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Doctoral School Materials Science and Engineering

DOCTORAL THESIS SUMMARY

CONTRIBUTIONS ON HYDRIDING OF Zr-Er MATERIALS SYSTEM, OBTAINED BY POWDER METALLURGY

PhD Supervisor

Prof. univ. dr. habil Adriana-Gabriela SCHIOPU

PhD candidate

Nicolae Tiberiu CIOBANU

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INTRODUCTION

Motivation for choosing the research topic

In the context of the transition to sustainable energy systems, hydrogen is considered a promising energy vector, but the main challenges remain related to its safe and efficient storage and transport. In this regard, materials capable of forming reversible metal hydrides have attracted particular interest, due to their high volumetric storage density and moderate operating conditions.

Metal hydrides are an important area of study, because they offer a high hydrogen storage capacity, can store the gas for a long period, and through dehydriding hydrogen is released at high purity. These systems offer a high degree of safety during operation.

Zirconium-based systems are recognized for their ability to form stable hydrides, characterized by favorable hydrogen absorption and desorption properties. The introduction of elements from the rare earth series, such as erbium, leads to significant changes in the crystal structure, metal-hydrogen binding energy and thermodynamic stability of hydride phases. Thus, the Zr-Er system stands out as a relevant candidate for optimizing the functional properties of hydrogen storage materials.

Relevance and significance of the research topic

By studying materials in the field of hydrogen storage, the correlation between the chemical composition of the materials, processing parameters and hydride behavior becomes essential, in order to optimize the functional performances of the developed materials.

The activities carried out within the framework of this thesis explore this direction by developing and characterizing materials from the Zr-Er system and studying the hydride/dehydride capacities of these materials. The study of zirconium-based materials is very important in the field of hydrogen storage, because these materials have physicochemical properties that make them suitable for modern energy applications, especially in the context of the transition to clean energy sources.

The multidisciplinary approach of the research within the present doctoral thesis offers significant contributions in the field of metal hydrides, by developing innovative methods and advanced characterization of materials from the Zr-Er binary system, but also by studying the hydriding/dehydriding of these materials.

The justification for choosing the research topic lies in the fact that zirconium and zirconium-based alloys can form metal hydrides, having the ability to absorb hydrogen in the crystal lattice, this process being reversible, a very important aspect in the study of hydrogen storage batteries, stability at high temperatures and providing safety. Research in this field supports the development of sustainable energy technologies and the transition to a low-carbon energy system.

The degree of novelty offered by the doctoral research carried out in this work includes the development of materials from the binary Zr-Er system, of different compositions, through powder metallurgy, a method that has not been used for the development of these materials, globally, the analysis of the hydriding method of Zr-Er materials, of different concentrations, and the analysis of the dehydriding capacity of samples from the ternary Zr-Er-H system, these thermal treatments being very little studied globally.

The novelty of this thesis consists in the systematic investigation of the hydriding behavior of materials from the Zr-Er system obtained through powder metallurgy, with an emphasis on the influence of composition and processing parameters on the structural and functional properties. The study contributes to filling the gaps in the specialized literature regarding this system and offers new perspectives for the development of advanced materials intended for hydrogen storage.

The purpose and objectives of the doctoral research

The purpose of this thesis is to study the hydriding behavior of materials in the Zr-Er system prepared by powder metallurgy.

The **main objectives** are:

(i) the development of materials with controlled compositions;
(ii) structural and morphological characterization;
(iii) the evaluation of the hydrogen absorption capacity;
(iv) the correlation of the obtained properties with the processing parameters.

Structure of the doctoral thesis

The doctoral thesis is structured in three distinct parts. The first part presents a bibliographic study of the specialized literature that includes elements regarding the importance of studying materials used in hydrogen storage, the properties of metal hydrides and metal-hydrogen systems of interest, the second part is intended for the original contributions, presenting the methods used in the experimental research, the analyses performed on the developed samples, results and discussions regarding the experimental work performed, and the third part includes elements regarding the general conclusions, own contributions and future perspectives regarding new research directions, which can be approached, using the data presented in this work.

The first part of the thesis, dedicated to the bibliographic study of the specialized literature, is structured in 2 essential chapters:

1. The importance of using hydrogen as an energy source;
2. The current state of research on hydrogen storage.

The first part of the thesis is dedicated to the theoretical substantiation of the use of hydrogen as an energy source and the analysis of the current state of research on its storage methods, constituting the conceptual framework necessary for the development of subsequent experimental studies. The current state of research highlights several main directions of hydrogen storage.

The critical analysis of the specialized literature highlights the existence of gaps in the study of ternary systems of the Zr-RE-H type (where RE represents rare earth elements), especially with regard to the mechanisms of hydride formation and the correlations between composition, structure and behavior in hydride-dehydride cycles.

In this context, the need to investigate the Zr-Er system is justified, in order to develop new materials with potential for hydrogen storage, thus contributing to the expansion of knowledge in the field of advanced energy materials.

The second part of the thesis, which includes the original contributions, is structured in five chapters, as follows:

3. Experimental research methodology;
4. Development of sintered Zr-Er compacts;
5. Hydriding of sintered Zr-Er compacts;
6. Studies on the decomposition of Zr-Er-H intermetallic hydrides;
7. Evaluation of the effectiveness of Zr-Er compacts used in hydrogen storage.

The second part of the thesis is dedicated to the original contributions and presents the results of experimental research on the development, characterization and evaluation of the Zr–Er system in the hydriding and dehydrating processes, with a view to its use for hydrogen storage.

Chapter 3 presents the methodology of the experimental research on the development of Zr-Er materials, describing the materials used, the equipment and the applied characterization techniques. An integrated experimental approach was adopted, based on the use of powder metallurgy, followed by complex characterizations by complementary methods, such as

scanning electron microscopy (SEM), elemental analysis EDS and X-ray diffraction (XRD). The experimental conditions used for the processes of developing materials in the Zr-Er system are also described.

Chapter 4 is dedicated to the development of sintered compacts in the Zr–Er system, for the compositions $Zr_{75}Er_{25}$, $Zr_{50}Er_{50}$ and $Zr_{25}Er_{75}$, by powder metallurgy, using hydride precursors. The study highlights the influence of the sintering temperature (1150–1250°C) on the densification, porosity, roughness and microstructure of the materials. Structural analyses confirmed the formation of phases specific to the Zr–Er system, and the results demonstrated direct correlations between the technological parameters and the physical-structural properties of the compacts.

Chapter 5 deals with the hydride process of sintered compacts, carried out at temperatures of 300°C, 500°C and 700°C, in a controlled hydrogen atmosphere. The experimental results highlighted the ability of the materials to absorb hydrogen, registering significant mass increases, dependent on composition and temperature. Structural analyses confirmed the formation of hydrides from the ternary system Zr–Er–H, along with binary hydrides, establishing favorable conditions for the formation of stable phases. The effect of hydriding on the structural integrity of the compacts, including the phenomenon of hydrogen-induced embrittlement, was also highlighted.

Chapter 6 is dedicated to the study of the dehydriding process of Zr–Er–H materials, carried out under vacuum and high temperature conditions. The characteristic hydrogen desorption ranges and the decomposition mechanisms of intermetallic hydrides were identified. XRD analyses confirmed the disappearance of hydride phases and the formation of oxide compounds, highlighting the sensitivity of the materials to oxidation after hydrogen release. Thermogravimetric studies (TGA/DTG) allowed the determination of the characteristic desorption temperatures and demonstrated the influence of the composition on the kinetics of the process, in particular the role of erbium in reducing the hydrogen release temperature.

Chapter 7 synthesizes the results obtained and evaluates the effectiveness of Zr–Er compacts in hydrogen storage applications. Comparative analysis of the studied compositions revealed that zirconium-rich materials exhibit a superior hydrogen absorption capacity, while materials with a high erbium content favor desorption process at lower temperatures. At the same time, the limitations of the system were identified, especially the tendency to oxidation after dehydriding, which influences the stability and reversibility of the processes.

The third part of the thesis synthesizes the results of the research carried out, highlighting the general conclusions, original contributions and future research directions regarding the use of materials from the Zr–Er system in the field of hydrogen storage and use as an energy source.

The original contributions are embodied in the development of new materials from the Zr–Er system, the systematic investigation of their behavior in the processes of interaction with hydrogen and the establishment of correlations between composition, structure and functional properties. Also, the optimal conditions for the formation of hydrides and the characteristic desorption intervals were identified, contributing to the understanding of the mechanisms involved in these processes.

Proposed **future research directions** aim to optimize the compositions of Zr–Er system to improve storage capacity and stability of hydride–dehydride cycles, reducing oxidation phenomena by using controlled atmospheres or protective coatings, as well as extending studies to multicomponent systems that include other rare earth elements. It is also proposed to investigate the kinetics of hydrogen absorption and desorption processes and evaluate the behavior of materials under conditions close to those in real applications.

