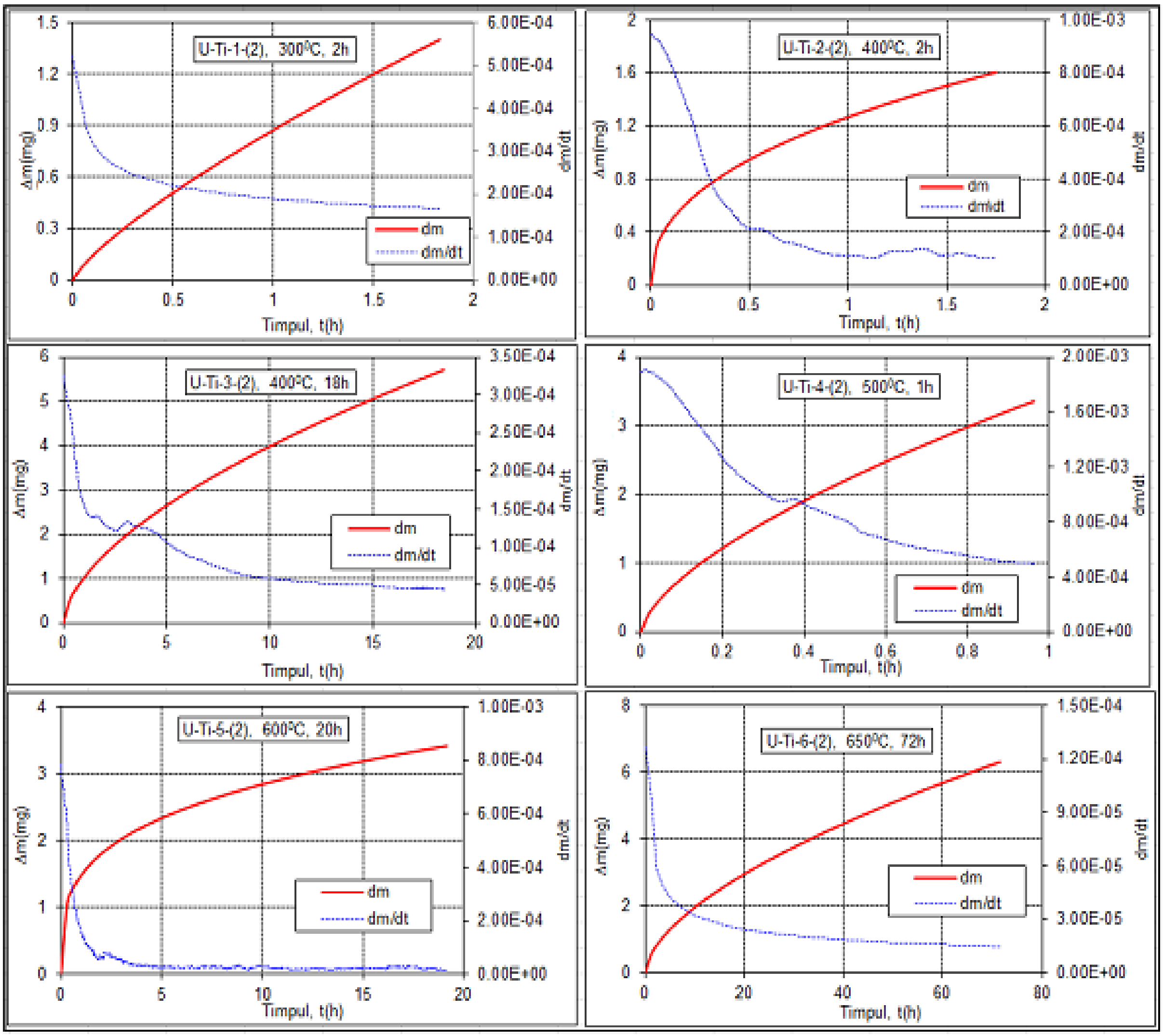


Figure 5.30: *Mass variation corresponding to the hydriding isotherms for the U-Ti-(2) alloy*

The kinetic coefficients were obtained by the method of thermogravimetric curves linearization and are presented in **Table 5.14**. The hydriding kinetics is given by the following law:

$$y = a \cdot x^b \qquad (5.5)$$

where the coefficients a and b are the coefficients of the linearization equation, y is the mass variation, and x is the time.

According to the data presented, the UTi-1-(2) sample follows a linear kinetic for the hydriding process. For the temperature range 400÷700°C, the law is parabolic, except the UTi-4 sample that follows a cubic law.

Table 5.14:*Data related to samples and measurements*

Samples	Weight (g)	Temp. (°C)	Time (h)	Reacted fraction, α_{max}	Rate constant, k	Correlation constant R^2
UTi-1-(2)	0.11626	300	2	0.80115	0.82849	0.997
UTi-2-(2)	1.19823	400	2	0.09425	0.42125	0.980
UTi-3-(2)	1.59491	400	70	0.24998	0.58729	0.995
UTi-4-(2)	1.97888	500	1	0.13472	0.54062	0.964
UTi-5-(2)	1.19823	630	20	0.20878	0.28249	0.989
UTi-6-(2)	1.73083	630	28	0.12801	0.44044	0.973
UTi-7-(2)	1.73083	650	70	0.25768	0.59669	0.991

6. Chapter VI – CONCLUSIONS. ORIGINAL CONTRIBUTIONS AND PROSPECTS

Numerous research on future energy have led in recent years to major pursuit of renewable energies, linked to the development of the "hydrogen economy". "The hydrogen economy represents all energy infrastructures at national and international levels which have hydrogen as primary energy source " [19]. Using hydrogen as an "energy carrier" has many advantages, but involves many scientific and technical obstacles, especially regarding storing it for later use.

The research activities conducted in this thesis aimed to bring new information on the storage of hydrogen as a metal hydride. A large number of materials have been studied as storage materials, but the evolution of these materials in a fully functional storage system still requires many years of research and development.

In order to achieve this goal, a comprehensive experimental program has developed, including synthesis of depleted metalic uranium alloys, as well as experimental measurements on samples taken from these alloys and research findings on the desired theme. The development of the experimental research involved: characterization of the alloys obtained; conducting experimental investigations to assess the effect of certain parameters (temperature, duration of exposure, type and concentration of alloying element) on the kinetics of the hydriding process and on the storage capacity, under isothermal conditions; assessing the structural changes and phase composition of the ternary alloys resulted after hydrogen absorbing; assessing of the physical stability of the hydrides formed, by thermal cycles of heating / cooling.

The originality of this thesis lies in applying the latest concepts in the field and the use of the most recent studies at European and international level. Also, it is to be mentioned that the approach of the hydrogen absorption properties in these types of alloys is a novelty in Romania. Other personal contributions, thus supplementing the data in the literature on the hydrogen asorbtion in U-Zr and Ti-U alloys are:

- ➢ theoretical, practical and technological approach of the synthesis and processing of materials based on depleted metalic uranium;
- ➢ preparation of a bibliographic study regarding the current methods for improving the hydrogen absorption properties of depleted metalic uranium by allying it with other elements;
- ➢ establishing methods for the synthesis and processing of material based on depleted metalic uranium, using raw materials and equipments from the Institute for Nuclear Research Pitesti, and the appropriate experimental facilities;
- ➢ obtaining information on the structure and composition of phases by XRD and SEM analysis, following the correlation between the chemical composition, the synthesis method and structure to improve the technological process (raw materials, homogenization, sintering temperature, etc.);
- ➢ preparation of intermetallic compounds, UZr_2 and U_2T, using original methods for synthesis of alloys;
- ➢ using a method less common in hydrogen absorbtion, i.e. the thermogravimetric method at constant pressure;
- ➢ providing results in the field of hydrogen isotopes storage to integrate the research activities from the Institute of Nuclear Research Pitesti in the thematic area of the EU.

Following the theoretical studies and experimental tests performed, as well as the results obtained, the following directions for future research are considered as necessary:

- ✓ performing hydrogen absorption tests at temperatures below 350°C;
- ✓ performing hydrogen absorption tests in non-isothermal conditions;
- ✓ using other methods that provide better understanding of the hydriding process such as neutron diffraction;

- ✓ using the transmission electron microscopy (TEM) that would allow the examination of microstructural effects of hydrogen absorption / desorption in these alloys;
- ✓ application of methods to improve the homogeneity of alloys;
- ✓ heat treatment tests to determine the absorption capacity and stability of the hydride after a large number of thermal cycles of hydrogen absorption / desorption;
- ✓ study of other alloying elements on the hydriding properties of uranium;
- ✓ determination of the kinetics of the hydriding process in non-isothermal conditions for the U-Zr and U-Ti alloys

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