PART I. CRITICAL REVIEW OF THE LITERATURE DATA

1. The Importance of Using Hydrogen as an Energy Source

The introduction of hydrogen as an energy source is a key option for reducing greenhouse gas emissions to zero, a commitment that many countries have recently announced [1]. The industry in this field is investing in large-scale projects to produce hydrogen from water electrolysis or from fossil fuels [1].

Many countries, particularly in Europe, are interested in the use of hydrogen as an energy source, as it represents a low-emission energy source and a means of reducing reliance on fossil fuels for energy production [1]. Hydrogen-based energy offers the opportunity to simultaneously contribute to decarbonization objectives and to enhance energy security [1].

Table 1. U.S. DOE requirements for hydrogen storage systems used in the automotive sector [2]

Storage parameters	Unit	2020 Objective	2025 Objective	Target
Gravimetric capacity	kWh/kg	1,5	1,8	2,2
Volumetric capacity	Kg H_2/L	0,030	0,040	0,050
System cost	$/kWh	10	9	8
Operating temperature	ºC	-40/60	-40/60	-40/60
Delivery temperature	ºC	-40/85	-40/85	-40/85
Cycle life	Cycles	1500	1500	1500
Pressure	Bar	5-12	5-12	5-12
Operating efficiency	%	90	90	90
Refueling time	minutes	3-5	3-5	3-5

Hydrogen storage in the form of metal hydrides presents significant advantages compared to gas compression or liquefaction, including high volumetric density, operational safety, and the possibility of operating at moderate pressures. Zirconium-based metals and alloys are recognized for their high affinity for hydrogen, chemical stability, and corrosion resistance. Zirconium forms stable hydrides (ZrH_x), exhibiting a notable hydrogen absorption capacity and favorable kinetics under controlled conditions [3].

Elements from the lanthanide series, including erbium, exhibit a strong interaction with hydrogen, forming stable hydrides and contributing to modifications of the crystal lattice parameters. The incorporation of erbium into the zirconium matrix may lead to:

- modification of the hydrogen bonding formation energy;
- adjustment of the equilibrium pressure in pressure–composition–temperature (P–C–T) diagrams;
- improved cyclic stability;
- optimization of microstructural properties and hydrogen diffusion.

2. Current State of Research on Hydrogen Storage

In principle, there are three methods for hydrogen storage: in gaseous form (in cylinders), in liquid form, and in the form of hydrides formed through the interaction of hydrogen with various materials under different conditions [4].

One kilogram of hydrogen occupies 11 m^3 at ambient temperature and pressure; consequently, its storage requires significant compression. The use of high-strength steel or other metals for conventional hydrogen storage is an option for safety reasons; however,

hydrogen diffusivity through steel and the high mass of steel represent major challenges for vehicular storage applications.

Liquid hydrogen is stored in a cryogenic container at approximately 20 K and ambient pressure, since hydrogen has a very low critical temperature of 33 K [5]. Its volumetric density is around 71 kg/m³, which is higher than that of gaseous hydrogen. However, liquid hydrogen storage systems require a large amount of energy during the liquefaction process, and boil-off losses of hydrogen gas limit potential applications.

Hydride-forming materials can safely store a higher hydrogen density compared to gaseous and liquid hydrogen storage systems [6]. Therefore, among hydrogen storage technologies, material-based storage systems are considered the most suitable, not only for mobile applications but also for stationary applications [7]. Recently, various types of materials have been investigated, for which the following properties are required:

1. High gravimetric and volumetric hydrogen density;
2. Suitable thermodynamic properties, such as reversible hydrogen absorption/desorption at moderate temperature and pressure;
3. Fast kinetics;
4. Easy handling;
5. Abundant resources and low cost.

2.2. Metal Hydrides

Metal hydrides have a wide range of applications. However, most research and development activities on metal hydrides are focused on two main applications: batteries and hydrogen storage. The main advantages of hydrogen storage in metal hydrides are the high volumetric hydrogen densities (sometimes even higher than in liquid hydrogen) and the possibility of reversible hydrogen absorption and desorption.

The bonding in ionic hydrides results from strong electrostatic forces between the different electrical charges of each atom. In general, ionic hydrides require high temperatures to release hydrogen due to their high formation enthalpies or high melting points.

Covalent hydrides are formed through bonding between hydrogen and elements from groups 3B–7B of the Mendeleev periodic table, which have higher electronegativity than hydrogen.

Interstitial hydrides occur when hydrogen penetrates into the interstitial sites between metal atoms in alloy structures (usually binary or ternary alloys) [8].

For optimal hydrogen storage, a metal should exhibit several important characteristics [9]:

- High hydrogen capacity per unit mass and per unit volume;
- Low dissociation temperature;
- Moderate dissociation pressure;
- Low heat of formation, in order to minimize the energy required for hydrogen release and to reduce heat dissipation during exothermic hydride formation;
- Reversibility with limited energy losses during hydrogen charging and discharging;
- Fast kinetics;
- High stability against O_2 and moisture for long cycle life;
- High resistance to a large number of hydriding–dehydriding cycles;
- Low cost of recycling and charging infrastructure;
- High safety.

2.3. Properties of Metal Hydrides

Hydrides that require high temperatures and pressures for operation are undesirable due to increased equipment and energy requirements. The specific requirements of metal hydrides

for mobile applications exclude many materials. A compromise may be possible depending on the values of different parameters [10]. The most stringent requirements regarding gravimetric and volumetric storage capacities are driven by automotive applications, where the acceptable weight and volume of a storage tank are approximately 100 kg and 100 L, respectively. Rehydriding is more critical over time than dehydriding; the rehydriding time corresponds to the time spent at the refueling station and should be less than 5 minutes [9].

Many metals and metallic alloys form a stable oxide layer on their surface under ambient conditions, which kinetically hinders hydrogen absorption. These natural oxides can be removed by surface sputtering under high vacuum conditions, followed by deposition of a protective layer, such as palladium or its alloys. This layer enables hydrogen chemisorption and protects the metal from oxidation [11].

Most natural elements are capable of forming hydrides. However, their dissociation pressures and temperatures are not suitable for most practical applications (0–100 °C and hydrogen pressures between 1 and 10 bar). Only vanadium satisfies these criteria, but its reversible hydrogen capacity is still too low [12]. Therefore, alloys must be developed in order to meet the specific requirements of a given practical application.

During hydriding, hydrogen atoms occupy specific interstitial sites. Only octahedral (O) and tetrahedral (T) sites are considered, as these are the only ones occupied by hydrogen atoms. However, some distinction should be made between different crystal structures [12].

Hydriding is a complex process in which a hydrogen molecule in the gaseous phase is dissociated into individual hydrogen atoms, which are then incorporated into the crystal lattice of the metal hydride [12]. The overall kinetics are limited by the slowest step, known as the rate-limiting step. For the research and development of new alloys, it is desirable that the hydride formation enthalpy and the reaction heat do not constitute rate-limiting steps in the hydriding process [13].

For practical applications, the key parameter is the reversible capacity of the materials (the amount of hydrogen released by the metal/alloy), denoted as $(H/Metal)_r$. The reversible capacity can be significantly lower than the maximum hydrogen absorption capacity $(H/Metal)_{max}$ [14].

For practical applications, it is important that the sorption properties (capacity, kinetics, reversibility, etc.) of the hydrogen storage system remain relatively constant over the entire lifetime of the storage materials. Different applications require different numbers of cycles, but in most cases the number of cycles should range from several hundred to many thousands. Cyclability has been studied mainly for magnesium-based compounds and AB_5-type alloys (e.g., $LaNi_5$) [15] [16] [17].

2.4. Thermodynamic Studies on Metal-Hydrogen Systems

2.4.1. Binary System Zr-H

The equilibrium phase diagram of the Zr–H system is of eutectoid type and consists of the following phases:

1. Terminal solid solution with a hexagonal close-packed structure and random interstitial hydrogen occupation (α-Zr);
2. Body-centered cubic solid solution (β-Zr);
3. Phase δ;
4. Phase ε.

2.4.2. Binary System Er-H

The phase diagram of Er-H shows a hydrogen gas phase and three solid phases [18]. These solid phases include:

1. α-Er solid solution;

2. Dihydride phase in the form of β-ErH_2;
3. Trihydride phase in the form of γ-ErH_3.

2.4.3. Binary System Er-Zr

The phase diagram of the Er–Zr system[19], illustrates two main solid solutions: an Er-rich solid at low temperatures with the hexagonal close-packed (HCP) allotrope of erbium (α-Er), and a Zr-rich solid at high temperatures with the body-centered cubic (BCC) allotrope of zirconium (β-Zr), separated by a simple eutectic reaction[19]. At the eutectic temperature of 1450 °C, a maximum of 27.3 at.% Zr is soluble in α-Er, and approximately 48 at.% Er is soluble in β-Zr. The solubility of Er in α-Zr and of Zr in β-Er is very limited[19].

2.4.4. The ternary Zr–Er–H system

In the literature, several isothermal sections of the Er–H–Zr system have been studied at temperatures of 350°C, 600°C, and 1100°C. At 350°C, six single-phase regions and five ternary equilibrium phases are identified. At 600°C, the two allotropes of zirconium can be observed. The ε-ZrH_2 phase is stable up to a hydrogen pressure of 1 bar, unlike the γ-ErH_3 phase [20]. The miscibility gap between β-ErH_2 and δ-ZrH_2 closes around 447 °C and is completely replaced by a solid-solution region [20]. At 1100°C, a large homogeneity range of the α-Er phase can be observed. Zirconium is present only in the β phase, and the only stable hydride at high temperatures is β-ErH_2 [20].

PART II. ORIGINAL CONTRIBUTIONS

3. Methodology of Experimental Research

3.1. Methods for the Fabrication of Zirconium-Based Materials

The fabrication of zirconium–erbium (Zr–Er) materials requires strict control of chemical composition and processing atmosphere, considering the high reactivity of zirconium at elevated temperatures and the affinity of both elements for oxygen. In practice, the main methods used are either based on melting routes or solid-state processing technologies.

In this doctoral research, the powder metallurgy route was selected for the fabrication of Zr–Er materials with different compositions, as it offers several significant advantages for this type of system, such as:

1. **Superior compositional control**, as powder mixing allows precise adjustment of composition, including low concentrations of erbium or zirconium [21];
2. **Reduced manufacturing temperature**, since sintering is performed below the melting point of the constituent elements, which minimizes volatilization losses, limits unwanted reactions with the atmosphere, and reduces energy consumption [21];
3. **Fine and homogeneous microstructure**, enabling uniform material distribution, reduced grain size, and controlled density of structural defects;
4. Possibility of obtaining **controlled porous materials**, which increases the specific surface area and enhances gas–solid reaction kinetics.

4. Fabrication of Zr-Er sintered compacts

For the fabrication of Zr–Er sintered compacts with different compositions, the powder metallurgy route was selected in this doctoral research. The first step in obtaining these compacts consists of the preliminary preparation of the erbium and zirconium raw materials. After raw material preparation, the next step involves the production of fine precursor powders, which will be used as constituents of the Zr–Er compacts with different compositions.

For powder fabrication, the initial stage consists of separately hydriding the raw materials under specific conditions (pressure, time, temperature), with the aim of embrittling the materials, which facilitates their subsequent mechanical processing. After the hydriding step of zirconium and erbium, the obtained hydrides are weighed, morphologically characterized (by electron microscopy), and structurally analyzed (by X-ray diffraction). Subsequently, zirconium and erbium hydrides are ground, sieved, weighed, and mixed.

The resulting mixtures of zirconium and erbium hydride powders are hydraulically pressed, followed by geometric characterization of the green compacts. In the final stage, the pressed compacts are sintered under predefined parameters (temperature, time, atmosphere). After the sintering process is completed, the samples are characterized in terms of geometry (mass, height, diameter), morphology (electron microscopy), and structure (X-ray diffraction).

Figure 1 presents the technological flowchart for obtaining Zr–Er materials with different compositions via powder metallurgy.

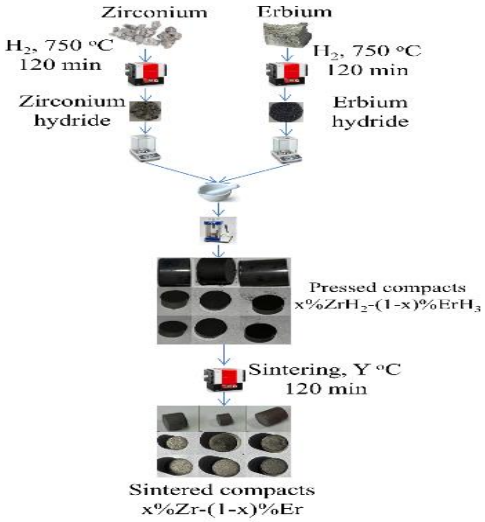


Figure 1. Technological flowchart for the fabrication of Zr_x–Er_{1-x} materials via powder metallurgy

4.1. Hydriding of Raw Materials

The raw materials used for the fabrication of Zr–Er sintered compacts with different compositions are individually hydrided, as the interaction between these metals and hydrogen leads to material embrittlement, which facilitates their subsequent processing.

For the hydriding treatments, a thermal furnace with a closed chamber is used, supplied with hydrogen at a pressure of 1.1 bar.

The hydriding treatment of erbium was carried out at 750°C in a thermal furnace, with a heating rate of 5 °C/min. After reaching the hydriding temperature, it was maintained for 2 hours. Following the isothermal holding stage, the furnace chamber was allowed to cool freely.

The hydriding treatment of zirconium was performed following the same procedure as in the case of erbium hydriding. Both metals share a common hydriding temperature (750°C). As a result of this treatment, zirconium hydride was obtained.

4.2. Preparation and Characterization of Hydride Powders

After obtaining the aforementioned metal hydrides, they were weighed and mixed according to the following proportions:

- 75%ZrH_2-25%ErH_3 (wt.%);
- 50%ZrH_2-50%ErH_3 (wt.%);
- 25%ZrH_2-75%ErH_3 (wt.%).

The mixed powder batches were manually milled using a granite mortar and pestle, and subsequently sieved through a stainless-steel sieve with a mesh size of 32 μm.

The three powder batches were analyzed by scanning electron microscopy (SEM), using a TESCAN VEGA II LMU electron microscope. The performed analyses confirmed the reduced particle size of ZrH_2 and ErH_3 powders, as well as a uniform elemental distribution.

Structural analysis of zirconium hydride and erbium hydride powders, performed by X-ray diffraction (XRD), confirmed the presence of ZrH_2 and ErH_3 phases obtained after the thermal hydriding treatments. In addition, the crystallographic characteristics of the identified compounds in the analyzed powders were determined.

4.3. Preparation of Pressed Compacts of x%ZrH_2-(1-x)%ErH_3

4.3.1. Pressing Powder Mixture x%ZrH_2-(1-x)%ErH_3

The pressed compacts were obtained using two cylindrical die sets with punches, made of stainless steel, each having a diameter of 10 mm and 15.5 mm. The compaction process was

carried out using a manual uniaxial hydraulic press. Pressing was performed at a pressure of approximately 115 bar, which was maintained for 60 seconds in order to stabilize the powder constituents.

4.3.2. Geometrical Characterization of the Pressed Compacts

After obtaining the pressed samples with a composition of x% ZrH_2 – (1 − x)% ErH_3, where x = 0.25, 0.50, and 0.75, the specimens were weighed using a KERN ABP 200-5M analytical balance. The geometrical properties of the samples were then determined by measuring their height and diameter using a digital micrometer. Measurements were performed at three distinct points for each sample. Table 2 present the properties of pressed compacts.

Table 2. Geometrical Characteristics of the Pressed Compacts of x%ZrH_2-(1-x)%ErH_3, Ø 10 mm; 15,5 mm

Content	Mass (grams)	Geometric density (g/cm^3)
75%ZrH_2-25%ErH_3	9,79	4,50
	1,93	4,71
	1,57	4,73
50%ZrH_2-50%ErH_3	9,64	4,65
	1,45	4,96
	1,52	4,97
25%ZrH_2-75%ErH_3	16,93	5,12
	1,523	5,32
	1,501	5,38

4.4. Fabrication of Sintered Compacts of Zr_x-Er_{1-x}

4.4.1. Determination of Sintering Parameters

The pressed samples were sintered at different temperatures in order to analyze how porosity, morphology, and the structure of the compacts are influenced by the sintering temperature and the initial composition.

The sintering parameters were selected to ensure the activation of solid-state diffusion mechanisms, promoting the formation of intergranular bonds and the reduction of porosity, without inducing excessive grain growth or phase segregation. As a reference sintering temperature, a value corresponding to 2/3 of the melting temperature of the material with the highest melting point was chosen ($ZrT_{melting}$ = 1852°C)[22].

Each heat treatment consisted of two stages: complete dehydriding of the samples, performed at 850°C, with the purpose of fully removing the hydrogen present in the powder mixtures and ensuring the fabrication of hydride-free sintered compacts, followed by the actual sintering stage. For each heat treatment, a different sintering temperature was applied, namely 1150°C, 1200°C, and 1250°C.

4.4.2. Sintering of pressed compacts x%ZrH_2-(1-x)ErH_3

For each heat treatment, a batch of pressed samples was placed in a closed-chamber thermal furnace equipped with a tantalum heating element. The furnace chamber was continuously purged with helium at a pressure of 1.1 bar throughout the entire heat treatment process. After completing the three heat treatments, nine compacts were obtained, with the following compositions: three Zr_{75}–Er_{25} samples, three Zr_{50}–Er_{50} samples, and three Zr_{25}–Er_{75} samples. Figure 2 present the sintered samples, with variable content of Zr-Er.

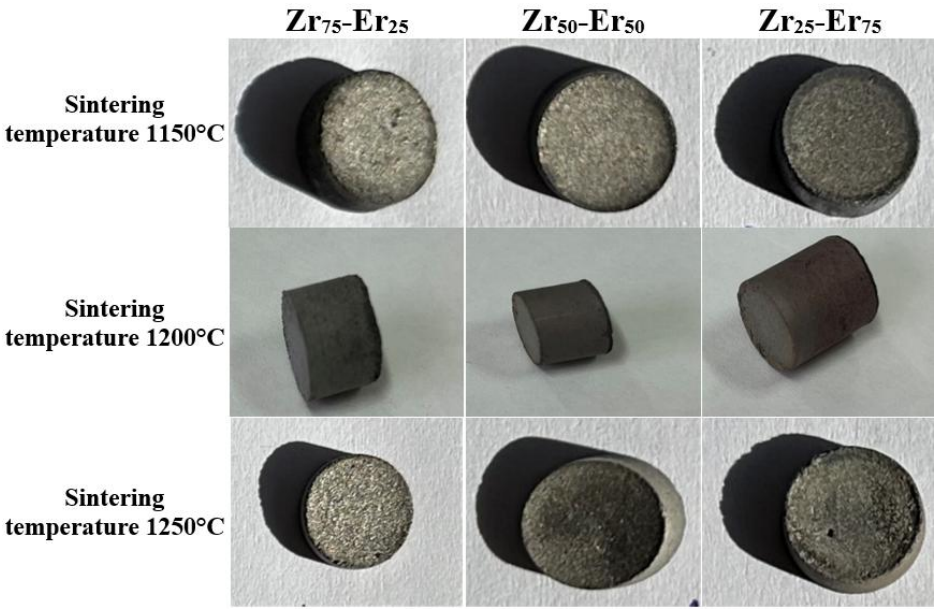


Figure 2. Zr_x-Er_{1-x}, x = 0,25; 0,50 and 0,75, sintered at 1150°C, 1200°C and 1250°C

4.5. Analysis and Characterization of the Sintered Compacts Zr_x-Er_{1-x}

4.5.1. Geometrical Characterization of the Samples Zr_x-Er_{1-x}

Following the measurements performed on the mass, diameter, and height of the samples, it was observed that all specimens exhibited an approximately 2wt.% loss. This difference between the pressed and sintered samples is attributed to the dehydriding stage of the compacts; during this process, the precursor compounds decompose through the release of hydrogen atoms.

The largest reductions in both diameter and height were recorded for the samples sintered at the highest temperature. By determining the real densities of the samples, the positive influence of higher sintering temperatures on sample densification was highlighted.

4.5.2. Roughness Analysis of the Sintered Samples Zr_x-Er_{1-x}

Following the roughness measurements performed, it was observed that the samples sintered at the highest temperature (1250°C) exhibited higher roughness values compared to those sintered at lower temperatures (1200°C and 1150°C).

In addition, another factor influencing the surface roughness of the samples is the Zr content. Specifically, samples with a higher Zr content present higher roughness values.

4.5.3. Morphological Analysis by Scanning Electron Microscopy

The SEM micrographs of the $Zr_{75}Er_{25}$ samples, obtained at magnifications of 100X and 500X using SE and BSE modes, clearly demonstrate a progressive microstructural evolution with increasing sintering temperature from 1150°C to 1250°C. Figure 3 shows the micrographs of sintered sample $Zr_{75}Er_{25}$, fabricated by powder metallurgy, obtain at 2000X magnification, using BSE mode.

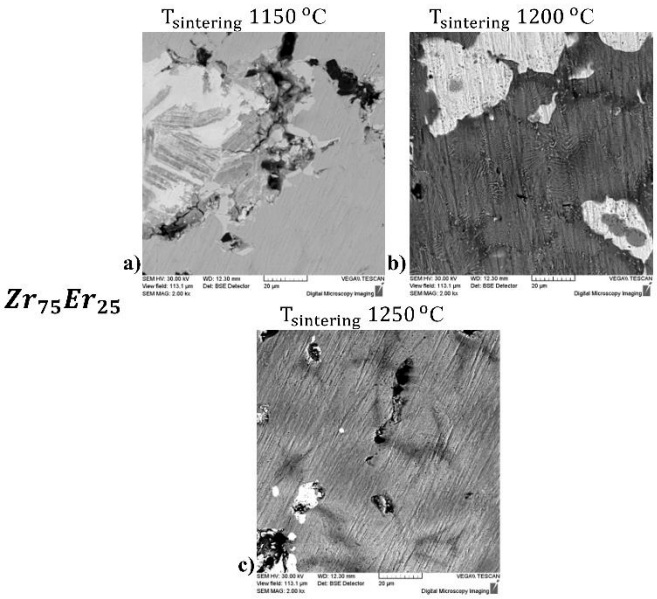


Figure 3. a) SEM micrograph of the $Zr_{75}Er_{25}$ sample, $T_{sintering}$ 1150 °C, 2000X magnification, BSE mode; b) SEM micrograph of the $Zr_{75}Er_{25}$ sample, $T_{sintering}$ 1200 °C, 2000X magnification, BSE mode; c) SEM micrograph of the $Zr_{75}Er_{25}$ sample, $T_{sintering}$ 1250 °C, 2000X magnification, BSE mode

Comparatively, the increase in sintering temperature promotes enhanced atomic diffusion, progressive densification, pore elimination, improved interparticle bonding, phase redistribution, and grain growth in the $Zr_{75}Er_{25}$ system. The sample sintered at 1250°C exhibits the most consolidated microstructure, indicating that higher sintering temperatures significantly improve the structural integrity and homogeneity of the samples.

The batch of $Zr_{50}Er_{50}$ samples was morphologically analyzed by scanning electron microscopy. The SEM micrographs of the $Zr_{50}Er_{50}$ samples, obtained at 500X magnification in both SE and BSE modes, show that higher sintering temperatures lead to an improvement in the microstructural characteristics of the samples. Figure 4 shows the micrographs of sintered sample $Zr_{50}Er_{50}$, fabricated by powder metallurgy, obtain at 2000X magnification, using BSE mode.

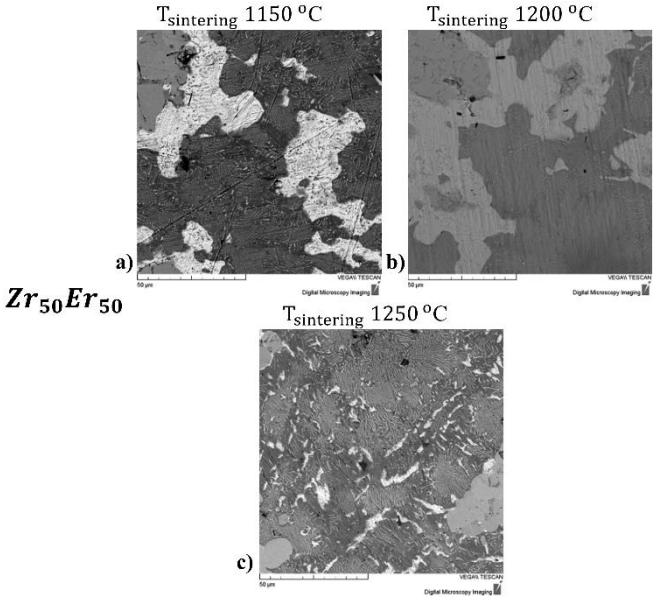


Figure 4. a) SEM micrograph of the $Zr_{50}Er_{50}$ sample, $T_{sintering}$ 1150 °C, 2000X magnification, BSE mode; b) SEM micrograph of the $Zr_{50}Er_{50}$ sample, $T_{sintering}$ 1200 °C, 2000X magnification, BSE mode; c) SEM micrograph of the $Zr_{50}Er_{50}$ sample, $T_{sintering}$ 1250 °C, 2000X magnification, BSE mode.

The SEM micrographs obtained in BSE mode at 2000× magnification for the $Zr_{50}Er_{50}$ samples sintered at 1150°C, 1200°C, and 1250°C clearly highlight the evolution of the microstructure and its homogenization with increasing sintering temperature.

By collectively analyzing the micrographs obtained for the $Zr_{25}Er_{75}$ samples, it can be observed that increasing the sintering temperature promotes enhanced atomic diffusion, progressive densification, pore elimination, improved interparticle bonding, phase redistribution, and grain growth within the $Zr_{25}Er_{75}$ system. Figure 5 shows the micrographs of sintered sample $Zr_{25}Er_{75}$, fabricated by powder metallurgy, obtain at 2000X magnification, using BSE mode.

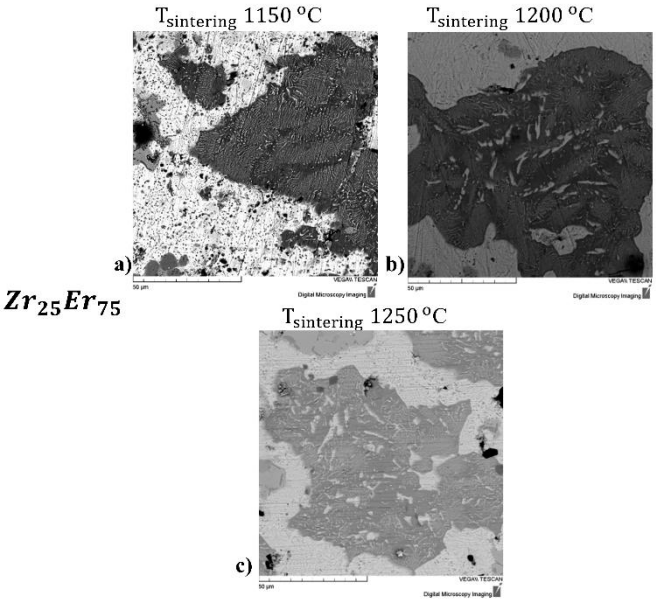


Figure 5. a) SEM micrograph of the $Zr_{25}Er_{75}$ sample, $T_{sintering}$ 1150 °C, 2000× magnification, BSE mode; b) SEM micrograph of the $Zr_{25}Er_{75}$ sample, $T_{sintering}$ 1200 °C, 2000× magnification, BSE mode; c) SEM micrograph of the $Zr_{25}Er_{75}$ sample, $T_{sintering}$ 1250 °C, 2000× magnification, BSE mode.

Comparatively, the sample sintered at 1250°C exhibits the most consolidated microstructure, indicating that higher sintering temperatures significantly improve the structural integrity and homogeneity of the samples.

4.5.4. Elemental analysis of Zr_x-Er_{1-x}

For $Zr_{75}Er_{25}$ sintered samples, through elemental analysis it was observed the simultaneous presence of Zr and Er, for all samples. The higher sintering temperature promotes compaction densification and advanced sintering through interdiffusion of Zr and Er elements and the formation of chemical bonds between them at this temperature.

Quantitative elemental analysis of the samples revealed a slight difference between the initial element concentrations of Zr and Er, determined by weighing, and those obtained by EDS analysis. These differences are associated with the influence of oxygen on the sample compositions.

Comparative analysis of the qualitative elemental characterization performed on the $Zr_{50}Er_{50}$ sintered samples shows that, as the sintering temperature increases, the interdiffusion of Zr and Er becomes more pronounced, indicating improved alloying of the elements with increasing temperature.

Qualitative elemental analysis of the batch containing $Zr_{25}Er_{75}$ sintered samples confirmed the simultaneous presence of the primary elements Zr and Er, indicating the formation of chemical bonds between the two elements as a result of the applied heat treatments.

4.5.5. Structural Analysis by X-Ray Diffraction

Chemical compounds identified by XRD in the $Zr_{75}Er_{25}$ sintered samples, obtained after heat treatments at 1150°C, 1200°C, and 1250°C, validate the SEM–EDS analyses and confirm the formation of chemical bonds between Zr and Er atoms in the form of a solid solution $Er_{0.15}Zr_{0.85}$. These solid solutions formed through heat treatments were also identified in the SEM micrographs, in regions where a eutectoid-like mechanical mixture between Zr and Er was observed.

Qualitative phase analysis of the $Zr_{50}Er_{50}$ sintered samples shows a variation in chemical compounds due to the temperature dependence of diffusion, phase stability, and the affinity of the elements for oxide formation. The $Zr_{50}Er_{50}$ samples exhibit multiple phases in the form of chemical compounds formed between Zr and Er, pure Zr and Er phases, as well as Zr and Er oxides. The formation of Zr–Er chemical compounds in the form of $Er_{0.15}Zr_{0.85}$, $Er_{0.89}Zr_{0.11}$, and ErZr is attributed to partial elemental diffusion and the limited mutual solubility of the elements.

According to X-ray diffraction analysis, the $Zr_{25}Er_{75}$ sintered samples contain the following Zr–Er phases: a Zr-rich solid solution in the form of $Er_{0.15}Zr_{0.85}$, and an Er-rich solid solution in the form of $Er_{0.89}Zr_{0.11}$. The formation of the Er-rich solid solution ($Er_{0.89}Zr_{0.11}$) is attributed to the diffusion of Zr atoms into the erbium matrix. The simultaneous formation of both solid-solution types, $Er_{0.15}Zr_{0.85}$ and $Er_{0.89}Zr_{0.11}$, is caused by atomic redistribution, mutual solubility limits, and the sintering temperatures applied, which allow atoms of one element to occupy the crystal lattice sites of the other element. Although the samples have a high erbium content, the formation of Zr-rich solid solutions is attributed to regions where zirconium is locally predominant.

5. Hydriding sintered compacts Zr-Er

5.1. Description of the Hydriding Experimental Model

To evaluate the efficiency of the fabricated Zr–Er binary system samples for hydrogen storage applications, experimental hydriding studies were performed. This approach aims to investigate the influence of composition on the amount of hydrogen that can be stored, as well as the way in which temperature and initial compositions affect the interaction between hydrogen and the samples.

In order to perform the hydriding of the sintered Zr_xEr_{1-x} compacts, where x = 0.25; 0.50, and 0.75, nine samples were selected, each containing the highest possible fraction of the chemical compound formed between Zr and Er, in order to facilitate the interaction of hydrogen with this type of material.

For a comparative study on the hydriding behavior of the Zr–Er system samples, three distinct temperatures were selected for the hydriding treatments, namely 300°C, 500°C, and 700°C.

5.2. Hydriding of Compacts from the Zr–Er System

The steps followed for carrying out the hydriding treatments of the samples are as follows:

1. Placement of the compacts from a batch into three identical alumina crucibles, positioned on the horizontal support inside the furnace chamber;
2. Initiation of the vacuum process to remove any possible impurities present inside the furnace chamber;
3. Filling the furnace chamber with helium in order to protect the samples from interaction with oxygen while the temperature is rising;
4. Heating the furnace by powering the tungsten resistance according to the thermal profile corresponding to each treatment, with temperature monitoring inside the chamber performed using a type K thermocouple connected to the control unit;

5. Once the required hydriding temperature is reached inside the furnace chamber, the helium supply is stopped and hydrogen gas is introduced into the chamber;
6. A hydrogen pressure of 1.1 bar is maintained for 60 minutes in order to complete the hydriding stage;
7. The hydrogen supply is stopped and helium is reintroduced into the furnace chamber until the temperature decreases to room temperature; cooling is performed under free cooling conditions;
8. In the final stage, the helium supply is stopped, the vacuum process is repeated, and the furnace is then opened to extract the hydrided samples.

The same procedure is applied for each of the three hydrided treatment. Figure 6 present the sintered samples of system Zr-Er, before and after hydriding.

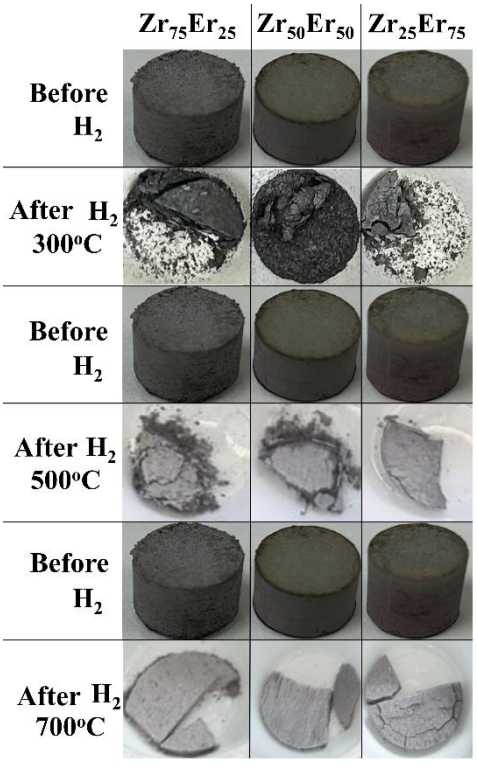


Figure 6. **Zr_x-Er_{1-x} samples, before&after hydriding**

5.3. Analysis of hydrides Zr-Er-H

5.3.1. Characterization of the Zr-Er-H Interaction, 300°C

By morphological analysis of the three Zr_xEr_{1-x} samples, where x is 0.25, 0.50, and 0.75, hydrided at 300 °C, it was comparatively observed that the sample with the highest zirconium content exhibits the least affected compactness due to hydrogen interaction at a pressure of 1.1 bar, the sample that completely lost its initial shape is the one with a $Zr_{50}Er_{50}$ composition.

According to the overlapping X-ray diffraction patterns recorded during the structural analysis of the samples hydrided at 300°C, the following phases were identified: intermetallic hydrides formed within the ternary Zr–Er–H system, in the form of chemical compounds $Er_{0.06}Zr_{0.94}H_{1.72}$, $Er_{0.95}Zr_{0.05}H_{1.96}$, and $Er_{0.06}Zr_{0.94}H_{1.63}$; metal hydrides formed within the binary Zr–H and Er–H systems, in the form of ErH_2, ErH_3, and ZrH_2 compounds; and oxide impurities, in the form of ZrO_2 and Er_2O_3 compounds.

The different types of chemical compounds formed between Zr–Er–H atoms are caused by the initial sample compositions. Thus, in the case of the sample with a predominant zirconium content, the compound $Er_{0.06}Zr_{0.94}H_{1.72}$ is identified, being the only sample exhibiting this phase. For the other two samples, with initial compositions of $Zr_{50}Er_{50}$ and $Zr_{25}Er_{75}$, the

$Er_{0.06}Zr_{0.94}H_{1.63}$ phase was identified, a compound formed through the interaction of hydrogen atoms with the constituent elements of the samples. The chemical compound formed within the ternary Zr–Er–H system and identified in all samples hydrided at 300°C is $Er_{0.95}Zr_{0.05}H_{1.96}$. Other types of hydrides identified in the samples include metal hydrides such as ErH_3, identified in the sample with an initial composition of $Zr_{75}Er_{25}$, and ZrH_2.

5.3.2. Characterization of the Zr-Er-H Interaction, 500°C

From the micrographs obtained through the analysis of the samples hydrided at 500°C, the $Zr_{75}Er_{25}$ sample exhibited the most pronounced morphological reconfiguration, disintegrating into distinct particles, unlike the other two samples, which showed only superficial cracking induced by interaction with H_2, without a complete transformation of their morphology into powder form. All these transformations are governed by the interaction mechanism between H_2 and the external surface of the material, which represents the primary contact zone, followed by the interaction of H_2 molecules with Zr and Er atoms through the dissolution of hydrogen into the metal lattice, a process with endothermic character. The shape and volume changes observed in the hydrided samples are generated by the specific diffusion and accommodation mechanism of hydrogen within the crystal lattice, as H_2 molecules tend to occupy interstitial sites, leading to structural deformation and volumetric expansion of the samples [23].

According to the overlapping X-ray diffraction patterns of the hydrided samples at 500°C, the following phases were identified: hydrides formed within the ternary Zr–Er–H system, in the form of $Er_{0.06}Zr_{0.94}H_{1.72}$, $Er_{0.95}Zr_{0.05}H_{1.96}$, and $Er_{0.06}Zr_{0.94}H_{1.63}$; hydrides formed within the binary Zr–H and Er–H systems, such as ErH_2, ErH_3, $ZrH_{1.801}$, and ZrH_2; as well as oxide impurities, in the form of ZrO_2 and Er_2O_3 compounds. The different types of chemical compounds formed between Zr–Er–H atoms are determined by the initial sample compositions. Thus, in the sample with a predominant zirconium content, the compound $Er_{0.06}Zr_{0.94}H_{1.72}$ is identified, being the only sample exhibiting this phase. For the other two samples, with initial compositions of $Zr_{50}Er_{50}$ and $Zr_{25}Er_{75}$, the $Er_{0.06}Zr_{0.94}H_{1.63}$ phase was identified, a compound formed through the interaction of hydrogen atoms with the constituent elements of the samples.The chemical compound formed within the ternary Zr–Er–H system and identified in all samples hydrided at 500°C is $Er_{0.95}Zr_{0.05}H_{1.96}$. Other types of hydrides identified in the samples include metal hydrides such as ErH_3 and ZrH_2, present in the samples with initial compositions of $Zr_{75}Er_{25}$ and $Zr_{50}Er_{50}$, while the sample with predominant erbium content exhibits hydrides in the form of ErH_2 and $ZrH_{1.801}$.

5.3.3. Characterization of the Zr-Er-H Interaction, 700°C

Following the morphological analyses performed on the samples hydrided at 700°C, it was observed that they preserve their initial geometric configuration, in contrast to the samples treated at lower temperatures, where significant morphological changes were identified. However, the interaction between H_2 and the sample surfaces at 700°C led to the formation of superficial cracks, similarly observed in all three samples. These transformations are attributed to the processes of adsorption, diffusion, and interstitial incorporation of H_2 at the sample surface, which represents the primary reaction front, followed by the processes of dissolution and incorporation of hydrogen into the Zr and Er metal lattice.

According to the qualitative phase analyses performed on the samples hydrided at 700°C, the following phases were identified: the $Zr_{75}Er_{25}$ hydrided sample contains hydrides formed within the ternary Zr–Er–H system, in the form of $Er_{0.95}Zr_{0.05}H_{1.96}$ and $Er_{0.06}Zr_{0.94}H_{1.72}$. In addition, hydrides formed within the binary Er–H and Zr–H systems were identified, such as ZrH_2 and ErH_3, as well as oxide impurities in the form of Er_2O_3. In the case of the sample with an equal Zr and Er composition, the only hydride phase identified was the binary Er–H hydride in the form of ErH_3. The remaining composition consists of oxide impurities such as Er_2O_3 and

ZrO_2, as well as a erbium-rich solid solution, in the form of the $Er_{0.89}Zr_{0.11}$ phase. For the $Zr_{25}Er_{75}$ sample hydrided at 700°C, hydrides from the ternary Zr–Er–H system were identified, in the form of $Er_{0.95}Zr_{0.05}H_{1.96}$ and $Er_{0.06}Zr_{0.94}H_{1.72}$, as well as metal hydrides from the binary Er–H system, in the form of ErH_3.

6. Studies on the Decomposition of Zr–Er–H Intermetallic Hydrides

6.1. Dehydriding of Materials from the Ternary Zr–Er–H System

To investigate the dehydriding temperature and time of materials from the ternary Zr–Er–H system, as well as to validate their hydrogen release capability, the hydrided Zr_xEr_{1-x} samples were dehydrided under vacuum conditions. The aim was to identify the temperature at which the intermetallic hydrides from the aforementioned ternary system release H_2, by monitoring pressure evolution inside the thermal furnace chamber. For the dehydriding treatment, samples with the highest content of ternary hydride compounds of the type $Er_{0.06}Zr_{0.94}H_{1.72}$, $Er_{0.95}Zr_{0.05}H_{1.96}$, and $Er_{0.06}Zr_{0.94}H_{1.63}$ were selected, while also ensuring a minimal content of oxide impurities.

According to the obtained results, at 300°C the intermetallic hydrides begin to decompose through a slow dehydriding stage. When the furnace temperature reaches approximately 600°C, a more rapid increase in pressure is observed, indicating that the desorption intensity of the ternary $Zr_xEr_{1-x}H$ hydrides is at its maximum. Subsequently, a further pressure increase is recorded in the temperature range of 750–820°C over a period of 10 minutes, followed by a negligible time-dependent pressure increase of approximately $1x10^{-4}$ bar/h. This final stage indicates pressure stabilization and the completion of the dehydriding process of the samples.

6.2. Structural Analysis by XRD of Dehydrided Zr–Er–H Samples

To confirm the decomposition of intermetallic hydrides from the ternary Zr–Er–H system, the dehydrided samples were structurally analyzed by X-ray diffraction in order to identify the phases formed after the thermal dehydriding treatment.

According to the results obtained from the qualitative phase analysis of the dehydriding Zr_xEr_{1-x} samples, where x = 0.25, 0.50, and 0.75, the identified phases confirm the complete dehydriding of the intermetallic hydrides from the Zr–Er–H ternary system, with the hydride phases being replaced by oxide compounds.

6.3. Thermogravimetric Studies of the Ternary Zr–Er–H System

Thermogravimetric analyses (TGA) are a fundamental thermal analysis technique used to identify mass changes in materials as a function of temperature and/or time under a controlled atmosphere. This type of analysis is employed to determine the thermal stability of materials and the mechanisms of reactions occurring at specific temperatures [24].

According to the curve obtained from thermogravimetric analysis performed under an Ar atmosphere on the Zr_{75}–Er_{25} –H sample, negligible mass variations are observed up to 350°C, indicating a high thermal stability of the hydride phases. The first dehydriding stage is noticeable in the temperature range of 350–450°C. Significant mass losses begin at approximately 525°C and continue up to 850°C, corresponding to a progressive hydrogen desorption process. The absence of abrupt reaction steps indicates a gradual dehydriding mechanism.

According to the mass evolution of the Zr_{50}–Er_{50}–H sample as a function of temperature, the sample remains stable in the range of 22–250°C, followed by a mass decrease between 250–280°C, representing the first dehydriding stage. The second decomposition stage of

intermetallic hydrides is identified in the temperature range of 350–400°C. In the 600–850°C interval, a continuous mass loss of up to 0.5% is observed over approximately 650 seconds, indicating an incipient stage of dehydriding.

The thermal evolution of the Zr_{25}–Er_{75}–H sample suggests a first mass-loss stage in the temperature range of 250–390°C, followed by a second region of mass decrease between 525–670°C.

To accurately identify the temperature intervals in which the Zr_xEr_{1-x}–H samples release hydrogen and to evaluate the intensity of the dehydriding stages, the derivative of the thermogravimetric curves (DTG) was determined. Comparatively, from the DTG curves it is observed that, as the erbium content increases, the dehydriding temperatures decrease, and H_2 desorption occurs at lower temperatures. This behavior is attributed to the increasing concentration of erbium-rich metal hydride phases, in the form of $Er_{0.95}Zr_{0.05}H_{1.96}$ compound, which, assuming a dehydriding behavior similar to erbium hydride, releases hydrogen at lower temperatures than zirconium hydride.

7. Evaluation of the efficiency of Zr–Er compacts in hydrogen storage

The experimental results obtained following the hydriding treatments applied to the sintered Zr–Er compacts highlight a clear dependence between material composition, treatment temperature, and hydrogen storage capacity.

According to the results obtained within the experimental research carried out in this study, the materials from the ternary Zr–Er–H system presented the following advantages:

- **the formation of metal hydrides** was achieved starting from 300°C, with a purity of metal hydrides in the form of various chemical compounds exceeding 90 wt%;
- **low formation pressure of hydrides** in the Zr–Er–H ternary system; the hydrides investigated in the experimental studies were formed at a hydrogen pressure of 1.1 bar, which provides a significant safety advantage for the operation of hydriding systems using these materials;
- **gravimetric hydrogen capacity** between 1–1.6 wt%; although the investigated systems exhibit relatively low gravimetric storage capacity, they are comparable with other similar hydrogen storage systems, namely intermetallic hydrides, which present gravimetric hydrogen storage capacities in the range of 1–3 wt% [25];
- **volumetric capacity** of Zr_xEr_{1-x}–H hydrides, where x is 0.25, 0.50, and 0.75, was found to range between 0.0852 kg H_2/L and 0.12 kg H_2/L;
- **reversible capacity**: according to experimental studies, Zr_x-Er_{1-x}–H hydrides, where x is 0.25, 0.50, and 0.75, exhibited desorption starting from 250°C;
- **thermal stability**: the investigated intermetallic hydrides showed mass stability up to temperatures of 250 °C, ensuring safe use in various applications.

Overall, the obtained results demonstrate that:

- Zr–Er–H hydrides exhibit a multi-steps dehydriding behavior;
- thermal stability increases with zirconium content;
- erbium-rich materials promote hydrogen desorption at lower temperatures;
- oxidation processes represent a major limiting factor in evaluating the reversibility of hydriding–dehydriding cycle.

PART III. GENERAL CONCLUSIONS, ORIGINAL CONTRIBUTIONS, AND FUTURE PERSPECTIVES

The demand for hydrogen, which can replace conventional energy sources (coal, oil, natural gas, etc.), has been steadily increasing worldwide in recent years. Researchers across the globe are seeking optimal solutions for transport and storage systems capable of meeting the requirements of hydrogen (H_2) applications.

This doctoral thesis primarily aimed to develop and characterize materials from the Zr–Er system, obtained by powder metallurgy, and to evaluate their behavior during hydriding and dehydriding processes in order to assess their potential for hydrogen storage applications.

In the first stage, sintered compacts of Zr_x–Er_{1-x} type, with compositions $Zr_{75}Er_{25}$, $Zr_{50}Er_{50}$, and $Zr_{25}Er_{75}$, were produced using hydride precursors (ZrH_2 and ErH_3). Sintering treatments were carried out at 1150°C, 1200°C, and 1250°C, resulting in nine compact samples. These were characterized in terms of geometry, roughness, morphology, elemental composition, and structure using scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and X-ray diffraction (XRD).

Geometrical analyses indicated an average mass loss of approximately 2 wt.%, attributed to the decomposition of hydride precursors and hydrogen release during sintering. Measurements also showed shrinkage in both diameter and height, caused by densification and sintering mechanisms, with more pronounced contraction at 1200°C and 1250°C. Density increased with sintering temperature, all materials reaching over 89% of theoretical density, confirming the efficiency of the sintering process and the formation of consolidated compacts.

The experimental densities were influenced by diffusion processes during thermal treatments, as well as by composition, with zirconium-rich samples exhibiting higher densities.

Open porosity analysis revealed that both sintering temperature and zirconium content affected pore characteristics, with higher zirconium content leading to increased porosity.

Roughness measurements showed an increase with both temperature and zirconium content, likely due to microstructural changes, intermetallic phase formation, and local surface reorganization.

Morphological characterization highlighted a heterogeneous structure typical of powder metallurgy materials, with eutectoid-like mechanical mixtures formed through Zr–Er interactions during heat treatment.

EDS analyses confirmed the presence of Zr and Er, along with oxygen and impurities such as Fe and W. Differences between theoretical and experimental compositions were attributed to partial oxidation and local inhomogeneities. The co-presence of zirconium and erbium in the same analyzed regions confirms their interaction and the formation of interatomic bonds.

Following the structural analyses by X-ray diffraction of the sintered Zr–Er materials, it was found that all samples contain alloys formed between zirconium and erbium, in different phase forms (ErZr, $Er_{0.15}Zr_{0.85}$, and $Er_{0.89}Zr_{0.11}$). The formation of these phases is influenced by the erbium content: samples with 75 wt.% erbium tends to form an erbium-rich solid solution, in the form of the $Er_{0.89}Zr_{0.11}$ phase. In all samples, a zirconium-rich solid solution, in the form of the $Er_{0.15}Zr_{0.85}$ phase, was identified, while the ErZr-type compound was found only in the $Zr_{50}Er_{50}$ samples. It was observed that as the zirconium concentration increases, the presence of the $Er_{0.15}Zr_{0.85}$ solid solution becomes more significant. Additionally, it was found that the use of higher sintering temperatures positively influences the degree of formation of chemical compounds between Zr and Er, with 1250°C favoring the formation of a higher amount of intermetallic phase.

During the hydriding stage, the sintered samples were treated in a hydrogen atmosphere at 300°C, 500°C, and 700°C, at a pressure of 1.1 bar, for 60 minutes. Based on post-hydriding analyses, the samples showed a mass increase ranging between 2.38% and 6.55 wt.%. The

identified mass increases may also be influenced by oxygen, through interaction with the atmosphere.

From a morphological perspective, hydriding produced significant changes in surface features and the integrity of the compacts. At 300°C, the $Zr_{50}Er_{50}$ sample completely lost its compact form, while the $Zr_{75}Er_{25}$ sample was less affected. At 500°C, the $Zr_{75}Er_{25}$ sample exhibited the most pronounced fragmentation. At 700°C, the samples retained their geometric shape but developed superficial macrocracks. These changes are associated with lattice expansion, stresses generated by hydrogen absorption, and embrittlement specific to metal hydride formation.

At 300ºC, for all hydride samples was confirmed the presences of intermetallic hydrides from ternary system Zr-Er-H.

At 500°C, the behavior of the samples depended on composition. The $Zr_{75}Er_{25}$ sample showed a significant amount of ZrH_2, while the $Zr_{25}Er_{75}$ sample favored the formation of the $Er_{0.95}Zr_{0.05}H_{1.96}$ phase and erbium-rich hydrides.

At 700°C, a reduction in ternary hydride content and an increase in oxide proportion were observed, especially for the $Zr_{50}Er_{50}$ sample. This behavior indicates that higher temperatures may limit the formation of stable hydrides and promote oxidation.

The dehydriding study was performed on samples hydrided at 300°C, selected due to their high content of ternary hydrides and lower impurity levels. Thermal analysis of the dehydriding process in vacuum, up to 800°C, revealed three distinct stages of hydrogen release: an initial slow stage starting around 300°C, an intense stage in the 600–700°C range, and a final stage up to approximately 820°C. These results confirm the stepwise nature of the desorption process.

XRD analyses performed after dehydriding confirmed the disappearance of hydride phases and the predominant formation of ZrO_2 and Er_2O_3 oxides. This transformation confirms hydrogen release from the crystal lattice but also highlights the sensitivity of Zr–Er materials to oxidation after dehydriding. The presence of oxide compounds is explained by the high affinity of Zr and Er for oxygen, as well as by sample exposure to the atmosphere after thermal treatment.

Thermogravimetric analyses carried out in an inert argon atmosphere allowed the identification of hydrogen desorption intervals for the $Zr_{75}Er_{25}H$, $Zr_{50}Er_{50}H$, and $Zr_{25}Er_{75}H$ samples. Zirconium-rich samples exhibited higher thermal stability, with dominant desorption stages above 500°C. In contrast, erbium-rich samples showed dehydriding processes at lower temperatures, in the 250–300°C range, indicating the significant influence of erbium in reducing the hydrogen release temperature.

DTG curves confirmed the stepwise nature of desorption. For the $Zr_{75}Er_{25}$-H sample, the main desorption processes were identified in the ranges 500–570°C, 600–650°C, and 770–790°C. For the $Zr_{50}Er_{50}$-H sample, the main peaks were located at 470–570°C, 620–660°C, and 770–790°C. For the $Zr_{25}Er_{75}$-H sample, the desorption peaks shifted to lower temperatures, namely 250–300°C, 500–550°C, and 600–650°C. Thus, it can be concluded that increasing erbium content reduces the characteristic hydrogen desorption temperature.

Overall, the obtained results demonstrate that Zr–Er system materials produced by powder metallurgy exhibit hydride-forming capability and can participate in reversible hydrogen absorption and desorption processes. Among the analyzed compositions, $Zr_{75}Er_{25}$ showed the best performance in terms of hydrogen absorption and ternary hydride formation. However, post-dehydriding oxidation represents an important limiting factor that must be controlled through optimization of the working atmosphere, handling in inert environments, and reduced oxygen exposure.

Therefore, the conducted research confirms the potential of the Zr–Er system for the development of hydrogen storage materials, while also highlighting the need to optimize sintering, hydriding, and dehydriding parameters to improve structural stability, reversibility, and oxidation resistance.

The personal contributions resulting from the experimental studies carried out within this doctoral thesis include:

- the development of the experimental model for obtaining Zr–Er system materials by powder metallurgy;
- the fabrication and characterization of zirconium and erbium hydrides powders;
- the fabrication of materials from the binary Er–Zr system by powder metallurgy;
- the analysis and interpretation of sintered compacts using various characterization methods;
- studies on the thermal influences on hydriding sintered Zr–Er materials;
- studies on the desorption capacity of Zr–Er–H intermetallic hydrides.

The experimental research studies conducted in this work demonstrated the efficiency of obtaining compacts from the binary Zr–Er system, with different compositions, by powder metallurgy, starting from zirconium and erbium raw materials.

The hydrogen storage capacity of Zr–Er based materials with different compositions was verified through hydriding tests at various temperatures and dehydriding treatments. Thermogravimetric analyses of Zr_x–Er_{1-x}–H samples (where x is 0.25, 0.50, and 0.75), obtained by hydriding at 300°C, confirmed the ability of the samples to release hydrogen under specific conditions (temperature, time).

The original scientific contributions provided by the experimental research carried out in this doctoral thesis include contributions regarding the formation conditions of erbium hydride, in the form of the ErH_3 phase [26]; the development of materials from the binary Zr–Er system by powder metallurgy using Zr and Er raw materials, resulting in homogeneous, uniform compacts with high density, uniform microstructure, low porosity, and a high content of chemical compounds formed between Zr and Er elements [21], [27]; contributions to the experimental model of hydriding/dehydriding of Zr–Er system materials; and the evaluation of the gravimetric and volumetric properties of hydrides in the ternary Zr–Er–H system. The Zr–Er system provides a balance between high absorption capacity (specific to Zr) and low desorption temperatures (induced by Er), making it suitable for applications where moderate thermal cycles are essential.

Through the doctoral research work, new approaches for the development of Zr–Er system materials were identified, and new data were collected and interpreted regarding the formation mechanisms of intermetallic hydrides in the ternary Zr–Er–H system, as well as important data on H_2 desorption from these intermetallic hydrides.

This doctoral thesis makes significant original contributions to the field of hydrogen storage materials by developing and systematically investigating the Zr–Er system, which has been insufficiently explored in the literature in the context of ternary hydride formation.

A major contribution consists in the **design and controlled fabrication of Zr_x-Er_{1-x} materials by powder metallurgy using hydride precursors (ZrH_2 and ErH_3)**, an approach that enables simultaneous synthesis, dehydriding, and activation of the material for hydrogen interaction processes. This technological strategy represents a novel element compared to conventional methods used for similar systems.

For the first time in this work, **a systematic and correlative study was conducted on the influence of sintering parameters (1150–1250°C) on densification, porosity, and intermetallic phase formation in the Zr–Er system**, highlighting direct relationships between temperature, microstructure, and functional material properties.

A particularly original result is **the identification and experimental characterization of chemical compounds in the Zr–Er system (ErZr, $Er_{0.15}Zr_{0.85}$, $Er_{0.89}Zr_{0.11}$) and the establishment of their formation conditions depending on composition and thermal regime**. These results complement and extend the existing data in the literature for zirconium- and rare-earth-based systems.

The main contribution of the thesis consists in the experimental demonstration of the ability of the Zr–Er system to form stable ternary hydrides, an aspect insufficiently documented previously. Phases of the following types were identified and validated:

- $Er_{0.95}Zr_{0,05}H_{1,96}$;
- $Er_{0,06}Zr_{0,94}H_{1,72}$;
- $Er_{0,06}Zr_{0,94}H_{1,63}$.

These results represent an original contribution to the field of ternary Zr–RE–H systems (RE = rare earths).
It was explicitly demonstrated that:

- **zirconium-rich compositions ($Zr_{75}Er_{25}$) maximize hydrogen absorption capacity;**
- **erbium-rich compositions reduce desorption temperatures**, facilitating hydrogen release;
- **the hydriding temperature controls the hydride formation mechanism (ternary vs. binary).**

An important original contribution is the direct **correlation established between composition – microstructure – hydriding behavior**, enabling the definition of optimization criteria for hydrogen storage materials.

Through morphological analysis, the thesis contributes by highlighting **the mechanism of hydrogen-induced structural degradation**, demonstrating that:

- hydride formation generates significant internal stresses;
- these stresses lead to the formation of macro- and microcracks;
- material embrittlement depends on composition and temperature.

Regarding the reverse processes, a relevant contribution is **the experimental determination of the dehydriding mechanism of Zr–Er–H materials**, clearly identifying:

- characteristic desorption intervals (≈250°C – 820°C);
- the existence of a stepwise process;
- the influence of composition on hydrogen release kinetics.

By combining TGA and DTG analyses, it was originally demonstrated that:

- **increasing Er content leads to lower desorption temperatures**;
- **dehydriding processes are controlled by the type of previously formed hydride phases**;
- **ternary hydrides exhibit behavior different from classical binary hydrides**.

Another important result is the identification of the **limitations of the Zr–Er system**, particularly:

- high susceptibility to oxidation after dehydriding;
- the influence of oxygen on phase stability;
- the need for strict control of the working atmosphere.

Through these results, the thesis not only characterizes a material system but also **proposes a compositional optimization model for hydrogen storage materials**, based on the balance between absorption capacity (Zr) and ease of desorption (Er).
Overall, the original contributions of the work consist of:

- the development of a new material system for hydrogen storage;
- the demonstration of Zr–Er–H ternary hydride formation;
- the establishment of composition–structure–property relationships;
- the identification of hydriding and dehydriding mechanisms;
- the definition of limitations and optimization directions.

Through these elements, the thesis contributes to advancing knowledge in the field of hydrogen storage materials and opens perspectives for the development of hybrid systems based on zirconium and rare earths.

Future research directions regarding the efficiency of Zr–Er-based materials with different compositions include: the development of Zr–Er binary system materials by powder

metallurgy in a controlled inert atmosphere to completely eliminate oxide impurities; thermodynamic analyses of metal hydride formation in the Zr–Er–H ternary system using high H_2 pressures and lower temperatures; experimental and theoretical studies on the cycling behavior of intermetallic hydrides in the Zr–Er–H system; determination of the hydrogen quantities required for hydriding Zr–Er materials at 300°C; and long-term stability analyses of metal hydrides in the Zr–Er–H system at room temperature, in air and water environments.

Additionally, experimental studies can be conducted on the development of Zr–Er-based alloys with the addition of binders, such as graphite, which can improve the hydriding/dehydriding kinetics of these metallic alloys and enhance oxidation resistance when the materials come into contact with air or water.

PUBBLISHED ARTICLES

Articles published in Web of Science-indexed journals relevant to the doctoral thesis field:

1. **Nicolae Tiberiu Ciobanu**, Denis Aurelian Negrea, Mariana Postelnicu, Nina Gabriela Tudorache, Nicolae Valentin Olaru, Aurel David (2024). *„Analysis of sintered Zr_xEr_{1-x} obtained through powder metallurgy"*, Journal of Science and Arts, Vol. 24, Iss. 4, pp. 991-1002, https://doi.org/10.46939/J.Sci.Arts-24.4-b06 IF=0,3 (Q4)
2. **Nicolae Tiberiu Ciobanu**, Adriana-Gabriela Șchiopu, Daniela Diaconu, Cătălin Marian Ducu, Mihai Oproescu, Maria Magdalena Dicu, Denis Aurelian Negrea, Sorin Georgian Moga, Mariana Postelnicu, Vasile Radu (2026). *„Morphological and structural characterization of sintered compacts zirconium-erbium obtained by powder metallurgy"*, UPB Sci. Bull., Series B, Vol. 88, Iss. 1, pp. 285-300, IF=0,33 (Q4)

Articles published in journals indexed in International Databases (IDB) relevant to the field of the doctoral thesis:

1. **Ciobanu Nicolae Tiberiu**, Șchiopu Adriana Gabriela (2023). *„Hydrogen Production and Solid-State Storage: A review"*, The Annals of "Dunărea de Jos" University of Galați, Fascicle 9, No. 3, https://doi.org/10.35219/mms.2023.3.01

Participation in conferences in the field of the doctoral thesis:

1. **Ciobanu Nicolae Tiberiu**, *„Experimental studies on binary system Er-H"*, 15th International Conference on Electronics, Computers and Artificial Intelligence (ECAI), June 2023, https://doi.org/10.1109/ECAI58194.2023.10194023
2. **Ciobanu Nicolae Tiberiu**, Șchiopu Adriana Gabriela, Mariana Postelnicu, Gabriela Tudorache, Valentin Olaru, Aurel David, *„Experimental Studies of the Binary System Zr-Er"*, NUCLEAR Conference, May 2024

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